APPLIED
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QUANTUM
THEORY
OF
SOLIDS

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QUANTUM THEORY OF SOLIDS

NOTES

LECTURE I

Professor: Dr. Henry Ehrenreich
Room: Pierce 304, MWF at 11 AM

Topics to be covered:

1. Lattice Vibrations
2. Electron in a periodic potential
3. Many electron problem; statistics
4. Electron - phonon interaction
5. Transport Theory

Recommended Reading List:

1. Sommerfeld & Bethe, Hand. d. Phys., vol. 24/2, (1933)
2. Mott & Jones, Prop. of Metals & Alloys, (1936)
3. Seitz (1940)
4. Brooks (1950) Lecture Notes
5. Kittel (1953)
6. Wilson (1953) Theory of Metals
7. Born & Hrang (1954)
8. * Peierls (1955)
9. Seitz & Turnbull Series
   vol. I. Reitz
   Pines
   vol. 5. W. Kohn
10. Encyclopedia of Physics (1955) (German)
    Liepfried, vol. 7
    Bardeen, vol. 15 (electron-phonon interaction)
    Slater, vol. 19
    Jones, vol. 19 (transport Theory)
11. * Wannier (1959)
12. * Ziman (1960) Electrons and Phonons

* should buy

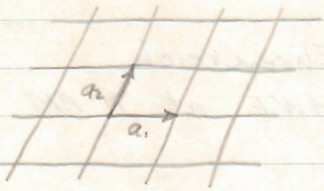
LATTICE VIBRATIONS:

Crystal Lattice:

Lattice vector definition:

$$\bar{l} \equiv \bar{R}_l = l_1 \bar{a}_1 + l_2 \bar{a}_2 + l_3 \bar{a}_3$$

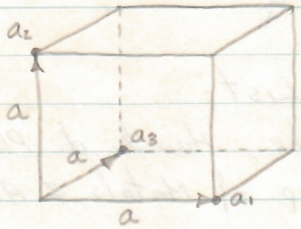
l's are integers less than the number of atoms.



1 atom/unit cell : Bravais lattice
2 or more : Basis Lattice

Cubic Types:

Simple:

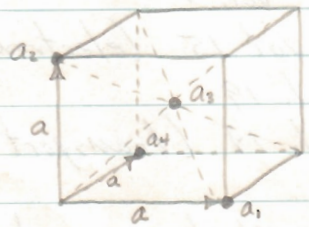


basic co-ordinates: $(a,0,0) = a_1$
$(0,a,0) = a_2$
$(0,0,a) = a_3$

other atomic co-ordinates may be found by a simple translation of these three

Body Centered Cubic (bcc):

basic co-ordinates: $(a,0,0) = a_1$
$(0,a,0) = a_2$
$(\frac{a}{2},\frac{a}{2},\frac{a}{2}) = a_3$



Now the position of a_4 may be found through a translation of the other three, viz,

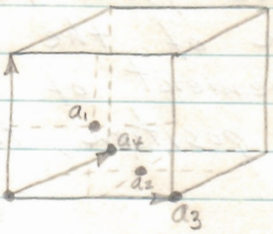
$$a_4 = (0,0,a) = 2a_3 - a_2 - a_1$$

Face Centered Cubic:

basic co-ordinates: $\left(\frac{a}{2}, \frac{a}{2}, 0\right) = a_1$

$\left(\frac{a}{2}, 0, \frac{a}{2}\right) = a_2$

$(a, 0, 0) = a_3$



Now,

$a_4 = (0,0,a) = 2a_2 - a_3$

Assuming Crystal Equilibrium, ie,

a) Equilibrium Configuration

b) Stable

and that atomic displacement is small, that is,

and $\frac{\langle \mu_\ell^2 \rangle^{1/2}}{\langle a \rangle} \ll 1$

we may write the following for the Hamiltonian:

$$H = \tfrac{1}{2} M \sum |\dot{\bar{r}}_\ell|^2 + V(\bar{r}_1, \bar{r}_2, \bar{r}_3, \ldots)$$

The potential function may be expanded by Taylor's expansion as follows:

$$V(\ldots, \bar{R}_\ell + \bar{\mu}_\ell, \ldots) = V_0 + \sum_{l\alpha} \left(\frac{\partial V}{\partial \mu_{l\alpha}}\right)_{\mu=0} \mu_{l\alpha}$$

$$+ \frac{1}{2} \sum_{l\alpha, l'\alpha'} \left(\frac{\partial^2 V}{\partial \mu_{l\alpha} \partial \mu_{l'\alpha'}}\right)_{\mu=0} \mu_{l\alpha} \mu_{l'\alpha'} + \frac{1}{6} \sum_{(\ )} (\quad) \mu\mu'\mu'' \ldots$$

Under Equilibrium, $\left(\frac{\partial V}{\partial \mu_{l\alpha}}\right)_0 = 0$

α is cartesian subscript, not subscript on l.

LECTURE II 9/28/60

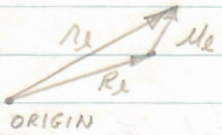
Continuing with the Hamiltonian for an atomic lattice of one atom per unit cell, viz.,

(1) $H = \frac{1}{2} M \sum_l |\dot{\bar{r}}_l|^2 + V(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_l, \ldots)$

in which $\bar{r}_l$ represents the distance at some instant from any arbitrary origin to the lth atom, $\bar{R}_l$ the distance from this origin to the equilibrium position of the lth atom, and $\bar{u}_l$ the displacement of the lth atom from its equilibrium position, that is,

(2) $\bar{r}_l = \bar{R}_l + \bar{u}_l$

with $\frac{\langle u_l^2 \rangle^{1/2}}{\langle a \rangle} << 1$



Expanding the potential in a Taylor series about $u = 0$

(3) $V(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_l, \ldots) = V(\ldots, \bar{R}_l + \bar{u}_l, \ldots)$

$= V_0 + \sum_{l\alpha} \left(\frac{\partial V}{\partial u_{l\alpha}}\right)_{u=0} u_{l\alpha} + \frac{1}{2} \sum'_{l\alpha, l'\alpha'} \left(\frac{\partial^2 V}{\partial u_{l\alpha} \partial u_{l'\alpha'}}\right)_{u=0} u_{l\alpha} u_{l'\alpha'} + \ldots$

in which α is the cartesian co-ordinates of displacement of the lth atom. It is usual to take $V_0 = 0$ for simplicity. Also, by the definition of equilibrium,

(4) $\left(\frac{\partial V}{\partial u_{l\alpha}}\right) = 0$, $u_{l\alpha} = 0$, and the linear terms disappear

The mixed partial in (3) is merely a constant when evaluated for all $u_{l\alpha} = 0$ and can be written

$$(5)\quad \left(\frac{\partial^2 V}{\partial u_{l\alpha}\,\partial u_{l'\alpha'}}\right)_0 = C_{\alpha\alpha'}(l,l')$$

Note that this has the dimensions of a force constant, as in a spring.

If the displacement is small, we may neglect higher order terms in V. However, these terms are called anharmonic terms and really give rise to the following phenomena:

1) thermal expansion
2) specific heat
3) thermal conductivity

The first term is called a harmonic term.

Symmetry Properties of harmonic terms:

a) all cells are physically equivalent with respect to their surroundings, thus,
$C_{\alpha\alpha'}(l,l') = C_{\alpha\alpha'}(l-l')$
that is, the "force constants" are dependent only on the difference between the positions of their atoms rather than on the positions themselves.

b) From (5), then, $C_{\alpha\alpha'}(l-l') = C_{\alpha'\alpha}(l'-l)$

c) For lattices having inversion symmetry, in which opposite directions on the same axis are equivalent, $C_{\alpha\alpha'}(l-l') = C_{\alpha\alpha'}(l'-l)$

d) Under a rigid displacement, $u_{l\alpha} = \text{epsilon}\ (\epsilon)$, the force constants are zero, i.e.,
$\sum_{l'} C_{\alpha\alpha'}(l-l') = 0$, from which follows
$\sum_{l} C_{\alpha\alpha'}(l) = 0$ by taking $l' = 0$ and summing on l.

The Hamiltonian now has the form:

$$(1A)\quad H = \tfrac{1}{2} M \sum_l |\dot{u}_l|^2 + \tfrac{1}{2} \sum_{l\alpha\, l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l\alpha}\, u_{l'\alpha'}$$

We will now define the canonical conjugates necessary to set up the equations of motion.

(6) $M_{l\alpha} \rightarrow q$, $M\dot{u}_{l\alpha} \rightarrow p$

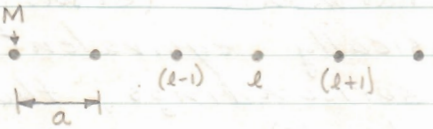
(7) From mechanics, $\dot{p} = -\frac{\partial H}{\partial q}$

Therefore,

(8) $M\ddot{u}_{l\alpha} + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l'\alpha'} = 0$

which is an equation of motion corresponding to Hooke's Law:

One Dimensional Case:



Take $C(l-l') = C(l'-l)$ from property (b)
and $\sum_l C(l) = 0$ from property (d)

Now (8) reduces to:

(9) $M\ddot{u}_l + \sum_{l'} C(l'-l)\, u_{l'} = 0$

of which a solution might be

(10) $u_l(t) = u_l(0)\, e^{-i\omega t}$

Substituting (10) into (9):

(11) $-M\omega^2 u_l(0) + \sum_{l'} C(l'-l)\, u_{l'}(0) = 0$

As there is no damping, there will be no exponential rise or decay along the lattice and the displacements will differ from one to the other only by a phase constant.

(12)[a] $u_{l+n}(0) = \Gamma^n u_l(0)$, or, with respect to a "$l=0$" reference,

[b] $u_l(0) = \Gamma^l u^\circ$ where u° denotes the displacement of the zeroth atom at $t=0$.

It is seen that Γ must be complex with modulus unity. Therefore,

(13) $\Gamma = e^{iqa}$, the qa being chosen with "foresight."

Substituting (12)[b] into (11); and using (13):

(14) $$-M\omega^2 e^{iqla} + \sum_{l'} c(l-l') e^{iql'a} = 0$$

(15) $$M\omega^2 = \sum_{l'} c(l-l') e^{-iq(l-l')a}$$

By taking into account the periodicity of the lattice, we may assign $l=0$ as a reference with $c(l') = c(l')$ by (b), then changing l' back to l, we have:

(16) $$M\omega^2 = \sum_{l} c(l) e^{iqla}$$

By using the same process, we could have initially assigned $l'=0$ as reference and obtained

(17) $$M\omega^2 = \sum_{l} c(l) e^{-iqla}$$

Adding (16) and (17) and dividing by two, we have,

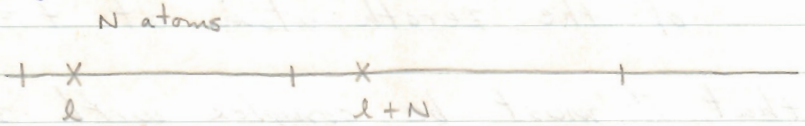
(18) $$M\omega^2 = \tfrac{1}{2} \sum_{l} c(l) \left(e^{iqla} + e^{-iqla}\right) = \sum_{l} c(l) \cos qla$$

From (18), the following important fact is apparent:

(19) $\omega^2(q) = \omega^2(-q)$

Boundary Conditions:

Assume (due to Born) we have periodic boundary conditions, that is,



(20) $u_l = u_{l+N}$

Since the displacements differ only by a phase factor, from (20) the phase factors of the u_l, u_{l+N} must be equal, that is,

(21) $e^{iqla} = e^{iq(l+N)a}$ or $e^{iqNa} = 1$

Thus,

(22) $qNa = 2n\pi$ or $q = \frac{2\pi n}{Na}$

which indicates the important fact that the q's are discrete, and with a bounded number of independent solutions because if $n = N+m$, $q = \frac{2\pi}{a} + \frac{2\pi m}{Na}$ with $n = m = N+m$ by periodicity.

Therefore: $0 \leq n \leq N-1$

N values of q

N values of ω

$0 \leq q \leq \frac{2\pi(N-1)}{Na}$, or, $0 \leq q < \frac{2\pi}{a}$

We may define the principle values of q as lying between $-\frac{\pi}{a}$ and π/a for convenience.

That is,

(23) $-\pi/a \leq q < \pi/a$ and which is the first Brillouin zone containing all the independent wave numbers.

Returning to (18), $M\omega^2 = \sum_l c(l) \cos qla$, we take the limit as $q \to 0$.

(24) $$\lim_{q \to 0} \left| \sum_l c(l) \left[1 - \tfrac{1}{2} q^2 a^2 l^2 + \dots \right] = -\tfrac{1}{2} q^2 a^2 \sum_l l^2 c(l) \right.$$

This indicates that $\omega \sim q$ which is typical of continuum motion, that is, as the wavelength grows larger, the wave moves much as if the lattice were a continuous solid. It is apparent that the condition must be made that $\omega^2 > 0$ as it must be real, and it follows that,

(25) $$\sum_l l^2 c(l) < 0$$

Now consider force constants between nearest neighbors, that is, only three force constants $c(0)$, $c(1)$, $c(-1)$. Now apply symmetry condition (d): $\sum_l c(l) = 0$

(26) $c(0) + c(1) + c(-1) = 0$ and $c(1) = -\tfrac{1}{2} c(0)$ by symmetry condition (b)

Substitute into (18) and sum from $l=0$ to $l=2$ or $l=-1$ to $l=+1$:

(27) $$M\omega^2 = \sum_{l=-1}^{l=+1} c(l) \cos qla = c(0) + 2c(1) \cos qa$$

$$= c(0) \left[1 - \cos qa \right] = 2 c(0) \sin^2 \tfrac{1}{2} qa$$

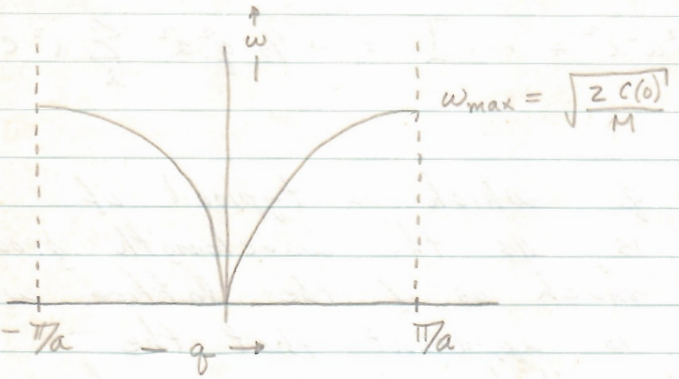
(28) $$\therefore \omega = \sqrt{\frac{2c(0)}{M}} \left| \sin \tfrac{1}{2} qa \right|$$

Taking the limit as $q \to 0$:

(29) $$\lim_{q \to 0} \left| \omega = \sqrt{\frac{c(0)}{2M}}\, a\, q = c\, q \right.$$

where c is the velocity of sound as it is usually taken for a continuous medium.

We plot ω versus q as given by equation (28)



Physical Significance of the Plot:

1) $u_\ell \propto e^{i q \ell a}$

$\therefore \frac{u_{\ell+1}}{u_\ell} = e^{iqa} = e^{i\frac{\pi}{a}a} = -1$ for $q = \pi/a$

2) Shows two different modes for high q.

LECTURE III 9/30/60

Recapitulation on One-Dimensional Case:

(1) $u_\ell(t) \sim e^{i(q\ell a - \omega t)}$; $q = \frac{2\pi}{\lambda}$

(2) $\omega = \left[-\frac{a^2}{2M} \sum_\ell \ell^2 c(\ell)\right]^{1/2} q$, for long λ

with $c(0)$, $c(1) = c(-1)$

For this long wavelength approximation:

(3) $C(1) = -1/2\, C(0)$

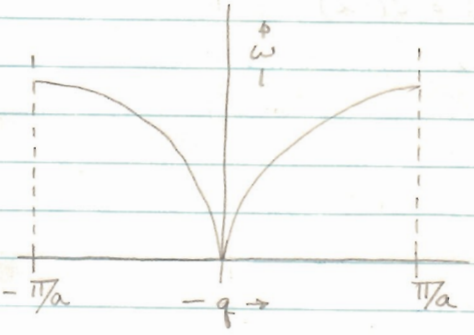
(4) $\sum_{l=-1}^{+1} l^2 C(l) = C(-1) + C(0) + C(1) = 0$

In general:

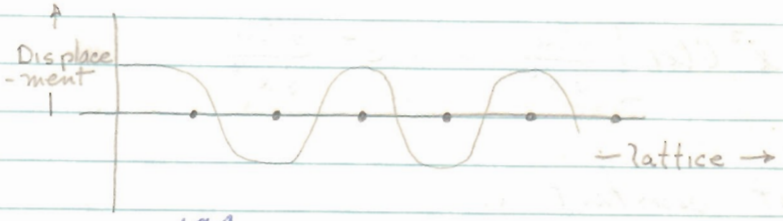
(5) $M\omega^2 = 2C(0)\sin^2 1/2 qa$; $\omega = \omega_{max} \sin \frac{n\pi}{2N}$, $0 \le n < N-1$

with $\omega_{max} = \sqrt{\frac{2C(0)}{M}}$

Graphical Explanation:



for $q = 0$: wave moves in phase
$q = \pi/a$: out of phase



e^{-iqa} → right traveling wave
e^{iqa} → left " "

This diagram represents the shortest possible wavelength of the system, $\lambda = 2a$. Anything shorter would be ridiculous as there would be no atoms there to vibrate.

The group velocity, $v_g = \frac{d\omega}{dq}$, is zero at $q = \pm \pi/a$ as can be seen from the simple diagrams above.

Demonstration That Long-wavelength Approximation Leads to Ordinary Wave Equation:

(6) Take $\sum_{l'} C(l-l')\, u_{l'} = \sum_{l''} C(l'')\, u_{l-l''}$

taking $l - l' = l''$

Expanding $u_{l-l''} = u_l - l'' \frac{du}{dl''} + \frac{1}{2} l''^2 \frac{d^2u}{dl''^2} - \ldots$

in a Taylor series considering u a function of l and substituting:

(7) $\sum_{l''} C(l'')\, u_{l-l''} = u_l \underbrace{\sum C(l'')}_{0} - \frac{du}{dl''} \underbrace{\sum l'' C(l'')}_{0} + \frac{1}{2} \frac{d^2u}{dl''^2} \sum l''^2 C(l'')$

$C(l) = C(-l)$

neglecting higher order terms in $\frac{du}{dl''}$.

Substituting (7) into II (9), viz.,

(8) $M \ddot{u}_l + \sum_{l'} C(l'-l)\, u_{l'} = 0$

we have,

(9) $\frac{\partial^2 u_l}{\partial t^2} = -\left[\frac{a^2}{2M} \sum_{l''} l^2 C(l)\right] \frac{\partial^2 u}{\partial x^2} = -c^2 \frac{\partial^2 u}{\partial x^2}$

Considering $\frac{d^2u}{dl''^2} = \frac{\partial^2 u}{\partial x^2}$ at constant l.

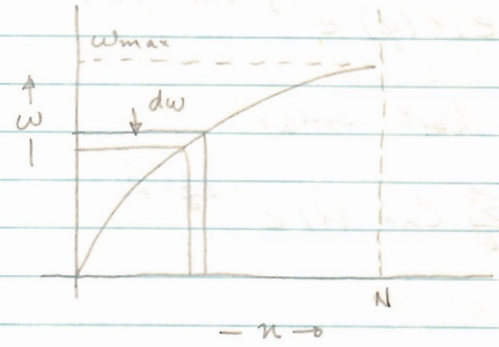
Thus it is right to think of wave motion in a continuum when $\lambda \gg a$. This connects us with elasticity theory. We can measure the elastic constants from which we can determine the force constants.

Density of Oscillators:

We ask the question: How many oscillators in the range $\Delta\omega = \omega + d\omega$. In other words, we want to calculate $\rho(\omega)$:

(10) $$\rho(\omega)\,d\omega = \frac{dn}{d\omega}\,d\omega$$

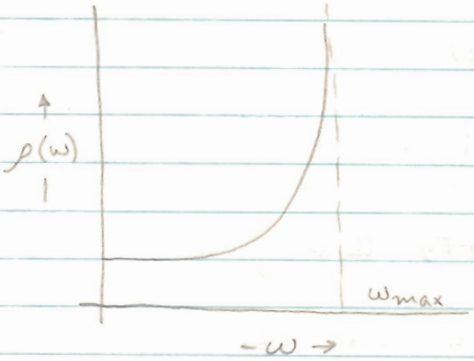
Plot ω versus n from relation (5):



From (5):

(11) $$n = \frac{2N}{\pi}\,\sin^{-1}\frac{\omega}{\omega_{max}}$$

(12) $$\frac{dn}{d\omega} = \frac{2N}{\pi}\,\frac{1}{\sqrt{\omega_{max}^2 - \omega^2}} = \rho(\omega)$$



$\rho(\omega)$ at ω_{max} is infinite because of $\frac{d\omega}{dn} = 0$ from above.

This difficulty disappears in the three dimensional case. Here it means that we have an infinite density of oscillators when $\omega = \omega_{max}$

Three Dimensional Case:

(13) From Before: $M\ddot{u}_{l\alpha} + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, u_{l'\alpha'} = 0$

Postulate the following solution:

(14) $u_{l\alpha'}(t) = e_{\alpha'}(q)\, e^{i(\bar{q}\cdot\bar{R}_l - \omega(q,j)t)}$

Substituting,

(15) $-M\omega^2 e_\alpha(q) + \sum_{l'\alpha'} C_{\alpha\alpha'}(l-l')\, e_{\alpha'}(q)\, e^{i\bar{q}\cdot(\bar{R}_{l'} - \bar{R}_l)}$

Performing a Fourier inversion: (not really)

(16) $\sum_{l'} C_{\alpha\alpha'}(l-l')\, e^{i\bar{q}\cdot(\bar{R}_{l'} - \bar{R}_l)} = \sum_{l} C_{\alpha\alpha'}(l)\, e^{-i\bar{q}\cdot\bar{R}_l}$

$= \hat{C}_{\alpha\alpha'}(q)$

On Substitution:

(17) $M\omega^2 e_\alpha(q) = \sum_{\alpha'} \hat{C}_{\alpha\alpha'}(q)\, e_{\alpha'}(q)$

Properties of $C_{\alpha\alpha'}(q)$ $[= \hat{C}_{\alpha\alpha'}(q)]$:

a) $C_{\alpha\alpha'}(l) = C_{\alpha'\alpha}(-l)$ from property II b.

b) $C^*_{\alpha\alpha'}(-q) = \sum_l C_{\alpha\alpha'}(l)\, e^{i(-\bar{q})\cdot\bar{R}_l} = C_{\alpha\alpha'}(q)$

from (16).

c) $C_{\alpha'\alpha}(q) = \sum_l C_{\alpha'\alpha}(l)\, e^{-i\bar{q}\cdot\bar{R}_l} = \sum_l C_{\alpha\alpha'}(-l)\, e^{i\bar{q}\cdot\bar{R}_l}$

$= C^*_{\alpha\alpha'}(q)$ which denotes the Hermiticity of the $C_{\alpha\alpha'}$'s.

d) From Inversion Symmetry: $C_{\alpha\alpha'}(l) = C_{\alpha\alpha'}(-l)$:

$C^*_{\alpha\alpha'}(-q) = C_{\alpha\alpha'}(q)$

$C_{\alpha'\alpha}(q) = C^*_{\alpha\alpha'}(q)$

Shifting our basis for l, we may form as before:

$$(18)\quad C_{\alpha\alpha'}(q) = \tfrac{1}{2}\sum_l C_{\alpha\alpha'}(l)\left[e^{-i\bar{q}\cdot\bar{R}_l} + e^{i\bar{q}\cdot\bar{R}_l}\right]$$

$$= \sum_l C_{\alpha\alpha'}(l)\cos\bar{q}\cdot\bar{R}_l$$

$$= -2\sum_l C_{\alpha\alpha'}(l)\tfrac{1}{2}\left[1-\cos\bar{q}\cdot\bar{R}_l\right] \quad \left\{\text{From } \sum_l C_{\alpha\alpha'}(l) = 0\right\}$$

$$= -2\sum_l C_{\alpha\alpha'}(l)\sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_l$$

which is analogous to our one-dimensional case. See equation II (18).

Returning to (15) and (16), we have on substitution:

$$(19)\quad \frac{1}{M}\sum_{\alpha'} C_{\alpha\alpha'}(q)\xi_{\alpha'} - \omega^2 \xi_\alpha = 0$$

We may now write three equations for each three directions:

$$(20)\quad \left(\frac{1}{M}C_{11}(q) - \omega^2\right)e_1 + \frac{1}{M}C_{12}(q)e_2 + \frac{1}{M}C_{13}(q)e_3 = 0$$

$$\frac{1}{M}C_{21}(q)\,e_1 + \left(\frac{1}{M}C_{22}(q) - \omega^2\right)e_2 + \frac{1}{M}C_{23}(q)e_3 = 0$$

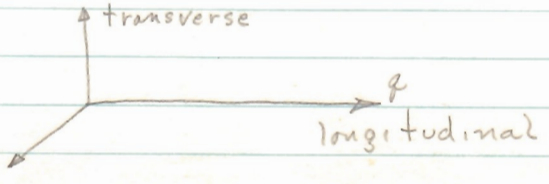
$$\frac{1}{M}C_{31}(q)\,e_1 + \frac{1}{M}C_{32}(q)\,e_2 + \left(\frac{1}{M}C_{33}(q) - \omega^2\right)e_3 = 0$$

Now we must have:

$$(21)\quad \left|\frac{1}{M}C_{\alpha\alpha'}(q) - S_{\alpha\alpha'}\omega^2\right| = 0$$

Thus we get our solution: $\omega(j,q)$ in which j is the index of the eigenvalues. $j = 1, 2, 3$

Also, $e(q,j)$ are the polarization vectors apparently



Significance of Symmetry:

(a) From Hermiticity of $C_{\alpha\alpha'}(q)$, i.e., $C_{\alpha\alpha'}(q) = C^*_{\alpha'\alpha}(q)$, the main diagonal must be real in the secular equation, so ω^2 is real.

(b) $\omega^2(q,j) > 0$, from common sense

(c) $\omega(q,j) = \omega(-q,j)$; because $C_{\alpha\alpha'}(-q) = C_{\alpha\alpha'}(q)$

(d) $e(q,j) = e^*(-q,j)$; see secular equation.

We will now look at the general solution and impose periodic boundary conditions:

(22) $$\bar{u}_l = \sum_{q,j}{}' e(q,j)\, e^{i(\bar{q}\cdot\bar{R}_l - \omega\{q,j\}t)}$$

as the sum of all solutions is a solution or as found by Fourier series solution.

Impose Periodic Boundary Conditions:

(23) $u_l = u_{l'}$, $l = (0, l_2, l_3)$
$l' = (G, l_2, l_3)$

considering G atoms per edge of sample. Although it is unrealistic to think of joining the boundarys of a four-dimensional object, we still do it for mathematical convenience.

"q" Space:

In q space there is a corresponding symmetry as in real lattice space.

Reciprocal Lattice Vector:

(24) $K = 2\pi (g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3)$

with g_i = integers

b_i = co-ordinates of q space

The lattice vector is $\bar{R}_l = (l_1 \bar{a}_1 + l_2 \bar{a}_2 + l_3 \bar{a}_3)$ with the important relation that,

(25) $\bar{a}_i \cdot \bar{b}_j = \delta_{ij}$

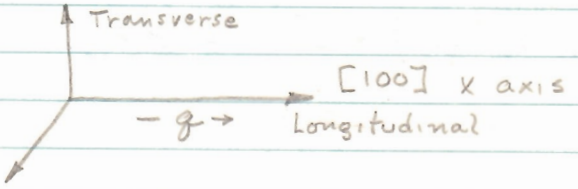
LECTURE IV 10-3-60

Continuation of 3 Dimensional Lattice Study:

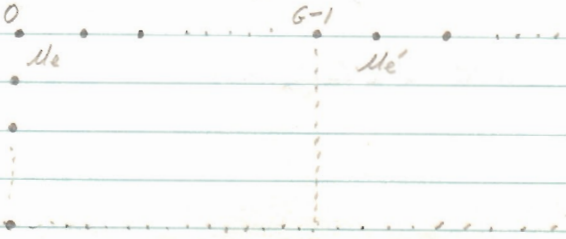
The general equation of a 3-D lattice has been given as:

(1) $\sum_{\alpha'} \left[\frac{1}{M} C_{\alpha\alpha'}(q) - \delta_{\alpha\alpha'} \omega^2(q,j) \right] e_{\alpha'}(q,j) = 0$

in which the eigenvectors are taken as the polarization vectors, with $\bar{u}_l \sim \bar{e}_q$



Taking periodic boundary conditions: $\bar{u}_l = \bar{u}_{l'}$ in all directions.



Reciprocal Lattice; system of axis representing "q" space which is analogous to coordinate space.

It is defined by 3 vectors, $\bar{b}_1, \bar{b}_2, \bar{b}_3$, such that $\bar{a}_\ell \cdot \bar{b}_j = \delta_{\ell j}$. Thus:

(2) $\bar{K}_g = 2\pi \left(g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3 \right)$

in which the relation to the real lattice is:

(3) $\bar{b}_i = \dfrac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \cdot \bar{a}_2 \times \bar{a}_3}$, etc., with dimensions of reciprocal length

In one dimension, $b = \frac{1}{a}$, $K = \frac{2\pi}{a}$ or the principal values of q, viz., $0 < q < \frac{2\pi}{a}$.

Now,

(4) $\bar{q} = \dfrac{2\pi}{G} \left(g_1 \bar{b}_1 + g_2 \bar{b}_2 + g_3 \bar{b}_3 \right)$ with $M_\ell = M_{\ell'}$

Take $\ell = (0, \ell_2, \ell_3)$
$\ell' = (G, \ell_2, \ell_3)$

(5) $M_\ell \sim e^{i \bar{q} \cdot \bar{R}_\ell}$
$M_{\ell'} \sim e^{i G \bar{q} \cdot \bar{a}_1}$

The periodic boundary conditions are satisfied if:

(6) $e^{i G \bar{q} \cdot \bar{a}_1} = 1$, now

(7) $G \bar{q} \cdot \bar{a}_1 = G \dfrac{2\pi}{G} \left(g_1 \bar{b}_1 + \dots \right) \cdot \bar{a}_1 = 2\pi g_1$

(8) $\therefore e^{i 2\pi g_1} = 1$

The spacing between points in "q" space is $\frac{2\pi}{G} \bar{b}_i$

There is no unique wave vector, i.e.

(9) $\bar{q}' = \bar{q} + K$

(10) $M_e \cong e^{i\bar{q}'\cdot\bar{R}_e} = e^{i\bar{q}\cdot\bar{R}_e} e^{i\bar{K}\cdot\bar{R}_e}$

with $\bar{K}\cdot\bar{R}_e = 2\pi \sum_i l_i q_i$ which is always some integer times π, thus showing $\bar{q}$ not unique. We then confine q so that $|\bar{q}| < |\bar{K}|$

The reciprocal lattice of a bcc is a fcc and vice-versa. Read article on reciprocal lattice in Ziman § 1.5, Rietz, vol. I., SSP.

Brillouin Zone: depends only on translational symmetry which is very important. Contains inversion symmetry.

How many independent eigenvalues are in a region of a crystal? The answer is 3G independent values of q. Thus number of independent eigenvalues equals the number of degrees of freedom.

Density of States in reciprocal space: The "volume" around each point is $\left(\frac{2\pi}{G}\right)^3 \bar{b}_1\cdot\bar{b}_2\times\bar{b}_3$. It can be shown that

(11) $$\bar{b}_1\cdot\bar{b}_2\times\bar{b}_3 = \frac{1}{\bar{a}_1\cdot\bar{a}_2\times\bar{a}_3}$$

Now $G^3[\bar{a}_1\cdot\bar{a}_2\times\bar{a}_3]$ is interpreted in real space as the volume V of the crystal, therefore, the volume in "q" space $= \frac{8\pi^3}{V}$

No. of points in "q" space / per volume $= \frac{V}{8\pi^3}$. This result is important because we can change a sum on q into an integration in "q" space, viz.,

(12) $$\sum_q \rightarrow \frac{V}{8\pi^3}\int d^3q$$

Interpretation of Eigenvectors:

Translational and Longitudinal properties result from the orthogonality of the eigenvectors, e_j.

Theorem: $S = \sum_l e^{i(\bar{q}-\bar{q}')\cdot \bar{R}_l} = G^3 \delta_{q', q+K}$

Proof: Shift origin: $\sum_l e^{i(q-q')\cdot(R_l + R_{l'})}$

$= S\, e^{i(\bar{q}-\bar{q}')\cdot \bar{R}_l}$

Now $S = 0$ unless $q - q' = K$ $\quad (e^{iK\cdot R_l} = 1)$

Then $S = \sum_l e^{i\bar{K}\cdot \bar{R}_l} = G^3$ (triple directions)

Theorem proved.

We note in all discussions a continual shift of thought between infinite and finite lattices.

Orthogonality of Eigenfunctions:

Orthogonality Condition:

(13) $\sum_l \left\{ e(\bar{q}, j)\, e^{i\bar{q}\cdot \bar{R}_l} \right\}^* \left\{ e(\bar{q}', j')\, e^{i\bar{q}'\cdot \bar{R}_l} \right\} = \eta\, \delta_{q,q'}\, \delta_{j,j'}$

where η is a normalization factor. We may write (13) as follows:

(14) $e(\bar{q}, j)^* \cdot e(\bar{q}', j') \sum_l e^{i(\bar{q}'-\bar{q})\cdot \bar{R}_l} = \eta\, \delta_{\bar{q},\bar{q}'}\, \delta_{j,j'}$

$\sum_l e^{i(\bar{q}'-\bar{q})\cdot \bar{R}_l} = G^3 \delta_{\bar{q},q'}$ from the above theorem

Choosing $\eta = G^3$, we have,

(15) $e(\bar{q}, j)^* \cdot e(\bar{q}', j') = \delta_{j,j'}$

We have thus shown the orthogonality of the eigenvectors from the orthogonality of the eigenfunctions. Thus, the polarization vectors in monatomic unit cell are all mutually orthogonal.

Assumption: $\omega(\bar{q},j)$ are non-degenerate

(16) $M\omega^2(\bar{q},j)\, e_\alpha(\bar{q},j) = \sum_{\alpha'} C_{\alpha\alpha'}(q)\, e_{\alpha'}(q)$

Change $j \to j'$

In tensor notation:

(17) $M\omega^2(\bar{q},j')\, \bar{e}(\bar{q},j') = \mathbb{C}(q)\, \bar{e}(\bar{q},j')$

Take the complex conjugate and transpose, knowing that the matrix $\mathbb{C}(q)$ possesses Hermiticity, that is, $\mathbb{C}(q) = \mathbb{C}^\dagger(q)$ where the dagger ($\dagger$) means complex conjugate and transpose.

(18) $M\omega^2(\bar{q},j')\, \bar{e}^\dagger(\bar{q},j') = \bar{e}^\dagger(\bar{q},j')\, \mathbb{C}(q)$

Multiply (17) by $\bar{e}^\dagger(\bar{q},j)$. Change $j' \to j$ in (18) and multiply by $\bar{e}(\bar{q},j')$. Subtract results:

(19) $M\left[\omega^2(\bar{q},j') - \omega^2(\bar{q},j)\right] \bar{e}^\dagger(\bar{q},j)\, \bar{e}(\bar{q},j')$

$= \bar{e}^\dagger(\bar{q},j)\, \mathbb{C}(q)\, \bar{e}(\bar{q},j') - \bar{e}^\dagger(\bar{q},j')\, \mathbb{C}(q)\, \bar{e}(\bar{q},j')$

$= 0$

Check assumption of non-degeneracy:

(20) For $j \neq j'$; $\bar{e}^\dagger(\bar{q},j) \cdot \bar{e}(\bar{q},j') = 0$

$j = j'$; $\bar{e}^\dagger(\bar{q},j) \cdot \bar{e}(\bar{q},j') \neq 0$

Thus $\omega^2(\bar{q},j)$ is non-degenerate

Evaluation of $\mathbb{C}$ or $C_{\alpha\alpha'}(q)$:

(21) $C_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{i\bar{q}\cdot\bar{R}_\ell}$

$= -2 \sum C_{\alpha\alpha'}(\ell) \sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_\ell$

Now the $C_{\alpha\alpha'}(\ell)$'s form a matrix:

Examine the symmetry of the crystal, for example, the rotation symmetry in a cubic crystal.

(22) $\bar{u}'_{\ell\beta} = \sum_{\alpha} S_{\beta\alpha}\, \bar{u}_{\ell\alpha}$ may be written

(23) $\bar{u}'_{\ell} = \mathbb{S}\, \bar{u}_{\ell}$ and when

(24) $\bar{u}'^{T}_{\ell} = \bar{u}^{T}_{\ell}\, \mathbb{S}^{T}$, then

(25) $\mathbb{S}^{T}\mathbb{S} = \mathbb{1}$ and $\mathbb{S}$ is an orthogonal transformation.

Using the tensor notation, we may write the potential energy as follows:

(26) $\Phi = \frac{1}{2} \sum_{\ell\ell'} u_\ell^{T}\, \mathbb{C}(\ell-\ell')\, u_{\ell'}$ (u_ℓ transposed, see II-1A)

$= \frac{1}{2} \sum_{\ell\ell'} u'^{T}_{\ell}\, \mathbb{C}'(\ell-\ell')\, u'_{\ell'}$ (by rotation or translation in a simple cubic)

$= \frac{1}{2} \sum_{\ell\ell'} u_\ell^{T}\, \mathbb{S}^{T}\, \mathbb{C}'(\ell-\ell')\, \mathbb{S}\, u_{\ell'}$

Then $\mathbb{C}(\ell-\ell') = \mathbb{S}^{T}\, \mathbb{C}'(\ell-\ell')\, \mathbb{S}$

LECTURE V 10-5-60

We have from before:

(1) $\hat{C}_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{-i\bar{q}\cdot\bar{R}_\ell} = -2 \sum_{\ell} C_{\alpha\alpha'}(\ell) \sin^2 \tfrac{1}{2}\bar{q}\cdot\bar{R}_\ell$ (with inversion symmetry)

(2) $\sum_{\alpha'} \left[\frac{1}{M} \hat{C}_{\alpha\alpha'}(q) - \delta_{\alpha\alpha'}\omega^2(q) \right] e_{\alpha'}(q) = 0$

(3) $\Phi = \frac{1}{2} \sum_{\ell}{}' \bar{u}_\ell^{\,T}\, \mathbb{C}(\ell-\ell')\, \bar{u}_{\ell'}$

The transpose is written because of the form necessary for matrix multiplication, viz., $(\ )(\ )^T(\ )(\ )$.

Make a symmetry transformation:

(4) $\Phi = \frac{1}{2} \sum_{\ell}{}' \bar{u}'^{\,T}_{\ell}\, \mathbb{C}'(\ell-\ell')\, \bar{u}'_{\ell'}$

Make the transformation unitary:

(5) $\bar{u}'_\ell = \mathbb{S}\,\bar{u}_\ell$
$\bar{u}'^{\,T}_\ell = \bar{u}_\ell^{\,T}\,\mathbb{S}^T$
with the condition $\mathbb{S}^T\mathbb{S} = \mathbb{I}$

Then:

(6) $\mathbb{C}(\ell-\ell') = \mathbb{S}^T\,\mathbb{C}'(\ell-\ell')\,\mathbb{S}$

We may remove the prime from the right hand side and write it without because the nature of the force constants remain physically unchanged.

Take a simple cubic lattice - compute tensor when there is nearest neighbor interaction. Find $\mathbb{C}(100)$.

[100]
(a, 0, 0)

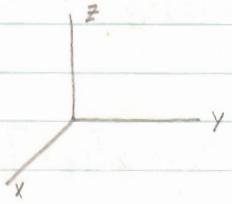
Nearest neighbor distance in simple cubic

(7) $\mathbb{C}(100) = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix}$

We would desire a transform such that $x, y, z \rightarrow x', y', z' = x, \pm y, \pm z$, leaving x invariant.

Use the transformation:

(8) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$



(9) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ -y \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$

↓ Rotate x axis

↓ Reflect in xz plane

Essentially, we make transformations keeping the direction of interest invariant.

Then:

(10) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ z \\ y \end{pmatrix}$

$\Leftrightarrow$ and is also symmetric about the diagonal,

Plug-in equation (6)

(11) $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & x & x \\ x & x & c_{22} \\ x & c_{33} & x \end{pmatrix}$

$= \begin{pmatrix} c_{11} & x & x \\ x & c_{33} & x \\ x & x & c_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}$

and we can conclude that $c_{33} = c_{22}$

Another transformation: $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$; from this $\Leftrightarrow$ would be:

(12) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$

Plug-in equation (6):

(13) $\begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}\begin{pmatrix} + & + & + \\ + & + & + \\ + & + & + \end{pmatrix}\begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix} = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}\begin{pmatrix} + & - & + \\ + & - & + \\ + & - & + \end{pmatrix}$

$= \begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix} = \begin{pmatrix} + & + & + \\ + & + & + \\ + & + & + \end{pmatrix}$, from which we conclude

(14) $C_{12} = -C_{12} = 0$

$C_{21} = -C_{21} = 0$

$C_{23} = -C_{23} = 0$

$C_{32} = -C_{32} = 0$

By performing the transformation $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$, we find that $C_{13} = -C_{13} = 0$

$C_{31} = -C_{31} = 0$

Thus we have shown that

(15) $\mathbb{C}(100) = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{bmatrix}$; also $\mathbb{C}(010) = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{bmatrix}$

and $\mathbb{C}(001) = \begin{bmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{bmatrix}$

Now we want to find $\hat{C}_{\alpha\alpha'}(q)$. Take nearest neighbors along axis with q propagating along the [100] direction. From (1), we get

(16) $\hat{\mathbb{C}}(q) = -2 \sum_{-1}^{1}{}' \mathbb{C}(l) \sin^2 \frac{qla}{2} = -4\,\mathbb{C}(100) \sin^2 \tfrac{1}{2} qa$

which gives: from (2):

(17) $\begin{bmatrix} -4\alpha \sin^2 \frac{1}{2} qa & 0 & 0 \\ 0 & -4\beta \sin^2 \frac{1}{2} qa & 0 \\ 0 & 0 & -4\beta \sin^2 \frac{1}{2} qa \end{bmatrix} = \hat{\mathbb{C}}(q)$

(18) $\begin{bmatrix} -\frac{4\alpha}{M} \sin^2 \frac{1}{2} qa - \omega^2 & 0 & 0 \\ 0 & -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa - \omega^2 & 0 \\ 0 & 0 & -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa - \omega^2 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$

The Determinant of the matrix must, of course, be zero. We then get:

(19) (a) $\omega^2 = -\frac{4\alpha}{M} \sin^2 \frac{1}{2} qa$

(b) $\omega^2 = -\frac{4\beta}{M} \sin^2 \frac{1}{2} qa$ for eigenvalues

For eigenvectors: Substitute eigenvalue one at a time back into (18): For (19) (a):

(20) $\begin{bmatrix} 0 & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$ It is apparent that e_2 and e_3 are zero, while e_1 may be finite.

$\begin{bmatrix} e_1 \\ 0 \\ 0 \end{bmatrix}$ will give a longitudinal wave

Using eigenvalue (19) (b):

(21) $\begin{bmatrix} A & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$, we will get $\begin{bmatrix} 0 \\ e_2 \\ e_3 \end{bmatrix}$ because the transverse mode has two directions. It is to be noted that we may only talk about longitudinal and transverse modes in high symmetry crystals.

Another simplifying assumption: look at long wavelengths, $\omega \sim q$, in a continuum. Measure elastic constants to match to coefficients. Sometimes we have more coefficients than constants. We sometimes search for a model to simulate reality. Use the central force model.

Central Force Model: Force between two atoms depends only on the distance between them.

Then:

(22) $V = \sum_l \varphi_x(r) = \frac{1}{2} k \sum_l (r-l)^2$ assuming a spring type relationship and nearest neighbor case

$$= \sum_l \left[\varphi(l) + \sum_\alpha \left(\frac{\partial \varphi}{\partial x_\alpha}\right)_{eq.} (x_\alpha - l_\alpha) + \frac{1}{2} \sum_{\alpha\alpha'} \left(\frac{\partial^2 \varphi}{\partial x_\alpha \partial x_{\alpha'}}\right)_{eq.} (x_\alpha - l_\alpha)(x_{\alpha'} - l_{\alpha'}) + \cdots \right.$$

with the usual assumptions about equilibrium. It can be shown that:

(23) $C_{\alpha\alpha'}(l) = \left(\frac{\partial^2 \varphi}{\partial x_\alpha \partial x_{\alpha'}}\right)_{eq.} = -k \frac{l_\alpha l_{\alpha'}}{l^2}$ this relation can be used to set up matrices

Look at [100] direction, $\alpha = 1, 2, 3$

$\therefore \quad C(l) = \begin{bmatrix} x & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$; thus reducing two force constants to one.

Important to remember the definition of the central force model.

This concludes the classical approach to lattice vibrations.

RESUME' OF CLASSICAL THEORY OF LATTICE VIBRATIONS

Hamiltonian (KE + V)

↓

Expand V → harmonic & anharmonic

↓

Hamilton's Equation of Motion

↓

Symmetry Properties of C's

- Vanishing of Forces under rigid displacements
- Periodicity of Lattice Fourier Analysis: $u_\ell \sim e^{i\vec{q}\cdot\vec{R}_\ell}$ Separation into different q's
- $C_{\alpha\alpha'}(q) = C_{\alpha'\alpha}(q)$ Hermiticity
  - ↓
  - ω's are real
- $C_{\alpha\alpha'}(q) = C_{\alpha\alpha'}(-q)$
  $\omega(-q) = \omega(q)$
  $e(q,j) = e^*(-q,j)$
  Displacement Real
  - ↓
  - Small q: $\omega \sim q$

} Time Reversibility

↓

Periodic Boundary Conditions

↓

(1) q's discrete
(2) not unique
(3) No. of q's = No. of Degrees of freedom

- Density of States in "q" space $\left(\frac{V}{8\pi^3}\right)$
- Brillouin Zone
  (1) Contains all about q's
  (2) Translational symmetry
  (3) Inversion symmetry

↓

Evaluate C's for specific systems: all symmetry properties

↓

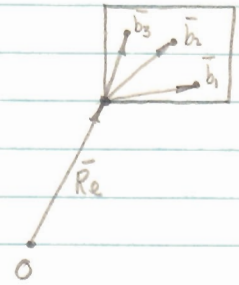
Specific Force Models

↓

$\rho(\omega)$: Density of States

Quantization of Lattice Vibrations

We previously considered only one atom/unit cell, now we will do the general case: Consider the following diagram for the unit cell:



$\bar{R}_\ell$ is the distance from some arbitrary origin to the origin of the unit cell. The $\bar{b}_i$'s are the vectors to the individual atoms in the unit cell from the unit cell origin.

For one atom/unit cell, the Hamiltonian in tensor terminology is:

$$(24)\quad H = V_0 + \frac{1}{2M}\sum_{\ell} \bar{p}_\ell \cdot \bar{p}_\ell + \frac{1}{2}\sum_{\ell\ell'} \bar{u}_\ell^{\,T}\, \mathbb{C}(\ell-\ell')\, \bar{u}_{\ell'}$$

In general:

$$(25)\quad H = V_0 + \frac{1}{2}\sum_{\ell,b} \frac{1}{M_b}\, \bar{p}_{\ell,b} \cdot \bar{p}_{\ell,b} + \frac{1}{2}\sum_{\ell\ell',bb'} \bar{u}_{\ell b}^{\,T}\, \mathbb{C}(\ell b, \ell' b')\, \bar{u}_{\ell' b'}$$

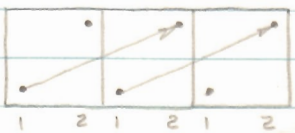
LECTURE VI 10-7-60

Quantum Mechanical Case

Our procedure will be to work with equation I(25) and combine it with the usual commutation rule, viz.,

$$(1)\quad [\bar{u}_{\ell b}, \bar{p}_{\ell b}] = i\hbar\, \delta_{\ell\ell'}\, \delta_{bb'}\, \mathbb{I}$$

The periodicy is such that $\ell-\ell'$ is the same when a particular atom in the unit cell is specified. Thus we have:



$$(2)\quad \mathbb{C}(\ell b, \ell' b') = \mathbb{C}(\ell-\ell', bb')$$

As the force tensor is really a mixed partial derivative, we may also write:

(3) $C_{\alpha\alpha'}(l-l', bb') = C_{\alpha'\alpha}(l'-l, b'b)$

The equation of motion is:

(4) $M\ddot{u}_{lb\alpha} + \sum_{\alpha' l' b'} C_{\alpha\alpha'}(l-l', bb')\, u_{l'b'\alpha'} = 0$

Under rigid displacement:

(5) $\sum_{l'b'} C_{\alpha\alpha'}(l', bb') = 0$

Now, we would like to transform our equations to "q" space. To do this, we need two theorems.

I. $\frac{1}{G^3}\sum_{l} e^{i(\bar{q}-\bar{q}')\cdot\bar{R}_l} = \delta_{q,q'+K}$

II. $\frac{1}{G^3}\sum_{q} e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = \delta_{ll'}$

Proof: $\bar{q} = \frac{2\pi}{G}\left(q_1\bar{b}_1 + q_2\bar{b}_2 + q_3\bar{b}_3\right)$

$\bar{R}_l - \bar{R}_{l'} = l_1\bar{a}_1 + l_2\bar{a}_2 + l_3\bar{a}_3$

$\therefore\ e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = e^{\frac{2\pi i}{G}(l_1q_1 + l_2q_2 + l_3q_3)}, \quad 0 \le q_i \le G-1$

$\frac{1}{G^3}\sum_{q} e^{i\bar{q}\cdot(\bar{R}_l-\bar{R}_{l'})} = \left[\frac{1}{G}\sum_{q_i=0}^{G-1} e^{\frac{2\pi i l_i q_i}{G}}\right]^3$

$= \left[\frac{1}{G}\,\frac{1-e^{i2\pi l_i}}{1-e^{i2\pi l_i/G}}\right]^3 = \delta_{ll'}$

$= \begin{cases} 0 & \text{if } l_i \neq 0 \\ 1 & \text{if } l_i = 0 \end{cases} = \delta_{ll'}$

We will use these theorems later.

We may define the following two transforms from coordinate space to q space:

(6) $\bar{u}_{\ell b} = \frac{1}{G^{3/2}} \sum_{q} \hat{\bar{u}}_{qb} e^{i q \cdot R_\ell}$

(7) $\bar{p}_{\ell b} = \frac{1}{G^{3/2}} \sum_{q} \hat{\bar{p}}_{qb} e^{-i q \cdot R_\ell}$, the minus sign being taken for later convenience.

Going back to the Hamiltonians; we shall first consider the kinetic energy term; using equation (7):

(8) $T = \frac{1}{2G^3} \sum_{\ell b} \frac{1}{M_b} \sum_{qq'} \hat{p}_{qb} \hat{p}_{q'b} e^{-i(\bar{q}+\bar{q}')\cdot \bar{R}_\ell}$

$= \frac{1}{2} \sum_{b,qq'} \frac{1}{M_b} \hat{p}_{qb} \hat{p}_{q'b} \delta_{q,-q'}$ (by Theorem I)

$= \frac{1}{2} \sum_{bq} \frac{1}{M_b} \hat{p}_{qb} \hat{p}_{-q,b}$ (removing Kronecker Delta)

Considering the potential energy term and applying equation (6):

(9) $V = \frac{1}{2G^3} \sum_{\substack{\ell\ell' \\ bb' \\ qq'}} \hat{\bar{u}}_{qb} \mathbb{C}(\ell-\ell', bb') \hat{\bar{u}}_{q'b'} e^{i(\bar{q}\cdot\bar{R}_\ell + \bar{q}'\cdot\bar{R}_{\ell'})}$

Now: $e^{i(\bar{q}\cdot\bar{R}_\ell + q'\cdot\bar{R}_\ell)} = e^{i\bar{q}\cdot(\bar{R}_\ell - \bar{R}_{\ell'})} e^{i(\bar{q}+\bar{q}')\cdot\bar{R}_{\ell'}}$

Define: $\bar{R}_\ell - \bar{R}_{\ell'} = \bar{R}_h$

(10) $V = \frac{1}{2G^3} \sum_{\substack{h\ell' \\ bb' \\ qq'}} \bar{u}_{qb} \mathbb{C}(h, bb') e^{i\bar{q}\cdot\bar{R}_h} \underbrace{e^{i(\bar{q}+\bar{q}')\cdot\bar{R}_{\ell'}}}_{G^3 \delta_{q,-q'} \text{ (by Theorem I)}} \bar{u}_{q'b'}$

$= \frac{1}{2} \sum_{\substack{bb' \\ q'}} \left[\underbrace{\sum_{h} \mathbb{C}(h, bb') e^{-i\bar{q}'\cdot\bar{R}_h}}_{\text{Fourier Invert}} \right] \bar{u}_{-q',b} \bar{u}_{q'b}$ (eliminating $\delta_{q,-q'}$)

$= \frac{1}{2} \sum_{\substack{bb' \\ q'}} \bar{u}_{-q'b} \mathbb{C}(q', bb') \bar{u}_{q'b}$

Because of the traveling waves in the "q" space, we find only a change in the sign of the exponent of e for the different directions:

(11) $p_{-q,b} = p^*_{qb}$
$u_{-qb} = u^*_{qb}$

and from the Fourier inversion performed to get (10):

(13) $\tilde{C}(q', bb') = \sum_n C(n, bb')\, e^{-i\bar{q}'\cdot\bar{R}_n}$

Using (11) on (10), we finally get the complete Hamiltonian:

(14) $H = \sum_q \left[\frac{1}{2} \sum_b \frac{1}{M_b} p^*_{qb} p_{qb} + \frac{1}{2} \sum_{bb'} u^*_{qb} C(q, bb') u_{qb} \right]$

$= \sum_q H_q$, changing $q' \to q$ in the potential energy term

We now examine the symmetry of the tensor C:

(15) a. $C^*_{\alpha\alpha'}(-q, bb') = C_{\alpha\alpha'}(q, bb')$ Time Reversal

b. $C^*_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(q, b'b)$ Hermiticity

c. $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q, b'b)$ From above properties

What are the commutation relations in "q" space? Multiply equation (6) by $\sum_l e^{-i\bar{q}'\cdot\bar{R}_l}$:

(16) $\sum_l \bar{u}_{qb} e^{-i\bar{q}'\cdot\bar{R}_l} = \frac{1}{G^{3/2}} \sum_q u_{qb} \sum_l e^{i(\bar{q}-\bar{q}')\cdot\bar{R}_l}$

$= \frac{1}{G^{3/2}} \cdot G^3 \sum_q u_{qb}\, \delta_{q,q'}$ (by Theorem I)

$= G^{3/2} u_{q'b}$; Finally:

(17) $u_{q'b} = \frac{1}{G^{3/2}} \sum_l \bar{u}_{lb} e^{-i\bar{q}'\cdot\bar{R}_l}$

In a similar manner, we find for the momentum:

$$(18)\quad p_{q'b} = \frac{1}{G^{3/2}} \sum_{l} p_{lb}\, e^{i\bar{q}'\cdot\bar{R}_l}$$

On multiplying (17) and (18) together, we may factor out all terms that commute and get:

$$(19)\quad \left[u_{qb}, p_{q'b'}\right] = \frac{1}{G^3} \sum_{ll'} e^{i(\bar{q}'\cdot\bar{R}_{l'} - \bar{q}\cdot\bar{R}_l)} \left[u_{lb}, p_{l'b'}\right]$$

$$= \frac{i\hbar}{G^3} \sum_{ll'} \delta_{ll'}\,\delta_{bb'}\, \mathbb{1}\, e^{i(\bar{q}'\cdot\bar{R}_{l'} - \bar{q}\cdot\bar{R}_l)}$$

$$= \frac{i\hbar}{G^3} \sum_{l} \delta_{bb'}\, \mathbb{1}\, e^{i(\bar{q}'-\bar{q})\cdot\bar{R}_l}$$

$$= i\hbar\,\delta_{bb'}\,\delta_{qq'}\,\mathbb{1} \quad \text{(by Theorem I)}$$

Thus we see that the commutation rules are analogous in "q" space to those in co-ordinate space. We now must make use of the Heisenberg equation of motion (from Schiff, Sec. 23), viz.,

$$(20)\quad i\hbar \frac{\partial F}{\partial t} = [F, H]$$

in which F is a quantum operator (coordinates or momentum, etc.) and H is the Hamiltonian of the system. We would like to find $\dot{u}$ and then $\dot{p}$. We see from the Hamiltonian (14) that if we choose u_{qb} as our quantum operator, it will commute with all terms of the Hamiltonian except the kinetic energy. Thus, we have:

$$(21)\quad i\hbar\,\dot{u}_{qb} = \left[u_{qb}, \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} p_{-q'b'}\, p_{q'b'}\right]$$

$$= \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} \left(u_{qb}\, p_{-q'b'}\, p_{q'b'} - p_{-q'b'}\, p_{q'b'}\, u_{qb}\right)$$

We now apply the commutation rules of equation (1).

(22) $u_{qb}\, p_{-q'b'}\, p_{q'b'} = (p_{-q'b'}\, u_{qb} + i\hbar\, \delta_{q,-q'}\, \delta_{bb'})\, p_{q'b'}$

(23) $u_{qb}\, p_{-q'b'}\, p_{q'b'} = p_{q'b'}(p_{-q'b'}\, u_{qb} + i\hbar\, \delta_{q,-q'}\, \delta_{bb'}) + i\hbar\, \delta_{q,-q'}\, \delta_{bb'}\, p_{qb}$

Substituting into equation (21), we finally obtain:

(24) $i\hbar\, \dot{u}_{qb} = \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} (2 i\hbar\, \delta_{q,-q'}\, \delta_{bb'})\, p_{q'b'}$

(25) $\dot{u}_{qb} = \frac{p_{qb}}{M_b}$

Equation (25) is just the classical result which one might have expected as we have only operated on the classical kinetic energy term of the Hamiltonian.

The next operation is to find: $M_b \ddot{u}_{qb} = \dot{p}_{qb}$
The proper Hiesenberg equation of motion is:

(26) $i\hbar\, \dot{p}_{qb} = [p_{-qb}, H]$

in which we will evaluate the potential energy part of the term (Hamiltonian).

LECTURE VII 10-10-60

Continuation of the Quantum Mechanical Case:
The following equations are given from before:

(1) $H = \frac{1}{2} \sum_q \left[\sum_b p^{\dagger}_{qb}\, p_{qb} + \sum_{bb'} u^{\dagger}_{qb}\, C(q, bb')\, u_{qb'} \right]$

(2) $u_{-qb} = u^{\dagger}_{qb}$
$p_{-qb} = p^{\dagger}_{qb}$

(3) $[u_{qb}, p_{q'b'}] = \delta_{qq'}\, \delta_{bb'}\, \mathbb{I}\, i\hbar$

(4) $\tilde{C}(q, bb') = \sum_l C(l, bb')\, e^{-iq \cdot R_l}$

(5) $C^{*}_{\alpha\alpha'}(-q, bb') = C_{\alpha\alpha'}(q, bb')$

(6) $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q, b'b)$

(7) $i\hbar \frac{\partial F}{\partial t} = [F, H]$

Take F to be u_{qb}, we get:

(8) $\dot{u}_{qb} = \frac{1}{M_b} p_{-qb}$, or, $M_b \ddot{u}_{qb} = \dot{p}_{-qb}$

Take F to be p_{-qb}, we then have from (6) and (7):

(9) $i\hbar \dot{p}_{-qb} = \left[p_{-qb} , \frac{1}{2} \sum_{b'b''} u_{-q'b'} C(q'; b'b'') u_{q'b''} \right]$

The following rules can be shown through manipulations in operator algebra:

(10) $[B, A_1 A_2] = -[A_1, B] A_2 - A_1 [A_2, B]$

Let $B \to p_{-qb}$, $A_1 \to u_{-q'b'}$, $A_2 \to u_{q'b''}$

Now:

(11) $i\hbar \dot{p}_{-qb} = -\frac{1}{2} \sum_{q' b'b''} \left\{ \underbrace{\left[u_{-q'b'}, p_{-qb}\right]}_{i\hbar \delta_{qq'}\delta_{bb'}} C(q'; b'b'') u_{q'b''} + u_{-q'b'} C(q'; b'b'') \underbrace{\left[u_{q'b''}, p_{-qb}\right]}_{i\hbar \delta_{qq'}\delta_{bb''}} \right\}$

$= -\frac{1}{2} i\hbar \sum_{b''} C(q, bb'') u_{qb''} - \frac{1}{2} i\hbar \sum_{b'} u_{qb'} C(-q, b'b)$

$= -i\hbar \sum_{b'} C(q, bb') u_{qb'}$

Because:

(12) $\left\{ \sum_{b'} u_{qb'} C(-q, b'b) \right\}_{\alpha} = \sum_{b'\alpha'} u_{qb'\alpha'} C_{\alpha'\alpha}(-q, b'b)$

$= \sum_{b\alpha'} C_{\alpha\alpha'}(q, bb') u_{qb'\alpha'} = \left\{ \sum_{b'} C(q, bb') u_{qb'} \right\}_{\alpha}$

The final result from (8) and (11) is:

$$(13)\quad M_b \ddot{u}_{qb} + \sum_{b'} C(q,bb')\, u_{qb'} = 0$$

which is the classical equation of motion except that the u's are now operators.

We now define a solution:

$$(14)\quad u_{qb} = \frac{1}{\sqrt{M_b}}\, \bar{e}(q,b)\, e^{i\omega t}\, u_q$$

where u_q is a quantum mechanical factor. Substitute this into the equation of motion:

$$(15)\quad \sum_{b'\alpha'} \left\{ \frac{1}{\sqrt{M_b M_{b'}}} C_{\alpha\alpha'}(q,bb') - \omega^2(q)\, \delta_{bb'} \delta_{\alpha\alpha'} \right\} \bar{e}_{\alpha'}(q,b')\, u_q = 0$$

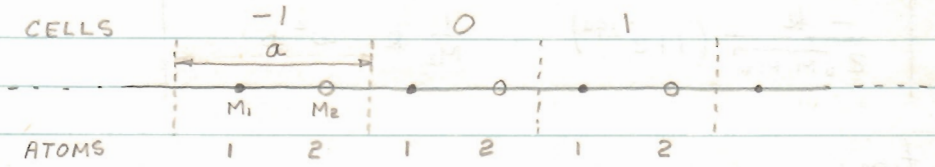
This looks like the corresponding equation for a unit cell without a basis. How many solutions are there? The upper limit on α' is three. Assume that there are k atoms per unit cell, then the upper limit on b' is k. So there are $3kG^3$ number of solutions which is also equal to the degrees of freedom of the system. Label each solution by j, q; that is, we have $\omega(q,j)$, $\bar{e}(q,j)$, u_{qj}. We also have an orthogonality-normality relationship between the $\bar{e}$'s similar to that before.

$$(16)\quad \sum_{b} \bar{e}^*(qbj) \cdot \bar{e}(qbj') = \delta_{jj'}$$

Previously, there was no summation over b.

Example: The Linear Di-atomic Chain:

We will ignore M_q and assume only nearest neighbor forces:



From rigid displacement considerations, we have

(17) $\sum_{\ell bb'} C(\ell, bb') = 0$

For atom #1 of cell #0:

(18) $C(0,11) + C(0,12) + C(-1,12) = 0$

For atom #2 of cell #0:

(19) $C(0,21) + C(0,22) + C(1,21) = 0$

By symmetry considerations and equations (17) and (19):

(20) $C(0,12) = C(-1,12) = -\frac{1}{2} C(0,11)$
$C(0,21) = C(1,21) = -\frac{1}{2} C(0,22)$

Since $C(\ell, bb') = C(-\ell, b'b)$

(21) $C(0,12) = C(0,21) \Rightarrow C(0,11) = C(0,22) = k$ (a constant)

From equation (4):

(22) $\hat{C}(q,11) = C(0,11) = k$
$\hat{C}(q,22) = C(0,22) = k$
$\hat{C}(q,12) = C(0,12) + C(-1,12)\, e^{-iq(-a)} = -\frac{1}{2} k \left[e^{iqa} + 1 \right]$
$\hat{C}(q,21) = C(0,21) + C(1,21)\, e^{-iq(+a)} = -\frac{1}{2} k \left[e^{-iqa} + 1 \right]$

We can check these against the symmetry relationships for Hermiticity.

Setting up the secular equation:

$$(23)\qquad \begin{vmatrix} \frac{1}{M_1}k-\omega^2 & -\frac{k}{2\sqrt{M_1M_2}}\left(1+e^{iqa}\right) \\ -\frac{k}{2\sqrt{M_1M_2}}\left(1+e^{-iqa}\right) & \frac{1}{M_2}k-\omega^2 \end{vmatrix} = 0$$

Upon solution:

$$(24)\qquad \omega^4-\left(\frac{1}{M_1}+\frac{1}{M_2}\right)k\omega^2+\frac{k^2}{M_1M_2}\left[1-\frac{1}{4}\left(1+e^{iqa}\right)\left(1+e^{-iqa}\right)\right]=0$$

$$\left(1+e^{iqa}\right)\left(1+e^{-iqa}\right) = 4\sin^2 \tfrac{1}{2}qa$$

$$(25)\qquad \omega^2(q)=\frac{1}{2}\frac{k}{M_1M_2}\left[(M_1+M_2)\pm\left\{(M_1+M_2)^2-4M_1M_2\sin^2\tfrac{1}{2}qa\right\}^{1/2}\right]$$

Consider the long wavelength approximation: $qa \ll 1$.
Then $\sin^2 \tfrac{1}{2}qa \approx \tfrac{1}{4}q^2a^2 \ll 1$ and

$$(26)\qquad \omega^2(q)=\tfrac{1}{2}k\frac{(M_1+M_2)}{M_1M_2}\left[1\pm\left(1-\frac{1}{2}\frac{M_1M_2}{(M_1+M_2)^2}q^2a^2\right)^{1/2}\right]$$

For the positive solution: ⊕

$$(27)\qquad \omega^2 \approx k\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\quad \text{[optical branch]}$$
(a finite constant)

For the negative solution: ⊖

$$(28)\qquad \omega^2=\frac{k}{4}\frac{q^2a^2}{M_1+M_2}\quad \text{[acoustical branch]}$$

Let us now consider the polarization vectors:
For the ⊕ solution:

$$(29)\qquad -\frac{k}{M_2}e_1-\frac{k}{\sqrt{M_1M_2}}e_2=0$$

$$(30)\qquad \frac{e_1}{e_2}=-\sqrt{\frac{M_2}{M_1}}=\sqrt{\frac{M_1}{M_2}}\frac{M_1}{M_2}\Rightarrow M_1\mu_1+M_2\mu_2=0$$

(from (14))

Physically, the optical branch gives the picture of molecular vibration of two atoms moving against each other or two sublattices moving rigidly against each other. In this branch, ω^2 has the form:

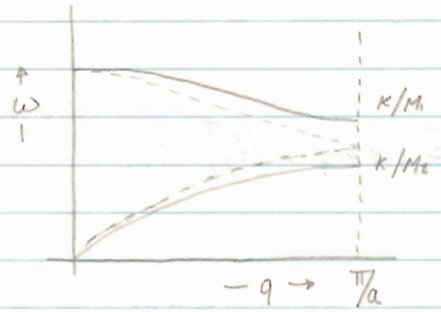
(31) $\omega^2 = A + B q^2$

Thus the group velocity $\frac{d\omega}{dq} = 0$, when $q = 0$ and the phase velocity $\frac{\omega}{q} = \infty$ at $q = 0$. The optical branch is so named because the opposed motion of ionic molecules in an $\mathcal{E}$ field to which case it corresponds.

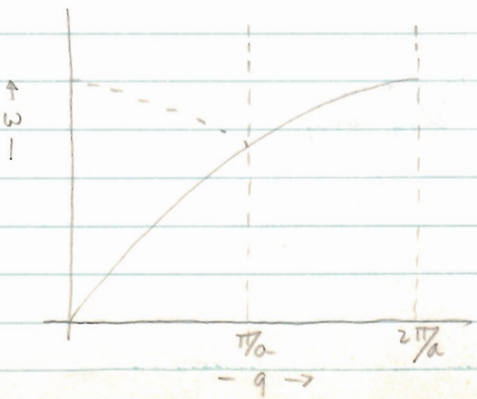
LECTURE VIII 10-14-60

Linear Diatomic Model: Continued:

(A) $\omega^2(q) = \frac{1}{2} \frac{k}{M_1 M_2} \left[(M_1 + M_2) \pm \sqrt{(M_1 + M_2)^2 - 4 M_1 M_2 \sin^2 \tfrac{1}{2} qa} \right]$



If $M_1 = M_2$, the problem reduces to the linear chain and the dotted line occurs in the graph. Why is there apparently an optical mode in the monatomic lattice? This can be explained in the fact the new unit cell has width $a/2$. Thus the new Brillouin zone is $2\pi/a$



Everything will be the same as before when the substitution $a \to \frac{a}{2}$ is made.

Return to Quantum Mechanical Considerations:

The object here will be to obtain a representation in occupation number space so as to quantize the lattice vibrations.

$$(1)\quad H = \frac{1}{2}\sum_{q}\left[\sum_{b}\frac{1}{M_b}p_{qb}^{\dagger}p_{qb} + \sum_{bb'}u_{qb}^{\dagger}\,C(q,bb')\,u_{qb'}\right]$$

with:

$$(2)\quad u_{qb} = \frac{1}{\sqrt{M_b}}\sum_{j}\bar{e}(qbj)\,u_{qj}$$

$$p_{qb} = \sqrt{M_b}\sum_{j}\bar{e}^{*}(qbj)\,p_{qj}$$

} Ignoring the time component or lumping it into the operator.

And the condition that:

$$(3)\quad \sum_{b}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj') = \delta_{jj'}$$

Substitute (2) and make use of (3) in to the Hamiltonian:

$$(4)\quad T = \sum_{b}\frac{1}{M_b}p_{qb}^{\dagger}p_{qb} = \sum_{b}\sum_{jj'}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj')\,p_{qj}^{\dagger}p_{qj'}$$

$$= \sum_{j}p_{qj}^{\dagger}p_{qj}$$

$$(5)\quad V = \sum_{bb'}\sum_{jj'}\frac{1}{\sqrt{M_bM_{b'}}}\bar{e}^{*}(qbj)\,C(q,bb')\,\bar{e}(qb'j')\,u_{qj}^{\dagger}u_{qj'}$$

Recall the secular equation:

$$(6)\quad \sum_{b'}\frac{1}{\sqrt{M_bM_{b'}}}C(q,bb')\,\bar{e}(qb'j') = \omega^2(qj)\,\bar{e}(qbj)$$

Then, upon substitution in (5):

$$(7)\quad V = \sum_{b}\sum_{jj'}\bar{e}^{*}(qbj)\cdot\bar{e}(qbj')\,\omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}$$

$$= \sum_{j}\omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}$$

Thus, finally:

$$(8)\quad H = \frac{1}{2}\sum_{qj}\left[P_{qj}^{\dagger}P_{qj} + \omega^2(qj)\,u_{qj}^{\dagger}u_{qj'}\right]$$

is the new Hamiltonian in terms of our quantum mechanical factors (operators) defined in equation VII (14), as part of the assumed solution.

We must inquire into the commutation rules between these operators. Multiply equations (2) by $\sum_b \bar{e}^*(qbj')$ and $\sum_b \bar{e}(qbj')$ and get:

$$(9)\quad u_{qj} = \sum_b \sqrt{M_b}\,\bar{e}^*(qbj)\cdot u_{qb}$$

$$P_{qj} = \sum_b \frac{1}{\sqrt{M_b}}\,\bar{e}(qbj)\cdot p_{qb}$$

Recall that:

$$(10)\quad [u_{qb\alpha}, p_{q'b'\alpha'}] = i\hbar\,\delta_{\alpha\alpha'}\delta_{bb'}\delta_{qq'}$$

Then, from (9) and (10):

$$(11)\quad [u_{qj}, P_{q'j'}] = \sum_{bb'}\sum_{\alpha\alpha'}\left[\sqrt{\frac{M_b}{M_{b'}}}\left\{\bar{e}_{\alpha}^*(qbj)\,u_{\alpha qb}\,e_{\alpha'}(q'b'j')\,p_{\alpha'q'b'} - e_{\alpha'}(q'b'j')\,p_{\alpha'q'b'}\,e_{\alpha}^*(qbj)\,u_{\alpha qb}\right\}\right]$$

$$= \sum_{bb'}\sum_{\alpha\alpha'}\sqrt{\frac{M_b}{M_{b'}}}\,e_{\alpha}^*(qbj)\,e_{\alpha'}(q'b'j')\left[u_{\alpha qb}, p_{\alpha'q'b'}\right] \quad (i\hbar\,\delta_{\alpha\alpha'}\delta_{bb'}\delta_{qq'})$$

$$= i\hbar\,\delta_{qq'}\sum_b\sum_{\alpha} e_{\alpha}^*(qbj)\,e_{\alpha}(qbj') = i\hbar\,\delta_{qq'}\delta_{jj'}$$

Therefore:

$$(12)\quad [u_{qj}, P_{q'j'}] = i\hbar\,\delta_{qq'}\delta_{jj'}, \text{ or, } [u_q, P_{q'}] = i\hbar\,\delta_{qq'}$$

Thus we have for the Hamiltonian:

(13) $$H = \frac{1}{2} \sum_q \left[P_q^\dagger P_q + \omega^2(q)\, u_q^\dagger u_q \right]$$

with $u_{-q}^\dagger = u_q$

$P_{-q}^\dagger = P_q$

which can be derived from equations (9) and considerations from previous lectures on the u's and e's.

Consider the following operators. We consider these because of their "interesting" properties which will soon be apparent.

(14) $$a_q = \frac{\imath}{\sqrt{2\hbar\omega_q}} P_q^\dagger + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q$$

$$a_q^\dagger = \frac{-\imath}{\sqrt{2\hbar\omega_q}} P_q + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q^\dagger$$

$$a_{-q}^\dagger = \frac{-\imath}{\sqrt{2\hbar\omega_q}} P_q^\dagger + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q$$

Manipulating:

(15) $$u_q = \sqrt{\frac{\hbar}{2\omega_q}} \left(a_q + a_{-q}^\dagger \right)$$

$$P_q^\dagger = \frac{\sqrt{2\hbar\omega_q}}{2\imath} \left(a_q - a_{-q}^\dagger \right)$$

then $P_q = \imath \sqrt{\frac{\hbar\omega_q}{2}} \left(a_q^\dagger - a_{-q} \right)$ and:

(16) $$\left[a_q, a_q^\dagger \right] = \frac{\imath}{\sqrt{2\hbar\omega_q}} \cdot \sqrt{\frac{\omega_q}{2\hbar}} \left\{ \underbrace{\left[P_{-q}, u_{-q} \right]}_{-\imath\hbar} - \underbrace{\left[u_q, P_q \right]}_{\imath\hbar} \right\}$$

$$= 1$$

$$\left[a_q, a_q \right] = 0$$

$$\left[a_q^\dagger, a_q^\dagger \right] = 0 \qquad \text{and in general:}$$

(17) $$\left[a_q, a_{q'}^\dagger \right] = \delta_{qq'}$$

Plugging in the Hamiltonian:

$$(18)\quad H = \frac{1}{2}\sum_q \left[\frac{1}{2}\hbar\omega_q \left(a_q - a_{-q}^\dagger\right)\left(a_q^\dagger - a_{-q}\right) + \omega_q^2 \frac{\hbar}{2\omega_q}\left(a_q^\dagger + a_{-q}\right)\left(a_q + a_{-q}^\dagger\right)\right]$$

$$= \frac{1}{2}\sum_q \frac{\hbar\omega_q}{2}\left[a_q a_q^\dagger + a_{-q}^\dagger a_{-q} + a_q^\dagger a_q + a_{-q}a_{-q}^\dagger\right]$$

We may change $-q$ to $+q$ because we know ω_q is even.

$$(19)\quad H = \frac{1}{2}\sum_q \hbar\omega_q \left(a_q a_q^\dagger + a_q^\dagger a_q\right)$$

$$= \sum_q \hbar\omega_q \left(a_q^\dagger a_q + \frac{1}{2}\right) \quad \text{by application of (16)}$$

Define $N_q \equiv a_q^\dagger a_q$; then:

$$(20)\quad H = \sum_q \hbar\omega_q \left(N_q + \frac{1}{2}\right)$$

We see that this bears a strong resemblence to the usual eigenvalue equation of the quantum mechanical harmonic oscillator.

Occupation Number Representation:

The object of choosing such a representation is to make N_q diagonal. The question is can one be found? At any rate, it must satisfy the commutation rules on the a's. We must prove:

$$(21)\quad \left[N_q, N_{q'}\right] = \left[a_q^\dagger a_q, a_{q'}^\dagger a_{q'}\right] = 0$$

which can be shown from the commutation rules for the a's. Also,

$$(22)\quad \left[a_q, N_q\right] = \left[a_q, a_q^\dagger a_q\right] = a_q$$

$$\left[a_q^\dagger, N_q\right] = \left[a_q^\dagger, a_q^\dagger a_q\right] = -a_q^\dagger$$

Suppose a wave function Ψ_λ describles the states in the occupation space. If:

(23) $N_q \Psi_\lambda = \lambda \Psi_\lambda$

then $a_q \Psi_\lambda$ is an eigenfunction of $\lambda - 1$
also $a_q^\dagger \Psi_\lambda$ is an eigenfunction of $\lambda + 1$
Proof:

$$N_q (a_q \Psi_\lambda) = (a_q N_q - a_q) \Psi_\lambda = (\lambda - 1)(a_q \Psi_\lambda)$$
$$N_q (a_q^\dagger \Psi_\lambda) = (a_q^\dagger N_q + a_q^\dagger) \Psi_\lambda = (\lambda + 1)(a_q^\dagger \Psi_\lambda)$$

LECTURE IX 10-17-60

Occupation Number Representation:

(1) $H = \sum_q \hbar \omega_q (N_q + \frac{1}{2})$; $N_q = a_q^\dagger a_q$

where q is taken to be the sum on q and γ.
Recall:

(2) $[a_q, a_{q'}^\dagger] = \delta_{qq'}$

$[a_q, a_q] = [a_q^\dagger, a_q^\dagger] = 0$

$[N_q, N_{q'}] = 0$ so diagonal representation is possible.

Also:

(3) $[a_q, N_q] = a_q$

$[a_q^\dagger, N_q] = -a_q^\dagger$

We now want to show that N_q's have eigenvalues which are either positive integers or zero. Now:

(4) $N_q (a_q^m \Psi_\lambda) = (\lambda - m)(a_q^m \Psi_\lambda)$, By continuous application of the proof for equation VIII (23).

There are two possibilities that preclude positive integers or zero for the eigenvalues.

1) $\lambda - m$ can be negative
2) one of the Ψ's vanishes

We can eliminate (1) because N_q is a positive, semi-definite number, since:

(5) $\langle N_q \rangle = (\Psi_\mu, a_q^\dagger a_q, \Psi_\mu) = (a_q \Psi_\mu, a_q \Psi_\mu) = \mu (\Psi_\mu, \Psi_\mu) \geq 0,$

therefore $\mu \geq 0$

(2) can be overcome by defining:

(6) $a_q \Psi_0 = 0 \quad , \therefore \lambda_0 = 0$

Now from the above considerations and the proof of equation VIII (23), we see that the states differ only by positive integers or zero.

Recognizitions:

Ψ_0 is the vacuum state : no particles
$N_q (a_q^\dagger \Psi_0) = 1 \cdot a_q^\dagger \Psi_0$, $\therefore$ one particle
Thus $a_q^\dagger$ are "creation" operators
We can then see that a_q are "annihilation" operators.
Therefore, we can associate $\lambda = n_q$, the number of particles and we can say:

(7) $N_q \Psi_{n_q} = n_q \Psi_{n_q}$

We can now find the expectation energy:

(8) $\langle E \rangle = \sum_q \hbar \omega_q \left(n_q + \frac{1}{2}\right) = (\Psi_{n_q}, E, \Psi_{n_q}) = \langle n_q | H | n_q \rangle$

as can be seen because $n_q = \int \Psi_{n_q}^* N_q \Psi_{n_q} \, dq$ (no!)

We can thus associate particles, called phonons, with the energy $\hbar \omega_q$.

The zero point energy is $\frac{1}{2}\sum_q \hbar\omega_q$. In field theory, this quantity is ∞, but finite in a solid because we sum over a number of finite q states.

Find the Matrix Elements:

We introduce the Dirac notation:

$$\langle n_{q'} | a_q | n_q \rangle = (\psi_{n_{q'}}, a_q \psi_{n_q})$$

$$\langle n_{q'} | a_q^\dagger | n_q \rangle = (\psi_{n_{q'}}, a_q^\dagger \psi_{n_q})$$

Consider:

$$(9)\quad \langle n_{q'} | [a_q, N_q] | n_q \rangle = \sum_{q''} \{ \langle n_{q'} | a_q | n_{q''} \rangle \langle n_{q''} | N_q | n_q \rangle - \langle n_{q'} | N_q | n_{q''} \rangle \langle n_{q''} | a_q | n_{q'} \rangle \}$$

Now $\langle n_{q''} | N_q | n_q \rangle = n_q \delta_{qq''}$

$\langle n_{q'} | N_q | n_{q''} \rangle = n_{q'} \delta_{q'q''}$

} because N_q is a diagonal

and $[a_q, N_q] = a_q$

Therefore:

$$(10)\quad (n_q - n_{q'}) \langle n_{q'} | a_q | n_q \rangle = \langle n_{q'} | a_q | n_q \rangle \quad \text{or}$$

$$(11)\quad (n_q - n_{q'} - 1) \langle n_{q'} | a_q | n_q \rangle = 0$$

Now, it is seen that $\langle n_{q'} | a_q | n_q \rangle$ vanishes unless $n_{q'} = n_q - 1$. Thus the matrix elements are:

$$(12)\quad \langle n_q - 1 | a_q | n_q \rangle$$

Also; in the same manner:

$$(13)\quad \langle n_{q'} | [a_q^\dagger, N_q] | n_q \rangle = \langle n_{q'} | a_q^\dagger | n_q \rangle (n_q - n_{q'})$$

$$= - \langle n_{q'} | a_q^\dagger | n_q \rangle$$

Thus $(n_q - n_{q'} + 1)\langle n_{q'}|a_q^\dagger|n_q\rangle = 0$, and the matrix element is non vanishing only if $n_{q'} = n_q + 1$ and our elements are given by:

(14) $\langle n_q + 1|a_q^\dagger|n_q\rangle$

Now:

(15) $\langle n_q|a_q^\dagger a_q|n_q\rangle = \langle n_q|a_q^\dagger|n_q - 1\rangle\langle n_q - 1|a_q|n_q\rangle = n_q$

with $\langle n_q|a_q^\dagger|n_q - 1\rangle = (\psi_{n_q}, a_q^\dagger \psi_{n_q - 1}) = (a_q \psi_{n_q}, \psi_{n_q - 1})$

$= (\psi_{n_q - 1}, a_q \psi_{n_q})^* = \langle n_q - 1|a_q|n_q\rangle^*$

Thus:

(16) $n_q = |\langle n_q - 1|a_q|n_q\rangle|^2$

and $\langle n_q - 1|a_q|n_q\rangle = e^{i\varphi}\sqrt{n_q}$

We choose the phase factors to be one because n_q's are separated by one. Once again:

(17) $\langle n_q|a_q a_q^\dagger|n_q\rangle = \langle n_q|a_q|n_q + 1\rangle\langle n_q + 1|a_q^\dagger|n_q\rangle = |\langle n_q + 1|a_q^\dagger|n_q\rangle|^2$

$\langle n_q|1 + a_q^\dagger a_q|n_q\rangle = n_q + 1$

Through the same argument:

(18) $\langle n_q + 1|a_q^\dagger|n_q\rangle = \sqrt{n_q + 1}$

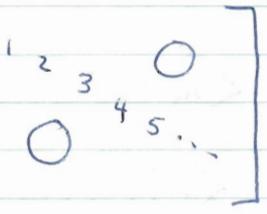
We may now describe these operator matrices in occupation space.

$a_q =$

	0	1	2	3	4	...
1	0	$\sqrt{1}$	0	0	0	...
2	0	0	$\sqrt{2}$	0	0	...
3	0	0	0	$\sqrt{3}$	0	...
4	0	0	0	0	$\sqrt{4}$	...
⋮	⋮	⋮	⋮	⋮	⋮	

$a_q^\dagger =$

	0	1	2	3	4	...
1	0	0	0	0	0	...
2	$\sqrt{1}$	0	0	0	0	...
3	0	$\sqrt{2}$	0	0	0	...
4	0	0	$\sqrt{3}$	0	0	...
⋮	⋮	⋮	⋮	⋮	⋮	

$\therefore N_q =$ 

We have been using only one direction of q or value of q. The total wave function is $\prod_q |n_q\rangle$

Having completed this analysis, we may now return to the meaning of u_{lb}.

Originally:

$$u_{lb} = G^{-3/2} \sum_q u_{qb}\, e^{i\bar{q}\cdot\bar{R}_l}$$

$$u_{qb} = \frac{1}{\sqrt{M_b}} \sum_j \bar{e}(qbj)\, \mathcal{U}_{qj}$$

$$\mathcal{U}_{qj} = \sqrt{\frac{\hbar}{2\omega_{qj}}}\left(a_{qj} + a^\dagger_{-qj}\right)$$

Therefore:

$$(19)\quad u_{lb} = \sum_{qj} \left(\frac{\hbar}{2 M_b G^3 \omega_{qj}}\right)^{1/2} \bar{e}(qbj)\left(a_{qj} + a^\dagger_{-qj}\right) e^{i\bar{q}\cdot\bar{R}_l}$$

It will be more convenient if we change $q \to -q$ which we can do because $\bar{e}(-q) = \bar{e}^*(q)$ and $\omega(-q) = \omega(q)$. Then:

$$(20)\quad u_{lb} = \sum_{qj}' \left[\frac{\hbar}{2 M_b G^3 \omega_{qj}}\right]^{1/2} \left[\bar{e}(q b_j) a_{qj} e^{i\bar{q}\cdot\bar{R}_l} + \bar{e}^*(q b_j) a_{qj}^\dagger e^{-i\bar{q}\cdot\bar{R}_l}\right]$$

This is the result of our whole lattice vibration study. What has been done is to describe the lattice displacements in terms of creation and annihilation operators. This is useful in phonon-electron interactions and permits the discussion of scattering between phonons and electrons.

Application to Specific Heats:

We take:

$$(21)\quad E(qj) = \sum_{qj}' \hbar\omega_{qj}\left(n_{qj} + 1/2\right)$$

The specific heat is that amount of heat which when added to a gram of a substance raises its temperature $1^\circ K$.

$$(22)\quad C_v = \left(\frac{\partial Q}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v \;; \quad dE = TdS + PdV,\ dV = 0$$

$$(23)\quad C_v = \frac{\partial E}{\partial T}$$

We make the assumption of neglecting changes in interatomic distances.

We now calculate the mean energy of the system at the temperature T:

$$(24)\quad \langle E(qj)\rangle = \sum_{qj}' \hbar\omega_{qj}\left(\langle n_{qj}\rangle + 1/2\right)$$

Introduce the following probability density function:

(25) P_n = probability of finding $n(q_j)$ particles in mode q_j

$$= \frac{e^{-\hbar\omega n/kT}}{\sum_{n=0}^{\infty} e^{-\hbar\omega n/kT}} \; ; \qquad \Sigma P_n = 1$$

Now: Define $\beta = 1/kT$

(26) $$\langle E_n \rangle = \sum_{n=0}^{\infty} P_n \hbar\omega (n + 1/2)$$

$$= \frac{\hbar\omega \sum_{n=0}^{\infty} n e^{-\beta\hbar\omega n}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}} + \frac{1}{2}\hbar\omega$$

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Specific Heats:

(1) $$\langle E(q_j) \rangle = \sum_{n=0}^{\infty} P_n \hbar\omega_{q_j} \left[n_{q_j} + \frac{1}{2} \right]$$

with

(2) $$P_n = \frac{e^{-\beta\hbar\omega n}}{\sum_n e^{-\beta\hbar\omega n}} \; ; \; \beta = 1/kT \; , \; \Sigma P_n = 1$$

(3) $$\langle E \rangle = \frac{\hbar\omega \sum_{n=0}^{\infty} (n+\frac{1}{2}) e^{-\beta\hbar\omega n}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}} = \frac{\hbar\omega \sum_{n=0}^{\infty} n e^{-\beta\hbar\omega n}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}} + \frac{1}{2}\hbar\omega$$

Consider:

$$(4)\quad -\frac{\partial}{\partial\beta}\ln\sum_n e^{-\beta\hbar\omega n} = \frac{\hbar\omega\sum_n e^{-\beta\hbar\omega n}\,n}{\sum e^{-\beta\hbar\omega n}}$$

$$= -\frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)^{-1} = -\left(1-e^{-\beta\hbar\omega}\right)\frac{\partial}{\partial\beta}\left(1-e^{-\beta\hbar\omega}\right)^{-1}$$

$$= \left(1-e^{-\beta\hbar\omega}\right)^{-1}\frac{\partial}{\partial\beta}\left(-e^{-\beta\hbar\omega}\right) = \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$= \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}.$$ Therefore:

$$(5)\quad \langle E\rangle = \hbar\omega\left[\frac{1}{e^{\beta\hbar\omega}-1}+\frac{1}{2}\right];$$

$$\langle n\rangle = \frac{1}{e^{\beta\hbar\omega}-1}$$ or the Bose-Einstein distribution.

Total Energy:

$$(6)\quad E = U_0 + \sum_{q_j}\langle E(q_j)\rangle = U_0 + E_z + E_T$$

where U_0 is the potential energy of the lattice

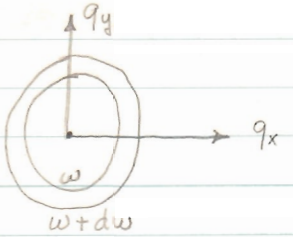
E_z is the zero point energy $= \frac{1}{2}\sum_{q_j}\hbar\omega(q_j)$

$$E_T = \sum_{q_j}\frac{\hbar\omega(q_j)}{e^{\beta\hbar\omega(q_j)}-1} = \sum_{q_j}\langle n(q_j)\rangle\hbar\omega(q_j)$$

Now $C_V = \frac{\partial E_T}{\partial T}$ and we must compute the sum over q_j but this is very difficult. However, the points in q space are very close, so we may make the approximation:

$$(7)\quad \sum_{q_j} \to \frac{V}{8\pi^3}\sum_j\int d^3q \to \sum_j\int d\omega_j\,\rho_j$$

where ρ is the density of states in q space.



Regarding the diagram, ρ is the number of states between the surfaces.

Now the distance between q and $q+dq$ is $\dfrac{d\omega}{|\nabla_q \omega|}$

The volume is $d\omega \int \dfrac{dS}{|\nabla_q \omega|}$

Thus $\sum_{q_j} \longrightarrow \dfrac{V}{8\pi} \sum_j \int_{\text{allowed volume}} d\omega_j \int \dfrac{dS}{|\nabla_q \omega|}$ where integration is carried out over the whole Brillouin zone

Then we see $\rho_j = \dfrac{V}{8\pi^3} \int \dfrac{dS}{|\nabla_q \omega|}$

Because $\nabla_q \omega$ is in the denominator, critical points occur when it vanishes as it is likely to do near the end of a Brillouin zone. See work by van Hove. Now:

(8) $E_T = \sum_j \int d\omega_j \, \rho_j \, \hbar\omega_j \, n_j(\omega_j)$

(9) $C_V = \dfrac{\partial \beta}{\partial T} \sum_j \int d\omega_j \, \rho_j \, \hbar\omega_j \, \dfrac{\partial n_j}{\partial \beta}$

$$\frac{\partial n_j}{\partial \beta} = \frac{-\hbar\omega \, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \; ; \; \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$$

(10) $\therefore \; C_V = \dfrac{1}{kT^2} \sum_j \int_0^\infty d\omega_j \left[\dfrac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1}\right]^2 e^{\beta\hbar\omega_j} \rho_j$

Introduce the dimensionless variable $z_j = \beta\hbar\omega_j$

$$(11)\quad C_V = k \sum_j \int_0^\infty dz_j \left[\frac{z_j}{e^{z_j}-1}\right]^2 e^{z_j} \rho_j$$

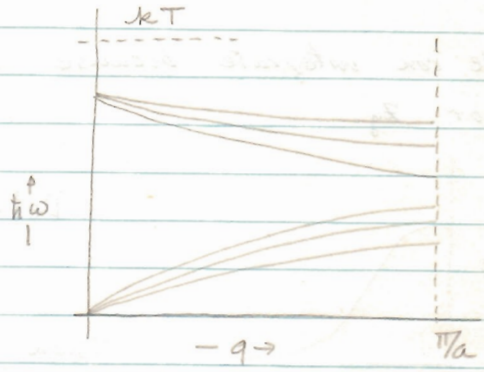
$$\left[\frac{z_j}{e^{z_j}-1}\right] = B(z_j)$$

There are two distinct cases for which we may evaluate (11) explicitly:

1) high temperatures: $kT \gg \hbar\omega_{max}$

$z_j \ll 1$

$B(z_j) \to 1$



Then:

$$C_V = k \sum_j \int_0^\infty d\omega_j \rho_j$$

$$\to k \sum_{q_j} = 3kG^3$$

↑ Take one atom per unit cell

which is the well-known law of Dulong and Petet

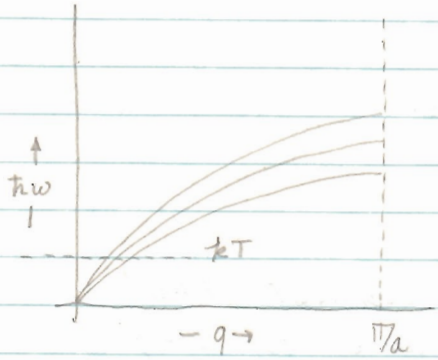
$E_T = 3G^3 kT$, each degree of freedom having energy kT.

2) Low temperature: kT of the order $\hbar\omega(q_j)$

where $\omega(q_j) = c_j(\theta,\varphi)\, q$

↑ sound velocity

Contributions to the integrand come only from $\omega(q_j)$ given by $c_j(\theta,\varphi)\, q$.



Now $\nabla_q \omega_j = c_j(\theta,\varphi)$

$dS = q^2 d\Omega$, Ω is solid angle.

Then: $\rho_j = \frac{V}{8\pi^3} \int \frac{q^2 d\Omega}{c_j(\theta,\varphi)}$

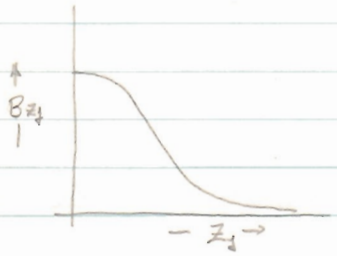
$$= \frac{V}{8\pi^3}\,\omega_j^2 \int \frac{d\Omega}{c_j^3(\theta,\varphi)} = \frac{V}{2\pi^2}\,\frac{\omega_j^2}{c_j^3}$$

taking $\frac{1}{c_j^3} = (4\pi)^{-1} \int \frac{d\Omega}{c_j^3(\theta,\varphi)}$

Then: $C_V = k \sum_j \int dz_j \, B(z_j) \, \frac{kT}{\hbar} \cdot \frac{V}{2\pi^2} \, \frac{\omega_j^2}{c_j^3}$

$$= k \left(\frac{kT}{\hbar}\right)^3 \frac{V}{2\pi^2} \sum_j \frac{1}{c_j^3} \underbrace{\int_0^\infty dz_j \, B(z_j) \, z_j^2}_{\frac{4\pi^2}{15}}$$

We can integrate because the integrand falls off at higher values for z_j.



Define: $\frac{1}{c_{eff}^3} = \frac{1}{3} \sum_j c_j^{-3}$

then $C_V = \frac{2\pi^2}{5} \frac{k^4 T^3 V}{\hbar^3 c_{eff}^3} \sim T^3$

Thus at low temperatures, the specific heat follows the Debye T^3 law.

Heuristic Discussion of Low Temperature Dependence:

$E_T \sim \int d^2q \, \hbar\omega_q \, n_q$

$\frac{\hbar\omega}{kT}$, $\omega \sim q$

In 3 dimensions: $q^2 dq \sim T^3$
2 dimensions: $q \, dq \sim T^2$ (graphite)
1 dimension: $dq \sim T$

We now use the Debye model to connect the two limiting cases. The model must reduce to $\omega \sim q$ at low temperatures and independence at high temperatures. At high temperatures, we assume only kT much higher than highest $\hbar\omega_{q\,max}$. Thus the assumption of a cutoff temperature seems likely.

Approximations in the Debye Model:

1) Continuum phenomenon: $\omega \sim q$, $\omega = cq$, where c is the velocity of sound, constant, and independent of direction, perhaps dependent on polarization.
2) Number of known modes are finite, that is, $q \leq q_{max}$
3) Replace the Brillouin zone by a sphere having the same number of states as the original zone.

Thus we require: $$\frac{V}{8\pi^3}\int_{q\leq q_{max}} d^3q = G^3 = \frac{V}{8\pi^3}\frac{4\pi}{3}q_{max}^3$$

This defines q_{max}: $$q_{max}^3 = \frac{G^3}{V}6\pi^2 = \frac{6\pi^2}{v_a}$$

where $v_a = \frac{V}{G^3}$ = volume of unit cell = a^3 for simple cubic.

in that case $$q_{max} = \frac{3.9}{a} = \frac{2\pi}{\lambda_{min}}$$

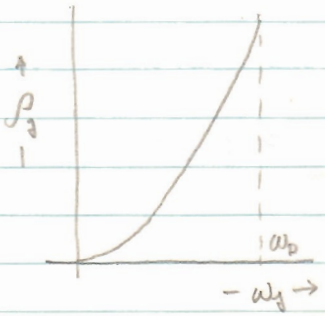
LECTURE XI 10-21-60

Debye Model Continuation:

1) $\omega_j = c_j q$
2) $q \leq q_{max} \longrightarrow \frac{V}{8\pi^3}\int d^3q = G^3$
3) Brillouin zone → Debye zone, $\therefore$ $q_{max}^3 = 6\pi\frac{G^3}{V}$

Define: $\omega_{Dj} = c_j q_{max}$

(1) $$\rho_j = \frac{V}{8\pi^3}\int \frac{dS}{|\nabla_q \omega|} = \frac{V}{8\pi^3}\frac{4\pi q^2}{c_j} = \frac{V}{2\pi^2}\frac{\omega_j^2}{c_j^3} = \frac{V}{2\pi^2}\left(\frac{\hbar}{T}\right)^2\frac{z_j^2}{c_j^3}\ ;\ z_j \leq z_{jD}$$
$$= 0\ ,\ z_j \geq z_{jD}$$



Debye Distribution

(2) $C_V = k \sum_j \int_0^\infty dz_j \; B(z_j) \left(\frac{k T \rho_j}{\hbar} \right)$

$= k \frac{V}{2\pi^2} \left(\frac{kT}{\hbar} \right)^3 \sum_j \frac{1}{C_j^3} \int_0^{z_{jD}} dz_j \; B(z_j) \; z_j^2$

where $B(z_j) = \frac{z_j^2 e^{z_j}}{(e^{z_j} - 1)^2}$

Now:

(3) $f_n(x) \equiv \int_0^x \frac{e^z z^n}{(e^z - 1)^2} dz$ which occurs commonly and is tabulated in Wilson

Debye Temperature: $\theta_{Dj} \equiv \frac{\hbar \omega_{Dj}}{k}$, then:

(4) $C_j = \frac{\omega_j}{q} = \frac{\omega_{Dj}}{q_{max}} = \frac{k \theta_{Dj}}{\hbar} \left(\frac{V}{6\pi^2 G^3} \right)^{1/3}$

(5) $C_V = k \frac{V}{2\pi^3} \left(\frac{kT}{\hbar} \right)^3 \frac{\hbar^3}{k^3} \frac{6\pi G^3}{V} \sum_j \frac{1}{\theta_{Dj}^3} f_4 (\theta_{Dj}/T)$

$C_V = 3 k G^3 \sum_j \left(\frac{T}{\theta_{Dj}} \right)^3 f_4 (\theta_{Dj}/T)$

Define: $\frac{1}{\theta_D^3} \equiv \frac{1}{3} \sum_j \frac{1}{\theta_{Dj}}$

Finally: $C_V = 9 k G^3 \left(\frac{T}{\theta_D} \right)^3 f_4 (\theta_D/T)$

Verification of the end points of the Debye Interpolation.

1) High temperature: $T \gg \theta_D$

$f_4(x) \approx \int_0^x z^2 dz = \frac{1}{3} x^3$

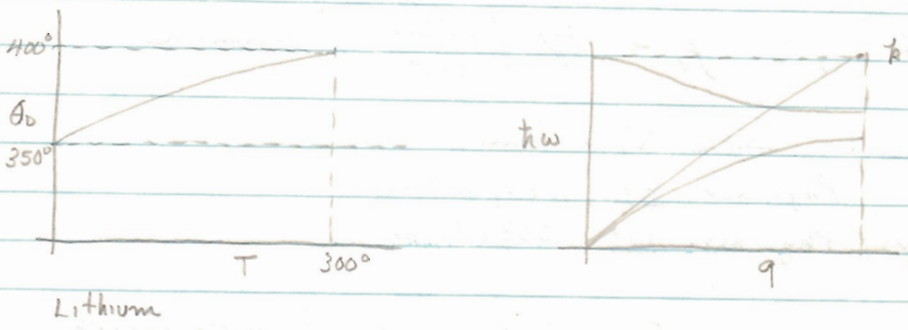
then $C_V = 9 k G^3 \left(\frac{T}{\theta_D} \right)^3 \frac{1}{3} \left(\frac{\theta_D}{T} \right)^3 = 3 k G^3$

2) Low Temperatures: $T \ll \Theta_D$

$$J_4(\Theta_D/T) \approx J_4(\infty) = \frac{4\pi^4}{15}$$

Then $C_V = \frac{2\pi^2}{5} \frac{k^4 T^3}{\hbar^3 c^3} \rightarrow C_{eff}$

Θ_D is found experimentally by fitting the C_V versus T data to equation (5). However, Θ_D is actually a slowly varying function of temperature.



$k\Theta_D$ is approximately equal to the optical mode energy.

Approximations in Debye Model:
1) c is a constant independent of direction
2) neglect of anharmonic terms
3) neglect of atomic structure in continuum model.

Einstein Model (1907):

Suggested by the decrease in C_V at low temperatures

1) Only single frequency ω_E for each atom, $k\Theta_E = \hbar\omega_E$
2) then $n = \frac{1}{e^{\hbar\omega_E/kT} - 1}$

$$E_T = \sum_{qj} \hbar\omega_{qj}\, n(qj) = \frac{k\Theta_E}{e^{\Theta_E/T} - 1} \cdot 3G^3$$

$$C_V = \frac{\partial E_T}{\partial T} = 3kG^3 \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1\right)^2}$$

High Temperatures: $T \gg \Theta_E$, $C_V = 3kG^3$

Low Temperatures: $T \ll \Theta_E$, $C_V = 3kG^3 \left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$

Applicability of Einstein Model:

(1) NG for acoustical modes because of interactions between atoms

(2) OK at high temperatures because of random motion of lattice points.

(3) Good for optical modes because of apparently independent vibrations of nearest neighbors.

See model discussed in Ziman, pp. 54-61

Odd Points:

1) Calculation of ρ_f: $\rho_f = \frac{V}{8\pi^3} \int \frac{dS}{|\nabla_q \omega|}$, examine

area of points where $\nabla_q \omega$ vanishes.

See: Van Hove, Phys. Rev. 89, 1189 (1953).
J.C. Phillips, Phys. Rev. 104, 1263 (1956).

2) Experimental measurements which give Dispersion Curves.

a) Neutron Diffraction:

b) Suppose neutron wave $\psi_n = e^{i(k\cdot r - \omega t)}$
lattice displacement $u_s \sim a_q e^{i(q\cdot r - \Omega t)}$

Collision: $\left.\begin{aligned} k' &= k + q + K \\ \hbar\omega' &= \hbar\omega + \hbar\Omega \end{aligned}\right\}$ phonon annihilation

from which the ω versus q relation can be found. Neutron scattering good because low energy gives sufficiently short wavelength.

LECTURE XII 10-24-60

ELECTRONS

SURVEY OF ELECTRON TRANSPORT THEORY:

The model is essentially this: we consider that all electrons are tightly bound in shells. These shells provide a potential of a periodic nature in which those loosely bound electrons move. We also assume interaction among the conduction electrons. The appropriate Schroedinger equation is:

$$(1)\quad \left[\sum_i \frac{\bar{p}_i^2}{2m} + \sum_i V(\bar{r}_i) + \sum_{i<j} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} \right] \psi(r_1, \cdots, r_N) = E\, \psi(r_1, \cdots, r_N)$$

① ② ③

Term ① is the usual kinetic energy of all the electrons.
Term ② is the lattice potential.
Term ③ is the interaction potential between the ith and jth electron. Also, the first two terms are further:

$$(2)\quad p_i \longrightarrow \frac{\hbar}{i} \nabla_i$$

$$(3)\quad V(r_i) = \sum_l V_a(\bar{r}_i - \bar{R}_l)$$ where V_a is the potential due to a single atom in the lattice.

We consider only static lattices and consequently disregard lattice vibrations. We will now discuss the possible approximations in the model.

Approximation A:
Simplest Case: Neglect ② and ③, then the equation of motion is:

$$(4)\quad \sum_i \frac{p_i^2}{2m} \psi(\bar{r}_1, \cdots, \bar{r}_N) = E\, \psi(\bar{r}_1, \cdots, \bar{r}_N)$$

We may always separate the variables in this type of equation and write the solution as a product, viz., $\Psi(\bar{r}_1, \cdots, \bar{r}_N) = \psi_1(\bar{r}_1)\,\psi_2(\bar{r}_2)\cdots\psi_N(\bar{r}_N)$, where each one will have the form of an exponential.

$$(5)\quad \psi_k(\bar{r}_k) = \frac{1}{\sqrt{\Omega}}\, e^{i\,\bar{k}_k\cdot\bar{r}_k}$$

where $\bar{k}_k$ is a constant of separation such that:

$$(6)\quad E = \sum_k \frac{\hbar^2 k_k^2}{2m}$$

We also have the subsidiary relation: $p_k\,\psi_k = \hbar\,k_k\,\psi_k$

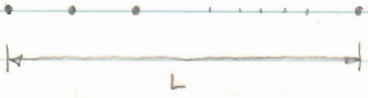
Our electrons can be thought of as forming a gas which obeys a certain type of statistics, viz., Fermi-Dirac statistics. This statistics states that the wave functions of the electrons must be anti-symmetric. We can express this in the following determinant:

$$(7)\quad \Psi(\bar{r}_1, \cdots, \bar{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\bar{r}_1) & \cdots & \psi_1(\bar{r}_N) \\ \psi_2(\bar{r}_1) & & \vdots \\ \vdots & & \vdots \\ \psi_N(\bar{r}_1) & \cdots & \psi_N(\bar{r}_N) \end{vmatrix}$$

assuming parallel spins on each and every electron. If any row or column is equal to another row or column, the determinant will vanish, therefore, no two electrons can occupy the same k state because the determinant will vanish. This is the exclusion principle without the spin.

This approximation is the Sommerfeld model of a metal.

What are the allowed values of $\bar{k}$? We look at one component with periodic boundary conditions.



(8) $e^{i k_x x} = e^{i k_x (x+L)}$

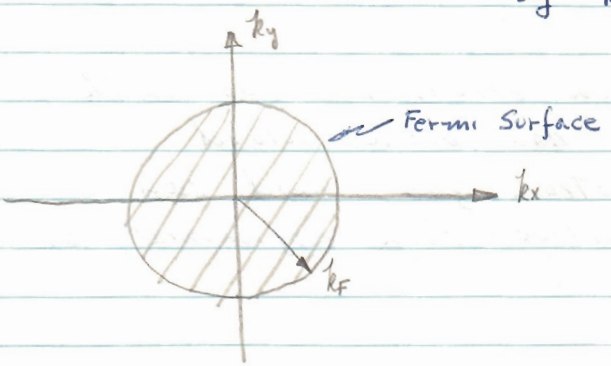
$e^{i k_x L} = 1$

$k_x = \frac{2n\pi}{L}$, $\Delta k_x = \frac{2\pi}{L}$

Thus, the volume per point in k space is $\left(\frac{8\pi^3}{\Omega}\right)$ and the density of states is $\left(\frac{\Omega}{8\pi^3}\right)$.

Ground State Energy:

At absolute zero, the electron gas can be thought of as condensing to a sphere in k space whose radius is defined by k_F, the Fermi radius.



The number of electrons is equal to the number of electrons per unit volume of k space times the total volume of k space time two for spin.

(9) $N = 2 \cdot \frac{V}{8\pi^3} \cdot \frac{4}{3}\pi k_F^3$; $k_F^3 = 3\pi^2 n$, with $n = \frac{N}{V}$

and the Fermi energy is defined as $E_F = \frac{\hbar^2 k_F^2}{2m}$.

The total energy of all the electrons is:

(10) $E = \frac{V}{4\pi^3} \int_0^{k_F} d^3k \, \frac{\hbar k^2}{2m} = \frac{V}{4\pi^3} \cdot \frac{\hbar^2 k_F^2}{2m} \cdot 4\pi \cdot \frac{1}{5} k_F^3$

$= \frac{V}{5\pi^2} E_F \cdot 3\pi^2 n = \frac{3}{5} E_F N$

Therefore, the energy per particle in the electron gas at absolute zero is $E/N = 3/5\, E_F$. When temperature is finite, the effect is to smear out the Fermi surface.

Approximation B:

Neglect ③ which gives for Schroedinger's Equation:

(11) $\sum_i \left(\frac{p_i^2}{2m} + V\{\bar{r}_i\} \right) \psi = E\psi$ which separates to

(12) $\left(\frac{p^2}{2m} + V\{\bar{r}\} \right) \psi(\bar{r}) = E\,\psi(\bar{r})$

which is the equation of motion of one electron in a periodic potential. We shall devote the major portion of our attention to this problem.

Approximation C:

Neglect ② which gives an electron gas with coulomb interactions. The problem has been solved exactly for a high density electron gas and can also be handled by Hartree, Hartree-Foch approximations.

Approximation D:

Neglect nothing. There are no exact solutions, however, Hartree-Foch approximations can be used.

The Single Electron in a Periodic Potential:

The Schroedinger Equation is:

(13) $-\frac{\hbar^2}{2m} \nabla^2 \psi(\bar{r}) + V(\bar{r})\,\psi(\bar{r}) = E\,\psi(\bar{r})$

with the condition $V(\bar{r}) = V(\bar{r} + \bar{R}_\ell)$

What are the form of the ψ's? To answer, we introduce the translation operator.

(14) $T_\ell\,\psi(\bar{r}) = \psi(\bar{r} + \bar{R}_\ell)$

We expand $\psi(\bar{r}+\bar{R}_\ell)$ in a Taylor series:

(15) $$\psi(\bar{r}+\bar{R}_\ell) = \sum_{n=0}^{\infty} \frac{(\bar{R}_\ell \cdot \nabla)^n}{n!} \psi(\bar{r}) = e^{\bar{R}_\ell \cdot \nabla} \psi(\bar{r})$$

(16) $$T_\ell = e^{\bar{R}_\ell \cdot \nabla} = e^{\frac{i}{\hbar} \bar{R}_\ell \cdot \bar{p}}$$ upon introducing the momentum operator.

It can be shown that T_ℓ commutes with H, that is,

(17) $$\left[\frac{p^2}{2m}, T_\ell\right] = 0$$ from expanding T_ℓ.

(18) $$\left[V(\bar{r}), T_\ell\right] = V(\bar{r})T_\ell - T_\ell V(\bar{r}) = V(\bar{r})T_\ell - V(\bar{r}+\bar{R}_\ell)T_\ell$$

$$= V(\bar{r})T_\ell - V(\bar{r})T_\ell = 0$$

(20) $$\therefore \quad [T_\ell, H] = 0$$

Assuming no degeneracy, commuting operators can be diagonalized by the same unitary transformation.

Consider $\psi(r) = e^{i\bar{k}\cdot\bar{r}}$

(21) $$T_\ell e^{i\bar{k}\cdot\bar{r}} = e^{\frac{i}{\hbar}\bar{R}_\ell\cdot\bar{p}} e^{i\bar{k}\cdot\bar{r}} = \psi(\bar{r}+\bar{R}_\ell) = e^{i\bar{k}\cdot\bar{R}_\ell} e^{i\bar{k}\cdot\bar{r}}$$

so $e^{i\bar{k}\cdot\bar{R}_\ell}$ are eigenvalues of $e^{i\bar{k}\cdot\bar{r}}$

Now consider $e^{i(\bar{k}+\bar{K})\cdot\bar{r}}$ as an eigenfunction, then:

(22) $$T_\ell e^{i(\bar{k}+\bar{K})\cdot\bar{r}} = \underbrace{e^{i(\bar{k}+\bar{K})\cdot\bar{R}_\ell}}_{e^{i\bar{k}\cdot\bar{R}_\ell}} e^{i(\bar{k}+\bar{K})\cdot\bar{r}}$$

Therefore, all eigenvalues are the same for each eigenfunction and all the states are degenerate. Then we can form solutions by linear combinations of the eigenfonctions.

(23) $$\psi(\bar{k},\bar{r}) = \sum_K A_{\bar{k}}(K) e^{i(\bar{k}+K)\cdot\bar{r}} = e^{i\bar{k}\cdot\bar{r}} \sum_K A_{\bar{k}}(K) e^{iK\cdot r}$$

Define:

(24) $u(\bar{k},\bar{r}) = \sum_K A_k(K)\, e^{\imath K\cdot r}$

we can easily see that this function has the property

(25) $u(k, r+Re) = u(k,r)$, and

(26) $\psi(k,r) = e^{\imath k\cdot r}\, u(k,r)$

where $u(k,r)$ is a periodic function with no degeneracy. This is called the Bloch Theorem (1928).

For a set of Schroedinger functions that are degenerate:

(27) $\psi_u(\bar{r}+\bar{Re}) = \sum_v T_{uv}\, \psi_v(\bar{r})$

Choose ψ's normalized and orthogonal:

(28) $\int \psi_u^*(\bar{r})\, \psi_v(\bar{r})\, d^3r = \delta_{uv}$, or

$$\int \psi_u^*\, \psi_{u'}\, d^3r = \delta_{uu'} = \sum_{vv'} T_{uv}^*\, T_{u'v'} \underbrace{\int \psi_v^*\, \psi_{v'}\, d^3r}_{\delta_{vv'}}$$

(29) $\therefore$ $\sum_v T_{uv}^*\, T_{u'v} = \delta_{uu'}$

with $T_{vu}^{*T} = T_{uv}^* = T_{vu}^\dagger$, then

(30) $\sum_v T_{u'v}\, T_{vu}^\dagger = \delta_{uu'}$

(31) $TT^\dagger = \mathbb{1}$

Thus a unitary matrix can be diagonalized.

LECTURE XIII 10-26-60

Bloch Theorem:

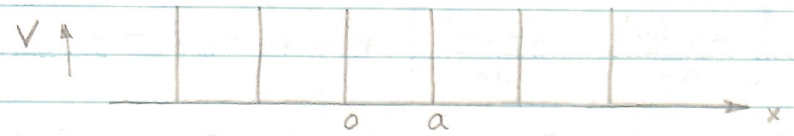
(1) $\psi(k,r) = e^{ik\cdot r}\, u(k,r)$

with degeneracy present,

(2) $T_R\, \psi(r) = \psi(r+R_R)$, $T_R = e^{i\bar{R}_R\cdot\nabla}$

Kronig - Penney Model:

Consider the one dimensional case where the potential is a series of periodic δ functions:



(3) $V(x) = a V_0 \sum_n \delta(x-na)$

(4) $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\,\psi(x)$

For $0 < x < a$:

(5) $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

(6) $\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0$, $\alpha^2 = \frac{2mE}{\hbar^2}$

(7) $\psi = A\sin\alpha x + B\cos\alpha x$

We now consider the Boundary Conditions:

(a) $\psi(x) = e^{ikx}\, u(k,x)$

then, $\psi(a) = e^{ika}\, u(k,0) = e^{ika}\,\psi(0)$

$\psi(0) = B$

and $\psi(a) = A\sin\alpha a + B\cos\alpha a = e^{ika}\, B$

$A = \frac{B}{\sin\alpha a}\left(e^{ika} - \cos\alpha a\right)$

Then: $\psi(x) = \frac{B}{\sin \alpha a}\left[\underbrace{(e^{ika} - \cos ka)\sin \alpha x + \sin \alpha a \cos \alpha x}_{\sin \alpha (a-x)}\right]$

Then: $\psi(x) = \eta\left[\sin \alpha (a-x) + e^{ika} \sin \alpha x\right], \quad 0 < x < a$

for one solution, the other is $k \to -k$

(b) Boundary Conditions on $\frac{d\psi}{dx}$: Take the Schroedinger equation and integrate over a small distance $\pm \epsilon$ about $x = 0$:

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon} \frac{d^2\psi}{dx^2}\,dx + a V_0 \sum_n \int_{-\epsilon}^{\epsilon} \delta(x - na)\,\psi(x)\,dx = E\int_{-\epsilon}^{\epsilon} \psi(x)\,dx$$

then: $$-\frac{\hbar^2}{2m}\left[\frac{d\psi(0)^+}{dx} - \frac{d\psi(0)^-}{dx}\right] + a V_0 \psi(0) = 0$$

because the δ function preserves ψ in the second integral on th LHS, but $\psi(0)^+ - \psi(0)^-$ vanishes on the RHS.

Define: $\eta = \frac{m V_0 a}{\hbar^2}$, then:

$$\frac{d\psi(0)^+}{dx} - \frac{d\psi(0)^-}{dx} = 2\eta\,\psi(0)$$

Thus showing that the derivatives are discontinuous. From previous consideration on the translational properties of the ψ's,

$$\psi(x) = e^{-ika}\,\psi(x+a) \;;\; \frac{d\psi(x)}{dx} = e^{-ika}\frac{d\psi(x+a)}{dx}$$

or $$\frac{d\psi(0)^-}{dx} = e^{-ika}\frac{d\psi(a)^-}{dx}$$

and combining with the above:

$$\frac{d\psi(0)^+}{dx} - e^{-ika}\frac{d\psi(a)^-}{dx} = 2\eta\,\psi(0)$$

Differentiating our previous solution for ψ; given in (a):

(8) $$\frac{d\psi}{dx} = \alpha\left[-\cos\alpha(a-x) + e^{ika}\cos\alpha x\right] \quad \text{(neglecting } \eta\text{)}$$

$$\frac{d\psi(0)}{dx} = \alpha\left[e^{ika} - \cos\alpha a\right]$$

$$\frac{d\psi(a)}{dx} = \alpha\left[e^{ika}\cos\alpha a - 1\right] \quad : \text{Multiply be } e^{-ika}$$

and substitute in the result of (b):

(9) $$\alpha\left[2\cos ka - 2\cos\alpha a\right] = 2\eta\sin\alpha a$$

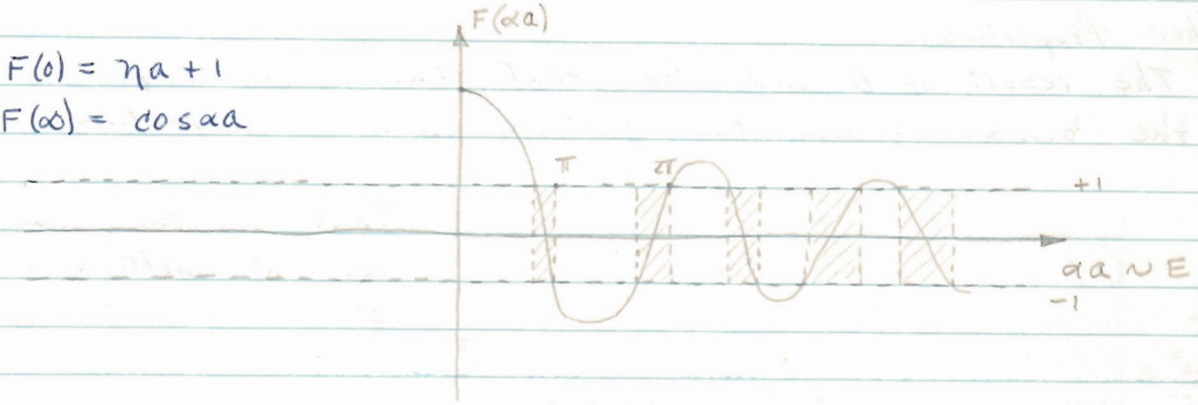
or Finally:

(10) $$\cos ka = \eta a\,\frac{\sin\alpha a}{\alpha a} + \cos\alpha a$$

Let us now examine the RHS, define it as $F(\alpha a)$ and plot it against αa:

$F(0) = \eta a + 1$

$F(\infty) = \cos\alpha a$



We note that the LHS of (10) cannot be greater than ± 1 because the function $\cos ka$ is real only between these values. Otherwise, k would be imaginary and damping would occur. Therefore α or E can only take on certain ranges of values which are called bands.

Properties of Bands:

A. For $\eta a \to 0$:

$$\cos ka = \cos \alpha a$$

$$k = \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\therefore E = \frac{\hbar^2 k^2}{2m}$$ or we have the case of the free particle.

B. For $\eta a \to \infty$ (tremendous δ functions!):

$$\frac{\sin \alpha a}{\alpha a} = \frac{\cos ka}{\eta a} \Rightarrow 0$$

$$\alpha a = n\pi \quad , n \neq 0$$

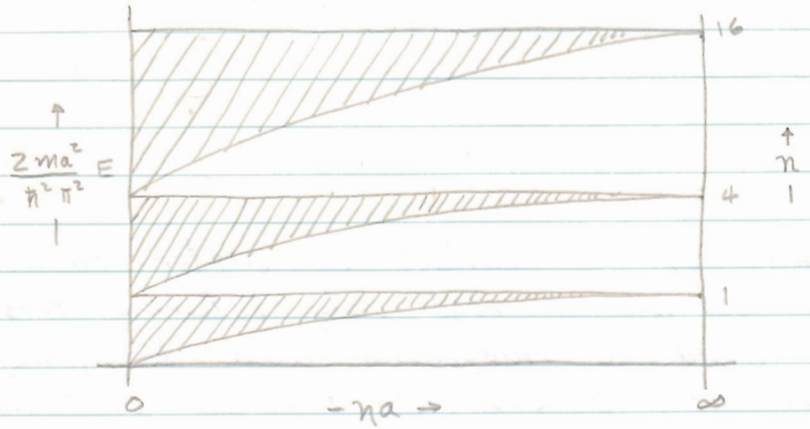
and $$E = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$ or we have the particle in a box.

Checking: $\psi(0) = \eta \sin \alpha a = 0$

$\psi(a) = \eta e^{ika} \sin \alpha a = 0$

Further Properties:

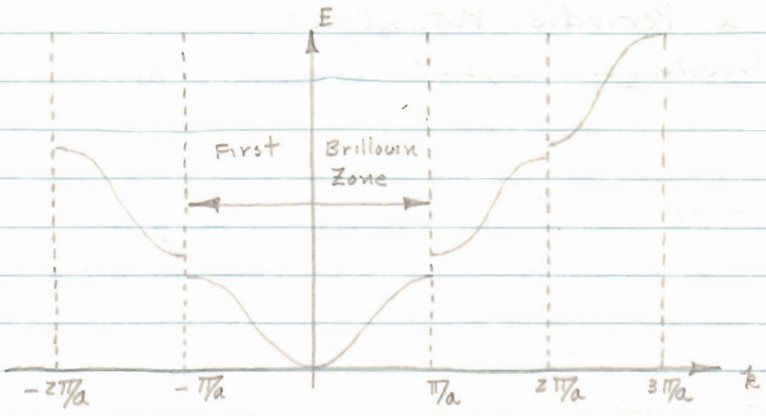
The result of B indicates that the upper edges of the bands follow the particle in a box equation:



That is, they always occur at multiples of π

In each band, $-1 < \cos ka < +1$, $(n-1)\pi \leq ka \leq n\pi$

Consider the plot of E versus k:



We shall see later that is possible to translate the zones by the reciprocal lattice vectors and can form the so-called reduced Brillouin zone.

Examine $k \sim 0$: in this region we may get $E = f(k)$ explicitly.

We have on expanding equation (10):

$$(11)\quad 1 - \tfrac{1}{2}k^2a^2 = \eta\,\frac{\sin a(\alpha_0+\delta\alpha)}{\alpha_0\left(1+\frac{\delta\alpha}{\alpha_0}\right)} + \cos a(\alpha_0+\delta\alpha)$$

$$= \frac{\eta a}{\alpha_0 a}\left(1-\frac{\delta\alpha}{\alpha_0}\right)\left(\sin a\alpha_0 + a\,\delta\alpha\cos a\alpha_0\right) + \cos a\alpha_0 - a\,\delta\alpha\sin a\alpha_0$$

$$= \underbrace{\frac{\eta a}{\alpha_0 a}\sin a\alpha_0 + \cos a\alpha_0}_{\text{1}} - \delta\alpha\left[\frac{\eta}{\alpha_0^2}\left(\sin a\alpha_0 - a\alpha_0\cos a\alpha_0\right) + a\sin a\alpha_0\right]$$

$$\text{mess}$$

Now $E = \frac{\hbar^2}{2m}(\alpha_0+\delta\alpha)^2 = \frac{\hbar^2\alpha_0^2}{2m} + \frac{\hbar^2}{m}\delta\alpha$

Then

$$(12)\quad E = \frac{\hbar^2k^2}{2m}a^2\left[\frac{\eta}{\alpha_0^2}\left(\sin a\alpha_0 - a\alpha_0\cos a\alpha_0\right) + a\sin a\alpha_0\right]^{-1} + \frac{\hbar^2\alpha_0^2}{2m}$$

$$= \frac{\hbar^2k^2}{2m^*};\quad m^* = \left\{a^2\left[\frac{\eta}{\alpha_0^2}\left(\sin a\alpha_0 - a\alpha_0\cos a\alpha_0\right)\right]^{-1} + 1\right\}^{-1} m$$

where m^* is the effective mass and can go from 0 to ∞ over both + and - values.

LECTURE XIV 10-28-60

Properties of Wave Functions in a Periodic Potential:

We begin with the Schroedinger equation and the periodicity conditions:

(1) $\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E\,\psi(r)$

(2) $V(r) = V(r+R_n)$

(3) $b(k,r) \equiv e^{ik\cdot r}\,u(k,r) = \psi(r)$

Operating with p on $b(k,r)$:

(4) $p\,e^{ik\cdot r} = e^{ik\cdot r}(\hbar k + p)$

and we get for the Schroedinger equation:

(5) $\left[\frac{1}{2m}(p+\hbar k)^2 + V(r)\right]u(k,r) = E\,u(k,r)$

$\left[\frac{-\hbar^2}{2m}(\nabla + ik)^2 + V(r)\right]u(k,r) = E\,u(k,r)$

Now k is a parameter of the equation, that is, the eigenfunctions $u_n(k,r)$ have the eigenvalues $E_n(k)$. Then:

(6) $\left[-\frac{\hbar^2}{2m}(\nabla + ik)^2 + V(r)\right]u_n(k,r) = E(k)\,u_n(k,r)$

We now observe the following properties of the Schroedinger equation (6):

(7) $b_n(k,r) = e^{ik\cdot r}\,u_n(k,r)$

$H^*(-k) = H(k)$ (potential is real)

$\therefore E_n(-k) = E_n(k)$ (eigenvalues are real)

$u_n^*(-k) = u_n(k)$

These are a direct consequence of the Schroedinger equation.

We now make the following transformation to momentum space:

(8) $$b_n(k,r) = \sum_K \chi_n(k,K)\, e^{i(k+K)\cdot r}$$

(9) $$u_n(k,r) = \sum_K \chi_n(k,K)\, e^{iK\cdot r}$$

We must have $u_n(k,r) = u_n(k, r+Re)$ and we see that this is so since $e^{iK\cdot Re} = 1$. Also, we must transform the potential.

(10) $$V(r) = \sum_K V(K)\, e^{-iK\cdot r}$$

We now transform the various parts of the Schroedinger equation operating on the Bloch functions:

a) $$-\frac{\hbar^2}{2m}\nabla^2 b_n(k,r) = \sum_K \frac{\hbar^2}{2m}(k+K)^2\, \chi_n(k,K)\, e^{i(k+K)\cdot r}$$

b) $$V(r)\, b_n(k,r) = \sum_{KK'} V(K)\, \chi_n(k,K')\, e^{i(k+K'-K)\cdot r}$$

c) $$E_n(k)\, b_n(k,r) = E_n(k) \sum_K \chi_n(k,K)\, e^{i(k+K)\cdot r}$$

To separate out the χ's, operate on a, b, c with $\int e^{-i(k+K'')\cdot r}\, d^3r$, knowing that:

(11) $$\int e^{i(K-K'')\cdot r}\, d^3r = \Omega\, \delta_{KK''}$$

Then:

a) $$\rightarrow \sum_K \frac{\hbar^2}{2m}(k+K)^2\, \chi_n(k,K) \int d^3r\, e^{i(K-K'')\cdot r}\, d^3r$$

$$= \frac{\hbar^2}{2m}(k+K'')^2\, \chi_n(k,K'')\, \Omega$$

b) $$\rightarrow \sum_{KK'} V(K)\, \chi_n(k,K') \int d^3r\, e^{i(K'-K-K'')\cdot r}$$

$$= \sum_K V(K)\, \chi_n(k, K+K'')\, \Omega \quad , \text{ when } K' = K+K''$$

c) $$\rightarrow E_n(k)\, \chi_n(k,K'')\, \Omega$$

We may now replace k'' with k everywhere and arrive at the momentum space representation of the Schroedinger equation:

$$(12)\quad \frac{\hbar^2}{2m}(k+K)^2 \chi_n(k,K) + \sum_{K'} V(K')\chi_n(k,K+K') = E_n(k)\chi_n(k,K)$$

We may think of this as no longer a differential equation, but as an algebraic equation in χ. When $V(K')=0$, it reduces merely to the energy as a function of k equation for the free particle. Examine the condition when $K \to K+K''$. Nothing changes with the consequence that, <u>in the first or same branch</u>,

$$(13)\quad E_n(k) = E_n(k+K) \text{ , and,}$$

$$(14)\quad \chi_n(k+K', K-K') = \chi_n(k,K)$$

The subscript n is now clear, that is, equation (13) only holds for the same value of n or branch. We now examine a proof of equation (14):

Let $k \to k+K''$
$K \to K-K''$

Now look at the Schroedinger Equation and note:
$k+K \to k+k$
$E_n(k) = E_n(k+K'')$
Then writing:

$$\frac{\hbar^2}{2m}(k+k)^2 \chi_n(k+k'', K-K'') + \sum_{K''} V(K'')\chi_n(k+K', K-K'+K'')$$
$$= E_n(k)\chi_n(k+K', K-K')$$

and we can make the identity
$\chi_n(k+K', K-K') = \chi_n(k,K)$
in the n branch.

Let us see how this concerns the Block Functions.

(15) $b_n(k,r) = \sum_K \chi_n(k,K)\, e^{i(k+K)\cdot r} = \sum_K \chi_n(k+K', K-K')\, e^{i(k+K)\cdot r}$

Let $K-K' \to K''$, $K \to K'+K''$, Then

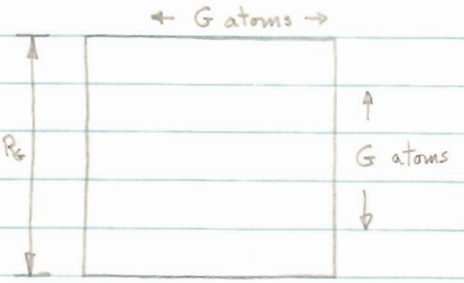
(16) $b_n(k,r) = \sum_{K''} \chi_n(k+K', K'')\, e^{i(k+K'+K'')\cdot r}$

$= b_n(k+K'', r) = b_n(k,r)$

This shows that the Bloch functions are periodic in a branch of the reciprocal space as well as the energy.

We now consider the problems of Boundary Conditions:
Periodic Boundary Conditions:

(17) $b_n(k, r+R_L) = e^{ik\cdot R_L}\, b_n(k,r)$



We would like to have the cyclic condition on the Bloch functions, viz.

$b_n(k, r+R_G) = b_n(k,r)$

then $e^{ik\cdot R_G} = 1$, or, $k\cdot R_G = 2\pi n$

We now recall the following relations and analogies from lattice vibration theory:

$$\bar{K} = 2\pi(g_1\bar{b}_1 + g_2\bar{b}_2 + g_3\bar{b}_3); \quad \bar{a}_j\cdot\bar{b}_k = \delta_{kj}$$

$$q \to k = \frac{2\pi}{G}(g_1\bar{b}_1 + g_2\bar{b}_2 + g_3\bar{b}_3); \quad \bar{R}_G = G\,\bar{a}$$

We then have: $k\cdot R_G = 2\pi(g_1+g_2+g_3)$

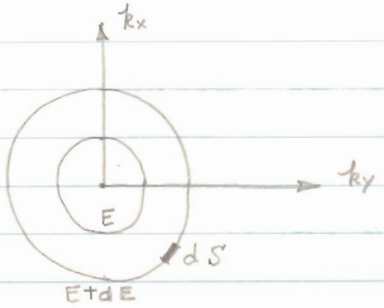
or that the spacing between the k's in the direction of a particular reciprocal lattice vector is $\frac{2\pi}{G}b_k$

and the density of states per unit volume is $\frac{\Omega}{8\pi^3}d^3k$

Therefore, the k's are discrete with $k = k+K$.

One important difference between electron motion and lattice vibrations is that for electrons there is no inherent short wavelength limit. The electronic vibrations are in a continuum whereas lattice vibrations are distributed over a space of discrete points. Therefore, there is more meaning to $k + K$.

As in Lattice Vibrations, we may introduce the notion of Brillouin zones, and define a density of states function.



(18) $\rho(E)\,dE = \frac{\Omega}{8\pi^3}\,d^3k$

The distance between E and $E+dE$ is

(19) $dk = \frac{dE}{|\nabla_k E|}$, and the volume element is

(20) $d^3k = dE \int \frac{dS}{|\nabla_k E|}$, Therefore,

(21) $\rho(E)\,dE = dE\,\frac{\Omega}{8\pi^3}\int \frac{dS}{|\nabla_k E|}$, or

(22) $\rho(E) = 2\,\frac{\Omega}{8\pi^3}\int \frac{dS}{|\nabla_k E|}$

(2 ↑ spin)

We now proceed to the construction of the Brillouin zones.

Construction of Brillouin Zones:

Consider a two dimensional square lattice. The reciprocal lattice of a square lattice is a square lattice.

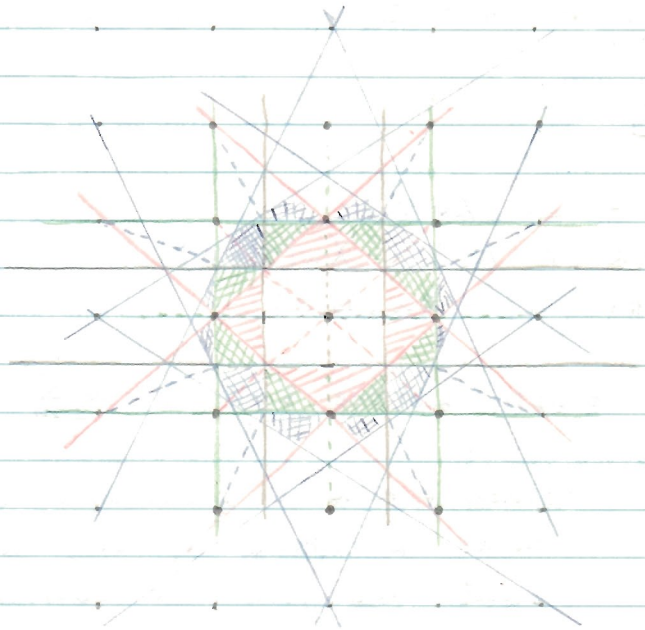
The rules are:

First BZ: Bisect the lines joining the nearest neighbors and extend the bisectors until they intersect.

Second BZ: Bisect the next nearest neighbor distances and proceed as before.

Third BZ: Bisect the third nearest neighbor distance and proceed as before.

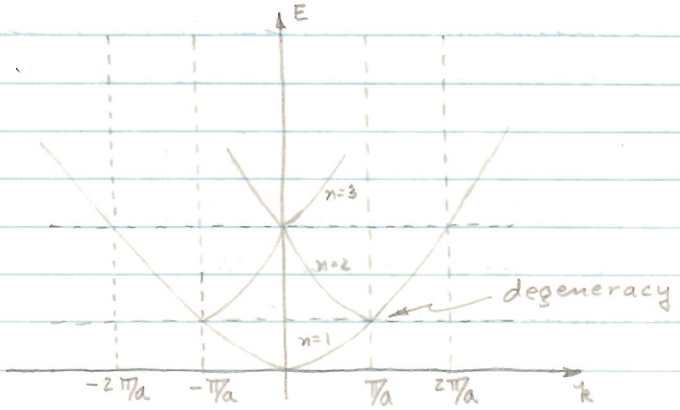
Any number of Brillouin zones can be constructed in this fashion.



First Zone
Second Zone
Third Zone
Fourth Zone

Reference: L. Brillouin: Wave Propagation in Periodic Structures

It is seen that the zones can be mapped back by a reciprocal lattice vector.



E vs k for empty lattice

$V(r) = 0$, $E = \frac{\hbar^2 k}{2m}$, $b_n(k,r) = u_n(k,r)\, e^{ikr} = e^{ikr}$

Reduced Zone Scheme:

It is possible to map everything into the first Brillouin zone. The diagram shown is for the free particle. Actually, the perturbation of the periodic potential will remove the degeneracy at the zone edge.

LECTURE XV 10-31-60

Clarification of Some Points in Lecture XIV:

Show $E_n(k) = E_n(k+K)$

Now:

$$b_n(k,r) = \sum_K \chi_n(k+K)\, e^{i(k+K)\cdot r}$$

Then: $\frac{\hbar^2}{2m}(k+K)^2 \chi_n(k+K) + \sum_{K'} V(K')\chi_n(k+K+K')$

$= E_n(k)\chi_n(k+K)$

Let $K \to K+K''$:

$$\frac{\hbar^2}{2m}(\underbrace{k+K''}+K)^2 \chi_n(\underbrace{k+K''}+K) + \sum_{K'} V(K)\chi_n(\underbrace{k+K''}+K+K')$$

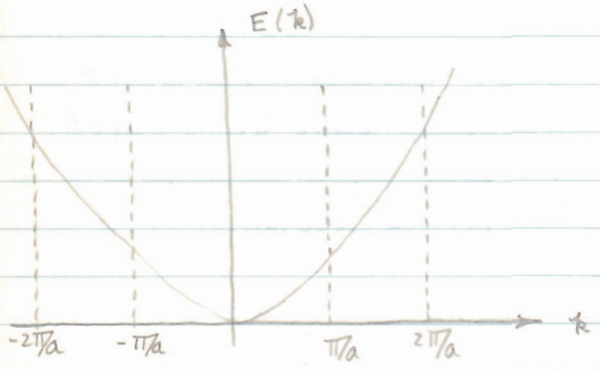
$$= E_n(k)\chi_n(\underbrace{k+K''}+K)$$

Then we see $E_n(k) = E_n(k+K'')$

and $\chi_n(k+K'+K-K'') = \chi_n(k+K)$

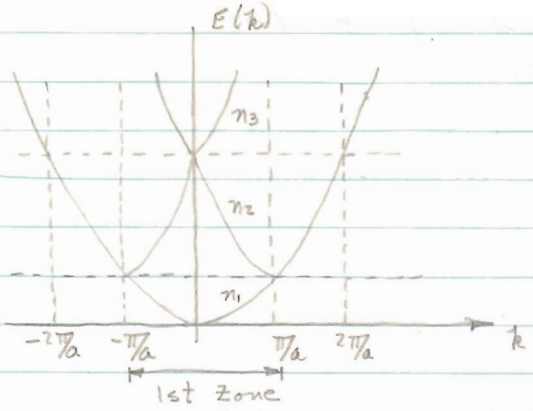
and $b_n(k+K,r) = b_n(k,r)$

Interpretive Illustration: Empty Lattice, $V=0$, $E = \frac{\hbar^2 k^2}{2m}$



Since E vs k is continuous, we can divide k space up any way we want. We can see obviously that $E_n(k) \neq E_n(k+K)$. However, we can interpret such an equality as was derived above in terms of the extended and reduced BZ schemes.

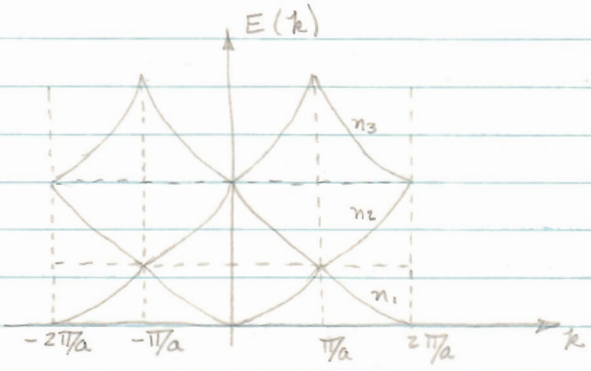
We know that we can map all solutions of the Schroedinger equation back into the first zone and form the reduced scheme. If this is not done we have the extended scheme.



Now $E_n(k)$ is multi-valued in the first zone and n is associated with each branch in the reduced zone.

Extended Zones	Reduced Zone
one solution corresponding to each k	Map into first BZ Infinite number of solutions corresponding to each k and labelled by n.

Now, since we have defined each branch by n we may consider them to be periodic in k space and draw the following.



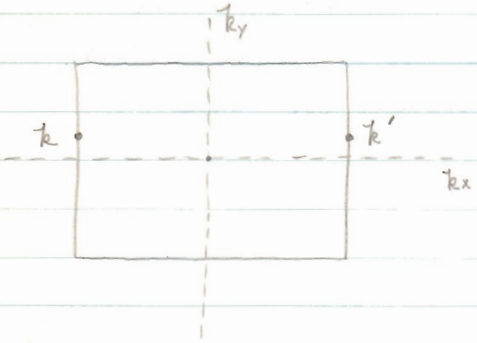
We now return to the discussion of Bloch functions. We see that the E_n's have the time reversibility property, viz. $E_n(k) = E_n(-k)$ and $u_n(k,r) = u_n^*(-k,r)$, quite analogous to the situation of the eigenvalues and eigenvectors of the lattice vibration theory.

We see that the Bloch functions, viz.,

$$b_n(k,r) = e^{ik\cdot r}\, u_n(k,r)$$

have the same form as the solutions to the lattice vibration equation of motion.

Let us examine the behaviour of the energy in the first Brillouin zone of a square lattice.



Now $E_n(k+K) = E_n(k)$
Then $E_n(k') = E_n(k)$
and $\nabla_k E_n(k') = \nabla_k E_n(k)$

If reflection through the origin is allowed:

$$\frac{\partial E_n(k)}{\partial k_x} = \frac{\partial E_n(k')}{\partial k_x} = 0$$

which holds for normal derivatives only. This means that the energy has an extremum at the BZ face or that it must be rounded. That this is so will be seen when the perturbation of a periodic lattice is applied.

Normality and Orthogonality of Bloch Functions:
We demand that:

(1) $b_n(k,r) = \eta\, e^{\imath k\cdot r}\, u_n(k,r)$

(2) $\eta^2 \int b_{n'}^*(k',r)\, b_n(k,r)\, d^3r = \delta_{nn'}\, \delta_{k'k}$. Then,

(3) $\eta^2 \int b_{n'}^*(k',r)\, b_n(k,r)\, d^3r = \eta^2 \int e^{\imath(k-k')\cdot r}\, u_{n'}^*(k',r)\, u_n(k,r)\, d^3r$

$$= \eta^2 \sum_R \int_{\text{unit cell}} e^{\imath(k-k')\cdot(r+R)}\, u_{n'}^*(k',r)\, u_n(k,r)\, d^3r$$

because the u_n's are periodic: $\left[b_n(k,r+R) = e^{\imath k\cdot(r+R)}\, u_n(k,r)\right]$

$$= \eta^2 \sum_R e^{\imath(k-k')\cdot R} \oint_{uc} e^{\imath(k-k')\cdot r}\, u_{n'}^*\, u_n\, d^3r$$

$$= \eta^2\, G^3\, \delta_{kk'} \oint_{uc} u_{n'}^*\, u_n\, d^3r$$

since we have shown previously in lattice vibration theory that:

$$\sum_R e^{\imath(k-k')\cdot R} = G^3\, \delta_{k'k}$$

As the u_n's are solutions of Schroedingers equation and form a complete set, we may regard them as orthogonal and normalized. Thus:

$$(4)\quad \eta^2 \int b_{n'}^*(k',r)\, b_n(k,r)\, d^3r = \eta^2 \Omega\, \delta_{kk'} \cdot \underbrace{\frac{1}{v_a}\int u_{n'}^* u_n\, d^3r}_{\delta_{nn'}}$$

$$= \delta_{kk'}\,\delta_{nn'}$$

$$\text{with } \eta = \frac{1}{\sqrt{\Omega}}$$

PERIODIC POTENTIAL PERTURBATION: THE NEARLY FREE ELECTRON

Refering to the figure of the reduced zone scheme, we will show that under a periodic potential distribution, the cusps at the face of the Brillouin zone will round off. We do this by applying the periodic potential as a perturbation, considering $V(K')$ in equation XIV (12) as being very small. When $K=0$:

$$(5)\quad \frac{\hbar^2}{2m} k^2 \chi_n(k) + \sum_{K'}' V(K')\, \chi_n(k+K') = E(k)\, \chi_n(k)$$

Now in the extended zone representation we may remove the n's since there is now periodicity. Then we have from before:

$$(6)\quad b_n(k,r) = \chi(k)\, e^{i k\cdot r} + \sum_K' \chi(k+K)\, e^{i(k+K)\cdot r}$$

where the prime denotes the deletion of $K=0$ in the sum. Following the usual perturbation methods, we may write:

$$(7)\quad \chi(k) = \chi^{(0)}(k) + \chi^{(1)}(k) + \chi^{(2)}(k) + \cdots$$

$$E(k) = E^{(0)}(k) + E^{(1)}(k) + \cdots$$

$$\chi(k+K) = \chi^{(1)}(k+K) + \cdots$$

$$V(r) = \sum_K' V^{(0)}(K)\, e^{-i K\cdot r}$$

In the Zeroeth Order:

(8) $\frac{\hbar^2 k^2}{2m} \chi^{(0)}(k) + V^{(0)} \chi^{(0)}(k) = E^{(0)}(k) \chi^{(0)}(k)$

We get $E^{(0)}(k) = V(0) + \frac{\hbar^2 k^2}{2m}$, or the free electron.

In the First Order:

(9) $\left[\frac{\hbar^2}{2m}(k+K)^2 + V(0)\right] \chi^{(1)}(k+K) + V(-K)\chi^{(0)}(k)$

$= E^{(0)}(k)\chi^{(1)}(k+K) = \left[V(0) + \frac{\hbar^2 k^2}{2m}\right] \chi^{(1)}(k+K)$

Solving for $\chi^{(1)}$:

(10) $\chi^{(1)}(k+K) = \frac{V(-K)}{\frac{\hbar^2}{2m}\left[k^2 - (k+K)^2\right]} \chi^{(0)}(k)$

Upon setting up the usual first order equation for the perturbed energy:

(11) $\left[\frac{\hbar^2}{2m} k^2 + V(0)\right] \chi^{(1)}(k) = E^{(0)}(k)\chi^{(1)}(k) + E^{(1)}\chi^{(0)}$

we see that $E^{(1)} = 0$, so we must proceed to the second order. In the second order:

(12) $\left[\frac{\hbar^2 k^2}{2m} + V(0)\right] \chi^{(2)}(k) + \sum_{K'} V(K') \chi^{(1)}(k+K')$

$= E^{(2)}\chi^{(0)}(k) + E^{(1)}\chi^{(1)}(k) + E^{(0)}\chi^{(2)}(k)$

or $E^{(2)}\chi^{(0)}(k) = \sum_{K'} V(K')\chi^{(1)}(k+K')$

Substituting (10) for $\chi^{(1)}(k+K')$:

(13) $E^{(2)}\chi^{(0)}(k) = \sum_{K'} \frac{V(K')V(-K')}{\frac{\hbar^2}{2m}\left[k^2 - (k+K)^2\right]} \chi^{(0)}(k)$

Since the potential is real, we see from equation XIV (10) that $V(-k) = V^*(k)$ and we obtain for the complete total energy of the first three orders of perturbation:

$$(14) \quad E = V(0) + \frac{\hbar^2 k^2}{2m} + \sum_{K}{}' \frac{|V(K)|^2}{E^{(0)}(k) - E^{(0)}(k+K)}$$

Only $\chi^{(1)}(k)$ contributes to the total wave function along with $\chi^{(0)}$:

$$(15) \quad b(k,r) = \frac{1}{\sqrt{\Omega}} e^{ik\cdot r}\left[1 + \sum_{K}{}' \frac{V(-K)\, e^{iK\cdot r}}{E^{(0)}(k) - E^{(0)}(k+K)}\right] \chi^{(0)}(k)$$

However, if $E^{(0)}(k) \to E^{(0)}(k+K)$ the solution diverges and we have a degeneracy condition. We will now consider this case as treated by the degenerate perturbation theory:
We write; for two different states, k, $k+K$:

$$(16) \quad \left[\frac{\hbar^2}{2m} k^2 + V(0)\right] \chi(k) + V(K)\, \chi(k+K) = E\, \chi(k)$$

$$(17) \quad \left[\frac{\hbar^2}{2m} (k+K)^2 + V(0)\right] \chi(k+K) + V(-K)\, \chi(k) = E\, \chi(k+K)$$

as the two Schroedinger equations in momentum space which we will now solve for the splitting of the degenerate levels.

LECTURE XVI 11-2-60

Recapitulation on Nearly Free electron Model:

The momentum representation equations for two different states, k, $k+K$ are:

$$(1) \quad \frac{-\hbar^2}{2m} (k+K)^2 \chi(k+K) + \sum_{K'} V(K')\, \chi(k+K+K') = E\, \chi(k+K)$$

$$\frac{-\hbar^2}{2m} k^2 \chi(k) + \sum_{K'}{}' V(K')\, \chi(k+K') = E\, \chi(k)$$

These states are perturbed by the following potentials:

(2) $V(K) \rightarrow V^{(1)}(K)$
$V(0) \rightarrow V^{(0)}(0)$

and the solution up to the second order for the total energy is:

$$(3)\quad E(k) = V(0) + \frac{\hbar^2 k^2}{2m} + \sum_K \frac{|V(K)|^2}{\frac{\hbar^2}{2m}\left[k^2 - (k+K)^2\right]}$$

$$E^{(0)}(k) - E^{(0)}(k+K)$$

in the non-degenerate case.

Degenerate Perturbation Treatment:

In the zeroeth order, we have for the two states:

$$(4)\quad \left[\frac{\hbar^2}{2m}k^2 + V(0)\right]\chi(k) + V(K)\chi(k+K) = E\chi(k)$$

$$\left[\frac{\hbar^2}{2m}(k+K)^2 + V(0)\right]\chi(k+K) + V(-K)\chi(k) = E\chi(k+K)$$

Solving for the coefficients of the χ's, we have the following secular equation

$$(5)\quad \begin{vmatrix} \frac{\hbar^2}{2m}k^2 + V(0) - E & V(K) \\ V(-K) = V^*(K) & \frac{\hbar^2}{2m}(k+K)^2 + V(0) - E \end{vmatrix} = 0$$

Put $\epsilon = E - V(0)$ and solve the determinant:

$$(6)\quad \left[\epsilon - \frac{\hbar^2 k^2}{2m}\right]\left[\epsilon - \frac{\hbar^2 (k+K)^2}{2m}\right] - |V(K)|^2 = 0$$

$$\epsilon^2 - \frac{\hbar^2}{2m}\left[k^2 + (k+K)^2\right]\epsilon + \left[\left(\frac{\hbar^2}{2m}\right)^2 k^2 (k+K)^2 - |V(K)|^2\right] = 0$$

We now solve for ϵ by the quadratic equation and get:

$$(7)\quad \epsilon = \frac{1}{2}\frac{\hbar^2}{2m}\left[k^2+(k+K)^2\right] \pm \left[\frac{1}{4}\left(\frac{\hbar^2}{2m}\right)^2\left\{k^2-(k+K)^2\right\}^2 + |V(K)|^2\right]^{1/2}$$

Then:

$$(8)\quad E = V(0) + \frac{1}{2}\left[E^{(0)}(k) + E^{(0)}(k+K)\right] \pm \left[\frac{1}{4}\left\{E^{(0)}(k) - E^{(0)}(k+K)\right\}^2 + |V(K)|^2\right]^{1/2}$$

This is the first order energy perturbation.

Let us now consider the following possibilities:

A. $E^{(0)}(k) - E^{(0)}(k+K) >> |V(K)|$

We get from equation (8):

$$\left.\begin{aligned} E &= V(0) + E^{(0)}(k) \\ &V(0) + E^{(0)}(k+K) \end{aligned}\right\}$$ case of free electrons.

B. $E^{(0)}(k) = E^{(0)}(k+K)$

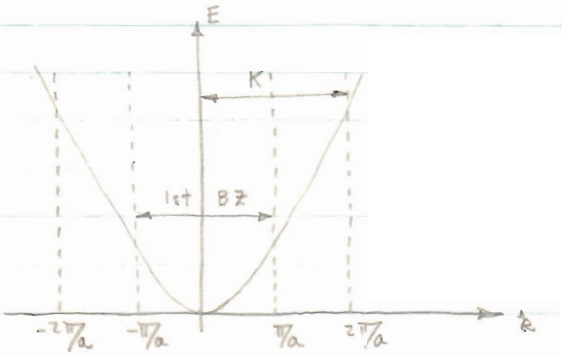
We get from equation (8):

$$E = V(0) + E^{(0)}(k) \pm |V(K)|$$

This occurs when $\frac{\hbar^2}{2m}\left[k^2-(k+K)^2\right] = 0$ which means that discontinuities are present. That is:

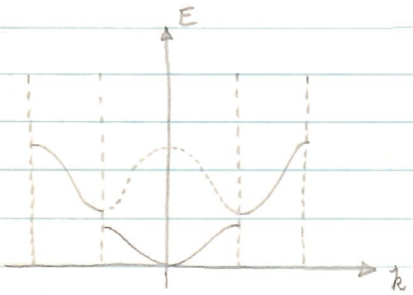
$(k+K)^2 - k^2 = 0$; $K^2 + 2k\cdot K = 0$

In one dimension: $k = \pm\frac{1}{2}K$ (K is either $\pm$) which is the definition of the BZ boundaries.



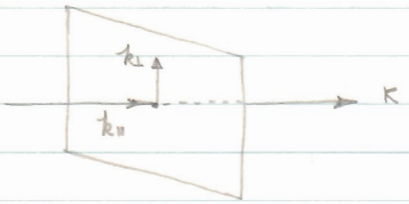
The equation $k = \pm\frac{1}{2}K$ denotes bisection of distances between reciprocal lattice points. This also indicates the two solutions of the energy equation in the B part.

We see that at $k = \pm \frac{1}{2}K$, there are two solutions for the energy, viz., $E = V(0) + E^{(0)}(k) + |V(K)|$
$= V(0) + E^{(0)}(k) - |V(K)|$,
That is, the energy of the unperturbed state has been split into two different levels by the perturbation. In one dimension, this appears as:



Splitting due to mixing of the unperturbed states by the small perturbing potential.

In Three Dimensions:



$k_\perp$ lies in the plane $\perp$ to K:

$K^2 + 2(k_\parallel + k_\perp)\cdot K = 0$,
but $k_\perp \cdot K = 0$
$\therefore\ k_\parallel = -\frac{1}{2}K$
Thus splitting will occur at a Brillouin zone face.

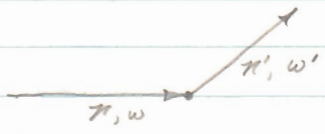
We now note that $K^2 + 2k\cdot K = 0$ is analogous to the Bragg reflection law related to the scattering of x-rays. We now examine this relationship.

We start with x-rays of wave number κ and frequency ω:

$$\psi_\kappa = \frac{1}{\sqrt{\Omega}} e^{i(\kappa\cdot r - \omega t)}, \quad \kappa = \frac{2\pi}{\lambda}$$

$$V(r) = \sum_K V(K) e^{-iK\cdot r}$$

Assume elastic scattering



We then have for the matrix elements of the scattering matrix:

$$(\psi_{\pi'}, V\psi_{\pi}) = \frac{1}{\Omega}\sum_{K} V(K)\, e^{i(\omega'-\omega)t} \underbrace{\int e^{i(\pi-K-\pi')\cdot r}\, d^3r}_{\Omega\,\delta_{\pi',\pi-K}}$$

and the matrix must be finite.

If: $\omega' = \omega$

$\omega = c\pi$

$|\pi'| = |\pi|$

$|\pi - K| = |\pi|$

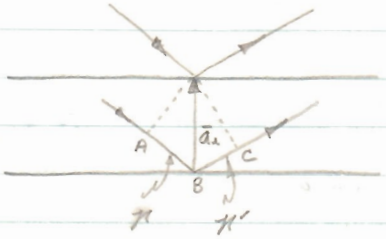
$\pi^2 - 2\pi\cdot K + K^2 = \pi^2$

or $K^2 - 2\pi\cdot K = 0$ (Bragg Reflection)

This means:

For constructive interference

$\overline{AB} + \overline{BC} = g_i \lambda$



$$AB = -\frac{\pi\cdot a_i}{|\pi|}$$

$$BC = \frac{\pi'\cdot a_i}{|\pi|}$$

We then get: $a_i\cdot(\pi'-\pi) = \pi g_i \lambda$, with $a_i\cdot b_j = \delta_{ij}$

Then $\pi' - \pi = \pi g_i \lambda b_i = 2\pi g_i b_i = K$

Return to Brillouin Zones:

At the BZ face, we have a splitting of energy levels by $\pm|V(K)|$. What happens when $V(K)$ vanishes? That is to say, one should not expect a discontinuity at every BZ face, because $V(K)$ might systematically vanish or accidently vanish, particularly when we are dealing with a lattice with a basis.

(atoms identical)

$$V(r) = \sum_{lb} V_a(r - R_l - b) = \sum_{K} V(K) e^{-iK\cdot r}$$

We will now find $V(K)$ explicitly:

Multiply by $e^{\imath K\cdot r}$ and integrate over co-ordinate space and get:

$$(9)\quad \Omega V(K) = \sum_{\ell b} \int d^3r\, V_a(r - R_\ell - b)\, e^{\imath K\cdot r}$$

make the substitutions:

$$r' = r - R_\ell - b$$
$$r = r' + R_\ell + b$$
$$e^{\imath K\cdot r} = e^{\imath K\cdot(r'+b)}$$
$$e^{\imath K\cdot R_\ell} = 1$$

$$(10)\quad \Omega V(K) = \sum_{\ell b} \int d^3r'\, V(r')\, e^{\imath K\cdot r'}\, e^{\imath K\cdot b}$$
$$= G^3 \sum_b e^{\imath K\cdot b} \int d^3r'\, V(r')\, e^{\imath K\cdot r'}$$

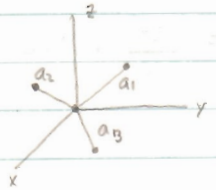
We define the structure factor to be:

$$(11)\quad S_K = \sum_b e^{\imath K\cdot b}$$

Usually the case when $V(K)$ vanishes is because the structure factor vanishes. This now brings us to the Jones zone.

Jones Zone (JZ): This is the zone each of whose faces correspond to energy discontinuities. In general, the JZ is larger than the BZ. For simple structures, they are identical.

Example: Face Centered Cubic Lattice:



Consider fcc with one atom per unit cell.

$$a_1 = \frac{a}{2}(011) \qquad b_1 = \frac{1}{a}(-111)$$
$$a_2 = \frac{a}{2}(101) \qquad b_2 = \frac{1}{a}(1-11)$$
$$a_3 = \frac{a}{2}(110) \qquad b_3 = \frac{1}{a}(11-1)$$

} bcc

$$\text{now } b_1 = \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3}$$

Now the atomic volume is: $v_a = a_1 \cdot a_2 \times a_3 = \begin{vmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{vmatrix} \frac{a^3}{8} = \frac{a^3}{4}$

and the reciprocal lattice vector is

$$K = \frac{2\pi}{a}\left[g_1 \begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix} + g_2 \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} + g_3 \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix} \right]$$

The nearest neighbors in reciprocal space are of the form

$$K = \frac{2\pi}{a}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}, \text{ etc.}$$

For next nearest: $K = \frac{4\pi}{a}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \frac{4\pi}{a}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \frac{4\pi}{a}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

and the bisectors will form a truncated octahedron for nearest and next neighbor interaction. The hexagonal side is $\perp$ to the nearest neighbor vectors. The square side is $\perp$ to the next nearest neighbor vectors.

LECTURE XVII 11-4-60

Jones and Brillouin Zones:

We introduce the notation nn for nearest neighbors and nnn for next nearest neighbors. In the fcc lattice; the distances in reciprocal space are:

nn: $K = \frac{2\pi}{a}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}$, etc. (hexagonal faces at surfaces)

nnn: $K = \frac{4\pi}{a}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$, etc. (square faces at surfaces)

Construction of the Jones Zone:

Consider the fcc equal to the sc with a basis. For a simple cubic, the BZ is a cube. The Jones zone is constructed so that $V(K)$ does not vanish at the faces, or, that energy gaps exist at the faces. We have:

(1) $V(K) \sim S_K = \sum_b e^{iK \cdot b}$ where the script b are basis vectors.

Now: $a_1 = a\begin{pmatrix}1\\0\\0\end{pmatrix}$, $b_1 = \frac{1}{a}\begin{pmatrix}1\\0\\0\end{pmatrix}$

and $S_K = \sum_{\mathcal{B}} e^{2\pi i (g_1 b_1 + g_2 b_2 + g_3 b_3)\cdot \mathcal{B}}$

with the basis vectors as:

$\mathcal{B} = (000)$, $\frac{a}{2}(110)$, $\frac{a}{2}(101)$, $\frac{a}{2}(011)$, therefore:

(2) $S_K = 1 + e^{\pi i (g_2+g_3)} + e^{\pi i (g_1+g_3)} + e^{\pi i (g_1+g_3)}$

Let us examine what happens to S_K when taking nn, nnn, etc.

A. nn in sc: $g_1 g_2 g_3 = 100$
$S_K = 1+1-1-1 = 0$

B. nnn: $g_1 g_2 g_3 = 110$
$S_K = 1-1-1+1 = 0$

C. nnnn: $g_1 g_2 g_3 = 111$; $S_K = 4$

D. nnnnn: $g_1 g_2 g_3 = 200$; $S_K = 4$

$\therefore V(K) \neq 0$

We have for the reciprocal lattice vector:

(3) $K = 2\pi (g_1 b_1 + g_2 b_2 + g_3 b_3) = \frac{2\pi}{a}\left[g_1\begin{pmatrix}1\\0\\0\end{pmatrix} + g_2\begin{pmatrix}0\\1\\0\end{pmatrix} + g_3\begin{pmatrix}0\\0\\1\end{pmatrix}\right]$

For case C above: $K = \frac{2\pi}{a}\left[\begin{pmatrix}1\\0\\0\end{pmatrix} + \begin{pmatrix}0\\1\\0\end{pmatrix} + \begin{pmatrix}0\\0\\1\end{pmatrix}\right]$

which is the same as the distance between nn when considering the fcc as with one atom per unit cell.

For case D above: $K = \frac{4\pi}{a}\begin{pmatrix}1\\0\\0\end{pmatrix}$ which is the same as the distance between nnn when considering the fcc as with one atom per unit cell.

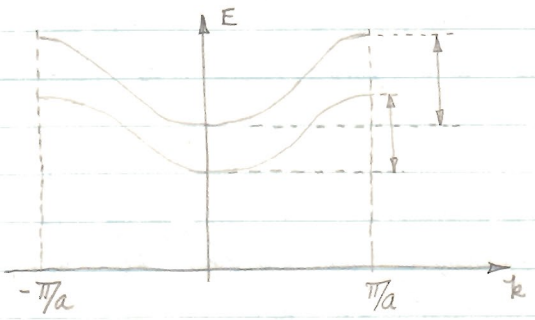
In this case, the Jones zone is the same as the Brillouin zone when taking the fcc as 1 atom/cell. In general, the BZ and the JZ are different as in the hcp for example.

BZ JZ

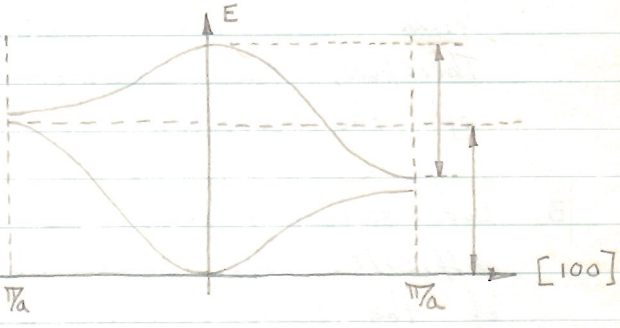
Summary of Brillouin Zone Properties:

A. All zones have the same volume in reciprocal space (from the mapping properties).
B. We can neglect all zones but the first if we regard the energy as a multiple-valued function of k (reduced zone scheme).
C. Each zone contains $2G^3$ states (2 for spin).
D. Correspondence to x-ray diffraction.
E. Translational symmetry applies to BZ. The construction of the BZ is by bisecting the nearest neighbor k vectors.
F. Two nearest neighboring zones may have overlapping energy bands.

In 1D:



In 3D:



In metals, this overlapping of bands is quite common. This can mean electrons spilling over into higher bands before the lower ones are completely filled.

WANNIER FUNCTIONS:

It is desired to find some wave functions in terms of cellular conditions in co-ordinate space. These will be more convenient than Block functions which are in terms of the periodic lattice. Such functions are found from the Fourier transform of the Block functions and are called Wannier functions:

$$(4)\quad a_n(R_\ell, r) = \frac{1}{\sqrt{N}} \sum_{k \in |BZ|} e^{-ik\cdot R_\ell}\, b_n(k, r)$$

N = G^3; sum over one BZ only; n = Band Index

Properties:

A. $a_n(R_\ell, r) = a_n(r - R_\ell)$

To show this, let: $r \to r+R$, $R_\ell \to R_\ell + R$, then

$$a_n(R_\ell + R, r+R) = \frac{1}{\sqrt{N}} \sum_k e^{-ik\cdot(R_\ell+R)}\, b_n(k, r+R)$$

$$= \frac{1}{\sqrt{N}} \sum_k e^{-ik\cdot(R_\ell+R)}\, e^{ik\cdot R}\, b_n(k, r)$$

$$= a_n(R_\ell, r) = a_n(r - R_\ell)$$

From the fact that $b_n(k, r+R) = e^{ik\cdot R}\, b_n(k, r)$
Therefore, the Wannier functions are invariant to translations of the origin.

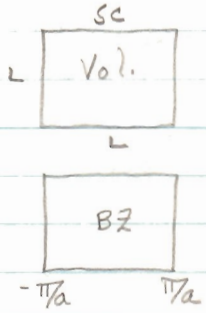
B. Localization Property. To show the localization property is difficult. We shall use an example in which the u's of the Block functions are independent of k.

$$b_n(k, r) = \frac{1}{\sqrt{\Omega}}\, u(r)\, e^{ik\cdot r}$$

Upon substitution in (4), we get:

$$a_n(r - R_\ell) = \frac{1}{\sqrt{N\Omega}}\, u(r) \sum_k e^{ik\cdot(r-R_\ell)}$$

Because k space is almost continuous, we can replace the summation with an integration which will be only over the first BZ of, say, a simple cubic structure.



For simplicity, we proceed only in one dimension.

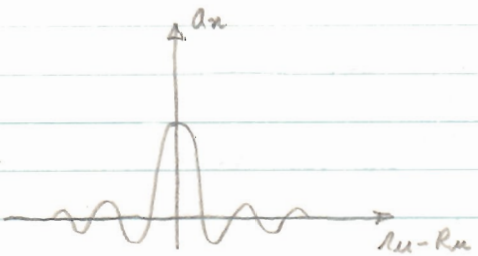
$$\sum_k e^{i k\cdot(r-R_\ell)} \rightarrow \frac{L}{2\pi}\int_{-\pi/a}^{\pi/a} dk_\mu\, e^{i k_\mu\cdot(r_\mu - R_\mu)}$$

$$= \frac{L}{2\pi i}\frac{1}{r_\mu - R_\mu}\left[e^{i\pi/a\,(r_\mu - R_\mu)} - e^{-i\pi/a\,(r_\mu - R_\mu)}\right]$$

$$= \frac{L}{\pi}\frac{\sin \pi/a\,(r_\mu - R_\mu)}{r_\mu - R_\mu}$$ where μ denotes a Cartesian component.

Then: $$a(r-R_\ell) = \sqrt{\frac{\Omega}{N}}\frac{L^3}{\pi^3}\frac{\sin\pi/a\,(x-R_x)\sin\pi/a\,(y-R_y)\sin\pi/a\,(z-R_z)}{(x-R_x)(y-R_y)(z-R_z)}$$

In 1D:



For the general case of the one dimensional model, we can choose the phase factor such that one and only one Wannier function exists that dies off exponentially or inversely: See W. Kohn, Phys. Rev. 115 809 (1959).

C. Inverse of Wannier Functions: Finding $b_n(k,r)$ as a function of $a_n(r-R_\ell)$

Multiply equation (4) by $e^{i k'\cdot R_\ell}$ and sum on ℓ. We get:

$$\sum_\ell e^{i k'\cdot R_\ell} a_n(r-R_\ell) = \frac{1}{\sqrt{N}}\sum_k b_n(k,r)\underbrace{\sum_\ell e^{i(k'-k)\cdot R_\ell}}_{N\,\delta_{k k'}}$$

or: $$b_n(k,r) = \frac{1}{\sqrt{N}}\sum_\ell e^{i k\cdot R_\ell} a_n(r-R_\ell)$$

D. Orthogonality of Wannier Functions:

$$\int a_n^*(r-R_\ell)\, a_{n'}(r-R_{\ell'})\, d^3r = \frac{1}{N}\sum_{k,k'} e^{i(k\cdot R_\ell - k'\cdot R_{\ell'})}$$

$$\cdot \underbrace{\int b_n^*(k,r)\, b_{n'}(k',r)\, d^3r}_{\delta_{nn'}\delta_{kk'}} = \frac{\delta_{nn'}}{N} \underbrace{\sum_k e^{ik\cdot(R_\ell - R_{\ell'})}}_{N\,\delta_{\ell\ell'}}$$

$$= \delta_{nn'}\,\delta_{\ell\ell'}$$

Let us now consider the operators $\hat{k}$ and $\hat{R}$ so that $\hbar k$ is called the crystal momentum and R is called the crystal coordinate. These operators are defined by:

(5) $\hat{R}\; a_n(r-R_\ell) = R_\ell\, a_n(r-R_\ell)$

$\hat{k}\; b_n(k,r) = k\, b_n(k,r)$

Consider a component of the operator $\hat{R}$; $\hat{R}_\alpha$:

(6) $$\hat{R}_\alpha\, b_n(k,r) = \frac{1}{\sqrt{N}}\sum_\ell e^{ik\cdot R_\ell} R_{\ell\alpha}\, a_n(r-R_\ell)$$

$$= \frac{1}{\sqrt{N}}\left(-i\frac{\partial}{\partial k_\alpha}\right)\sum_\ell e^{ik\cdot R_\ell}\, a_n(r-R_\ell)$$

$$= -i\frac{\partial}{\partial k_\alpha}\, b_n(k,r)$$

Performing a similar operation on the Wannier function with $\hat{k}_\alpha$ will give $i\frac{\partial}{\partial R_{\ell\alpha}}\, a_n(r-R_\ell)$.

LECTURE XVIII 11-7-60

Wannier Functions:

(1) $a_n(r-R_\ell) = \frac{1}{\sqrt{N}} \sum_k e^{-ik\cdot R_\ell} b_n(k,r)$

$b_n(k,r) = \frac{1}{\sqrt{N}} \sum_\ell e^{ik\cdot R_\ell} a_n(r-R_\ell)$

These functions form a complete orthogonal set. They have the important property of localization, viz:

Also, they are orthonormal:

(2) $\int a_{n'}^*(r-R_{\ell'})\, a_n(r-R_\ell)\, d^3r = \delta_{nn'}\delta_{\ell\ell'}$

We define the following diagonalized operators:

$\hat{R} \rightarrow$ crystal coordinate

$\hbar\hat{k} \rightarrow$ crystal momentum

with: $\hat{R}\, a_n(r-R_\ell) = R\, a_n(r-R_\ell)$

$\hat{k}\, b_n(k,r) = k\, b_n(k,r)$

Applying the operators to their opposite functions:

$\hat{R}_\alpha\, b_n(k,r) = \frac{1}{\sqrt{N}} \sum_\ell e^{ik\cdot R_\ell} R_{\ell\alpha}\, a_n(r-R_\ell) = \left(-i\frac{\partial}{\partial k_\alpha}\right) b_n(k,r)$

$\hat{k}_\beta\, a_n(r-R_\ell) = \frac{1}{\sqrt{N}} \sum_k e^{-ik\cdot R_\ell} k_\beta\, b_n(k,r) = \left(i\frac{\partial}{\partial R_{\ell\beta}}\right) a_n(r-R_\ell)$

Define a new representation as some system wave function expanded in terms of Bloch functions:

(3) $\psi(r) = \sum_{n,k} a_n(k)\, b_n(k,r)$

Take $H\psi(r) = E\psi(r)$, multiply by $\int b_{n'}^*(k',r)\, d^3r$, and get; letting $a_n(k) \rightarrow \varphi_n(k)$:

(4) $\sum_{nk} a_n(k) \int b^*_{n'}(k',r)\, H\, b_n(k,r)\, d^3r = \sum_{nk} a_n(k)\, E \underbrace{\int b^*_{n'}(k',r)\, b_n(k,r)\, d^3r}_{\delta_{nn'}\,\delta_{kk'}}$

or $\sum_{nk} \langle n'k'|H|nk\rangle\, \varphi_n(k) = E\, \varphi_{n'}(k')$

which is the Schroedinger equation in a new representation called the crystal momentum representation (Adams, 1953).

Now consider:

(5) $\hat{R}_\alpha\, \psi(r) \Rightarrow \sum_{nk} \varphi_n(k) \left(-i \frac{\partial}{\partial k_\alpha}\right) b_n(k,r)$

We replace the sum in k space by an integration:

(6) $\hat{R}_\alpha\, \psi(r) \rightarrow \sum_n \int d^3k\, \varphi_n(k) \left(-i \frac{\partial}{\partial k_\alpha}\right) b_n(k,r)$

$= \sum_n \int d^3k \left(-i \frac{\partial}{\partial k_\alpha}\right) \left(\varphi_n(k)\, b_n(k,r)\right) = 0$ (reduced zone)

$- \sum_n \int d^3k\, b_n(k,r) \left(-i \frac{\partial}{\partial k_\alpha}\right) \varphi_n(k)$

We then have a surface integral over the B.Z. Replacing the integral with a sum:

(7) (6) $\rightarrow$ $\sum_{nk} b_n(k,r) \left(i \frac{\partial}{\partial k_\alpha}\right) \varphi_n(k)$

Now multiply by $\int b^*_{n'}(k',r)\, d^3r$:

(8) $\int b^*_{n'}(k',r)\, \hat{R}_\alpha\, \psi(r)\, d^3r = \sum_{nk} \int b^*_{n'}(k',r)\, b_n(k,r)\, d^3r \left(i \frac{\partial}{\partial k_\alpha}\right) \varphi_n(k)$

$\Downarrow$

$\sum_{nk} \langle n'k'|\hat{R}_\alpha|nk\rangle\, \varphi_n(k) = i \frac{\partial}{\partial k'_\alpha}\, \varphi_{n'}(k')$

We see that the matrix of $\hat{R}_\alpha$ is diagonal or:

(9) $\langle n'k'|\hat{R}_\alpha|nk\rangle = i \frac{\partial}{\partial k_\alpha}\, \delta_{nn'}\, \delta_{kk'}$

A similar relation also holds for $\hat{k}_\beta$ in the crystal momentum representation:

$$(10)\quad \langle n'k' | \hat{k}_\beta | nk \rangle = k_\beta \delta_{nn'} \delta_{kk'}$$

How do $\hat{k}_\beta$, $\hat{R}_\alpha$ commute?

Evaluate the elements of the commutator matrix:

$$(11)\quad \langle n'k' | \hat{R}_\alpha \hat{k}_\beta - \hat{k}_\beta \hat{R}_\alpha | nk \rangle$$

$$= \sum_{n''k''} \left\{ \langle k'n' | \hat{R}_\alpha | k''n'' \rangle \langle k''n'' | \hat{k}_\beta | kn \rangle - \langle k'n' | \hat{k}_\beta | k''n'' \rangle \langle k''n'' | \hat{R}_\alpha | kn \rangle \right\}$$

$$= \sum_{n''k''} \left\{ \imath \frac{\partial}{\partial k'_\alpha} \delta_{k'k''} \delta_{n'n''} k_\beta \delta_{kk''} \delta_{nn''} - k_\beta \delta_{k'k''} \delta_{n'n''} \imath \frac{\partial}{\partial k_\alpha} \delta_{kk''} \delta_{nn''} \right\}$$

$$= \delta_{nn'} \delta_{kk'} \left\{ \imath \frac{\partial}{\partial k_\alpha} k_\beta - \imath k_\beta \frac{\partial}{\partial k_\alpha} \right\} = \langle n'k' | \imath \delta_{\alpha\beta} | nk \rangle$$

$$\therefore \quad [\hat{R}_\alpha, \hat{k}_\beta] = \imath \delta_{\alpha\beta}$$

In the crystal coordinate representation with wave functions $\psi(r) = \sum_l \psi_n(R_l)\, a_n(r - R_l)$, $k_\alpha = \frac{1}{\imath} \frac{\partial}{\partial R_\alpha}$ must hold.

This can be shown by: $R_\alpha \frac{1}{\imath} \frac{\partial}{\partial R_\beta} - \frac{1}{\imath} \frac{\partial}{\partial R_\beta} R_\alpha = \imath \delta_{\alpha\beta}$

These relations will not be used now. However, the two representations are entirely equivalent.

Limitations: R_α, k_β are discrete and they can only operate on periodic functions of k. That is, they are valid if:

$$f(k) = \sum_l F(R_l)\, e^{\imath k \cdot R_l}, \quad f(k) = f(k + K)$$

Consider:

(12) $[\hat{R}, f(k)] = [i\nabla_k, f(k)] = i\nabla_k f(k)$

Keep in mind that $e^{ik\cdot R_\ell}$ is an eigenvalue of T_ℓ and we will show that functions expanded in terms of T_ℓ are valid for the operators.

(13) $f(k) = e^{ik\cdot R_\ell}$, $i\nabla_k f(k) = -R_\ell e^{ik\cdot R_\ell}$

$\therefore [\hat{R}, e^{ik\cdot R_\ell}] = \hat{R}T_\ell - T_\ell\hat{R} = -R_\ell T_\ell$

Then $T_\ell \hat{R} = (\hat{R} + R_\ell) T_\ell$ and this shows that the operators are consistent with the effects of T_ℓ.

Now suppose we operate on $f(R)$ with some function of k when we want $k = -i\frac{\partial}{\partial R_\ell}$. Again we can use only functions of k which are periodic. For example:

(14) $T_\ell f(R) = e^{ik\cdot R_\ell} f(R) = e^{R_\ell\cdot\nabla_\ell} f(R) = f(R+R_\ell)$

Therefore, $-i\frac{\partial}{\partial R_\ell}$ can be formally used when functions of k can be expanded in terms of T_ℓ.

Return to Wannier Functions: Tight Binding approximation: Find $E_n(k)$ in terms of Wannier functions. Recall:

(15) $H b_n(k,r) = E_n(k) b_n(k,r)$, $H = \frac{p^2}{2m} + V(r)$

Now:

(16) $\sum_\ell e^{ik\cdot R_\ell} H a_n(r-R_\ell) = E_n(k) \sum_\ell e^{ik\cdot R_\ell} a_n(r-R_\ell)$

Multiply by $\int a_{n'}^*(r-R_{\ell'})\, d^3r$ and get

(17) $\sum_\ell e^{ik\cdot R_\ell} \langle n'\ell' | H | n\ell\rangle = E_{n'}(k) e^{ik\cdot R_{\ell'}} \delta_{nn'}$

It is clear that $\langle n'l'|H|nl\rangle$ has only diagonal components. We then define $\langle nl'|H|nl\rangle \equiv H_n(l';l)$ and:

(18) $$E_n(k) = \sum_l e^{-ik\cdot(R_l - R_{l'})} H_n(l';l)$$

And since H is periodic, we can apply our cosmological principle, $H_n(l',l) = H_n(l-l')$. Choose $R_l = 0$, $l' \to l$ and get:

(19) $$E_n(k) = \sum_l H_n(l)\, e^{-ik\cdot R_l}$$

This is a general equation which permits the states to be found by the matrix elements of H in terms of Wannier functions.

Tight Binding: Take the atoms to be far enough apart such that Wannier functions do not overlap.

We write for the potential: $V(r) = \sum_l \underbrace{V_a(r - R_l)}_{\text{atomic potential}}$

For a single atom: $\left[\frac{p^2}{2m} + V_a(r)\right] a_n(r) = E_n^{(a)} a_n(r)$

which is good only for non overlapping Wannier functions.

LECTURE XIX 11-9-60

The Tight Binding Approximation:

Equations from last lecture:

(1) $H = \frac{p^2}{2m} + V(r)$; $H\, b_n(k,r) = E_n(k)\, b_n(k,r)$

(2) $E_n(k) = \sum_l e^{-ik\cdot R_l} H_n(l)$

with $H_n(l) = \int a_n^*(r-R_l)\, H\, a_n(r)\, d^3r$

We take the space between atoms large enough so that the wave functions do not overlap. We can start with localized wave functions and form bands from the overlap of the perturbed wave functions: Notice that $w^2 \sim \sum_l c(l)\, e^{-ik\cdot R_l}$ is very similar to equation (2).

Tight Binding Wave functions:

(3) $V(r) = \sum_l V_a(r-R_l)$

(4) $\left[\frac{p^2}{2m} + V_a(r)\right] a_n(r) = E_n^a\, a_n(r)$

V_a is the potential due to the field of the nucleus and other electrons of a single atom. The net potential at any point is the sum of all these potentials. For non-overlapping wave functions, we could write a Schroedinger equation like (4), with E_n^a as the hydrogenic energy level.

We demand that the Wannier functions be orthonormal and that they be Fourier related to the Bloch functions:

(5) $$\int a_{n'}^{*}(r-R_{\ell'})\, a_n(r-R_\ell)\, d^3r = \delta_{nn'}\delta_{\ell\ell'}$$

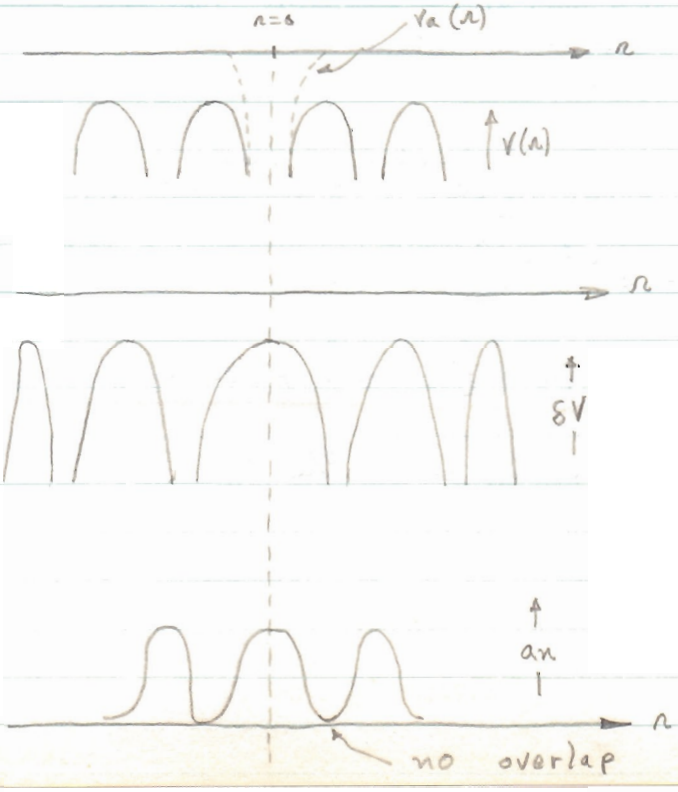
(6) $$b_n(k,r) = \frac{1}{\sqrt{N}} \sum_{\ell} e^{ik\cdot R_\ell}\, a_n(r-R_\ell)$$

Consider the a_n's as atomic orbitals. The following is called LCAO, linear combination of atomic orbitals. Now:

(7) $$H_n(k) = \int a_n^*(r-R_\ell)\left\{ \underbrace{\frac{p^2}{2m} + V_a(r)}_{E_n^a} + \underbrace{\sum_{\ell}{}' V_a(r-R_\ell)}_{\delta V = V(r)-V_a(r)} \right\} a_n(r)\, d^3r$$

$$= E_n^a \delta_{\ell 0} + \int a_n^*(r-R_\ell)\, \delta V\, a_n(r)\, d^3r$$

This brings in the interaction of the rest of the atoms in the crystal. The wave functions still do not overlap but the field of the other atoms δV has now been introduced. The following illustrates the situation graphically.



How may we evaluate the above integrals? We take the atomic states n to correspond to s functions which are non-degenerate and spherically symmetric. Thus the integrals will be the same regardless of which atom they are taken over. We now define these integrals as constants:

$$(8)\quad \int |a_n(r)|^2\, \delta V\, d^3r = -\alpha_n$$

$$(9)\quad \int a_n^*(r-R_l)\, \delta V\, a_n(r)\, d^3r = -\beta_n(l)$$

} both constants are positive

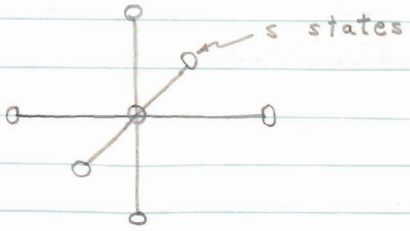
Applying equation (2) to (7) with (8) and (9) gives:

$$(10)\quad E_n(k) = E_n^a - \alpha_n - \sum_l{}' e^{-ik\cdot R_l}\, \beta_n(l)$$

It is seen that it is the last term which introduces the band nature.

Example: Simple cubic with NN Interaction:

$$a_1 = \begin{pmatrix}1\\0\\0\end{pmatrix}a,\quad a_2 = \begin{pmatrix}0\\1\\0\end{pmatrix}a,\quad a_3 = \begin{pmatrix}0\\0\\1\end{pmatrix}a$$



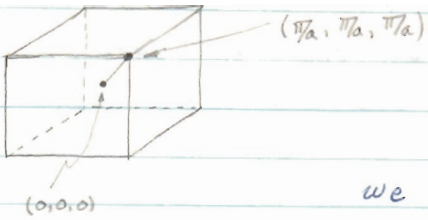
$\beta(l)$ is the same for each atom:
Therefore:

$$E_n(k) = E_n^a - \alpha_n - \beta_n(1)\left[\left(e^{-ik_xa} + e^{ik_xa}\right) + \left(e^{-ik_ya} + e^{ik_ya}\right) + \left(e^{-ik_za} + e^{ik_za}\right)\right]$$

$$= E_n^a - \alpha_n - 2\beta_n(1)\left[\cos k_xa + \cos k_ya + \cos k_za\right]$$

with $\quad -\pi/a < k_x, k_y, k_z \leq \pi/a$

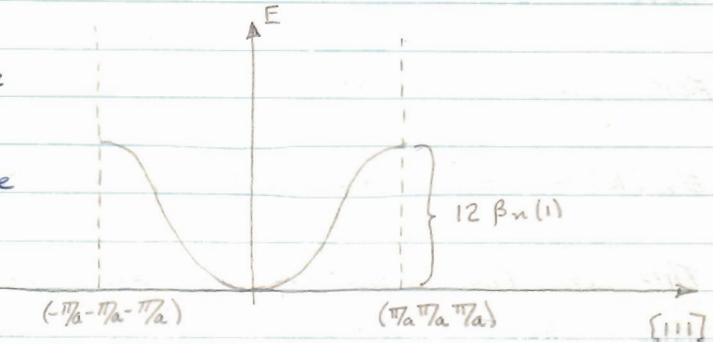
We now have the following BZ structure:



$(0,0,0)$: $E_n(0) = E_n^a - \alpha_n - 6\beta_n(1)$

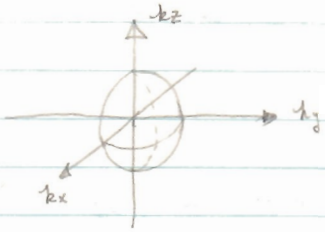
$(\pi/a\ \pi/a\ \pi/a)$: $E_n(\pi/a) = E_n^a - \alpha_n + 6\beta_n(1)$

we take (000) as reference level of energy



① Around $k \approx 0$: $E_n(k) = E_{min} + \beta_n(1)\, k^2 a^2$; $k^2 = k_x^2 + k_y^2 + k_z^2$

where E_{min} is $E_n^a - \alpha_n - 6\beta_n(1)$. The surfaces of constant energy are then spheres.

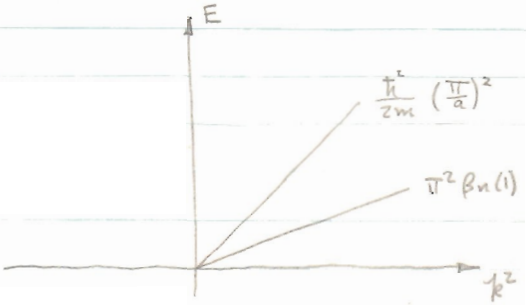


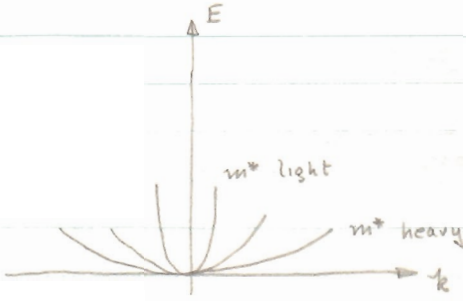
By analogy with the free electron case, we can write for $E_n(k)$ and $\beta_n(1)$:

$$E_n(k) = E_{min} + \frac{\hbar^2 k^2}{2m^*}, \text{ and}$$

$$\frac{m^*}{m} = \frac{\hbar^2}{2\beta_n(1) m a^2} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \frac{1}{\pi^2 \beta_n(1)}$$

$$= \frac{E_{free}(100)}{E'(100)}$$





We now examine the nature of the energy surfaces near the surfaces of the BZ:

② Around $(\pi/a, 0, 0)$: We let $k_x = \pi/a - K_x$ where K_x is measured in from the BZ face,

Then: $\cos k_x a = \cos(\pi - K_x a) = -\cos K_x a = -\cos(\pi/a - k_x)a$

For small $\pi/a - k_x$:

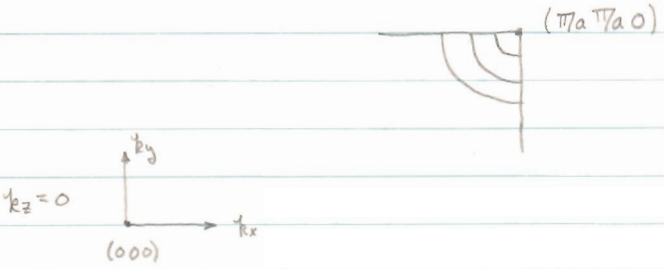
$$E_n(k) = E_n^a - \alpha_n - 2\beta_n(1) + \beta_n(1)\, a^2 \left[-(\pi/a - k_x)^2 + k_y^2 + k_z^2\right]$$

This is the equation of an equilateral hyperboloid of one sheet centered about $(\pi/a\ 0\ 0)$, That is, an equilateral hyperboloid of revolution of one sheet about the k_x axis.

③ Around $(\pi/a\ \pi/a\ 0)$: Using the same procedure as in ②:

$$E_n(k) \sim \left[-(\pi/a - k_x)^2 - (\pi/a - k_y)^2 + k_z^2\right]$$

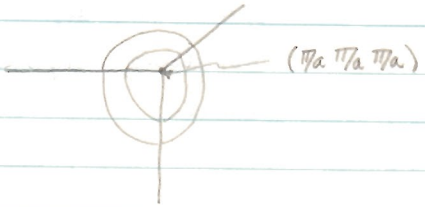
This is the equation of an equilateral hyperboloid of revolution of two sheets about the k_z axis centered at $(\pi/a\ \pi/a\ 0)$.

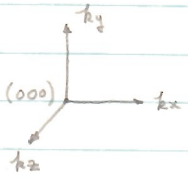


④ Around $(\pi/a\ \pi/a\ \pi/a)$:

$$E_n(k) \sim \left[-(\pi/a - k_x)^2 - (\pi/a - k_y)^2 - (\pi/a - k_z)^2\right]$$

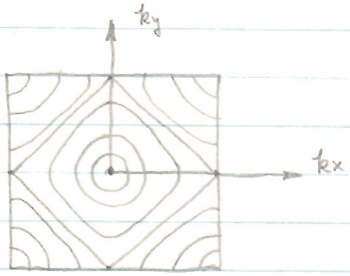
This is a sphere whose center is at $(\pi/a\ \pi/a\ \pi/a)$.





For more diagrams, see Sommerfeld & Bethe, Hand. d. Phys. 24/2 p. 400.

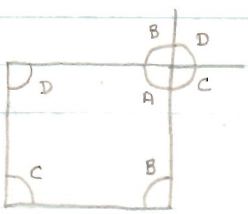
A k_x-k_y plane cross-section of the constant energy surfaces in the first BZ follows:



As the band fills up, it is seen that the Fermi surface will become far from spherical.

Some very good diagrams are in Zuman, pp 75-80.

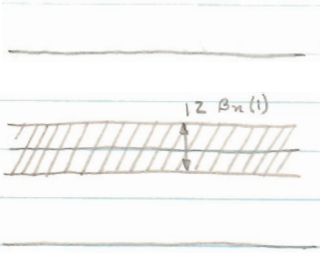
It is obvious that $E(\pi/a\ 00) < E(\pi/a\ \pi/a\ 0) < E(\pi/a\ \pi/a\ \pi/a)$ and as we fill up the band, there will be little pockets left in the corners of the cube. In the repeated zone scheme, we will have something like:



These pockets can be thought of as "holes" (particles of + charge).

We have seen how one band can be drawn in the Brillouin zone and how the surface of constant energy is constructed within the zone.

The treatment given here is only valid for widths of the band small compared to the band separation. That is, width $\ll |E_{n+1} - E_n|, |E_n - E_{n-1}|$

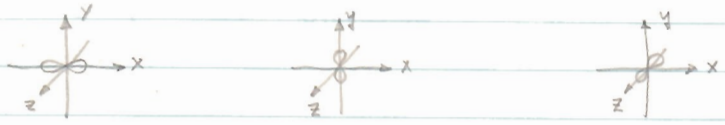


Otherwise, the wave functions will overlap and the tight binding approximation does not hold.

The Tight Binding Approximation for p functions:

Now $a_n(r)$ will be three fold degenerate (see Pauling and Wilson on the Hydrogenic atom).

$$a_n(r) = \underset{p=1}{x f(r)}\ ,\ \underset{p=2}{y f(r)}\ ,\ \underset{p=3}{z f(r)} = a_n^{(p)}(r)$$



We wish to find a single wave function which will be a linear combination of the degenerate set.

(11) $$a_n(r - R_l) = \sum_p \alpha_p a_n^{(p)}(r - R_l)$$

with the $a_n^{(p)}$ taken to be orthonormal; viz:

(12) $$\int a_n^{*(p')}(r)\, a_n^{(p)}(r)\, d^3r = \int xy\, f^2(r)\, d^3r = 0$$ since the integrand is antisymmetric.

LECTURE XX 11-14-60

Calculations of the Energy Bands in a Crystal where the Wave Functions are p Functions for the Tight Binding Approximation:

Recall from last lecture:

(1) $a_n(r) = x f(r), y f(r), z f(r) = a_n^{(\nu)}(r)$

(2) $\int a_{n'}^{(\nu')*}(r-R_{\ell'})\, a_n^{(\nu)}(r-R_\ell)\, d^3r = \delta_{\nu\nu'}\delta_{nn'}\delta_{\ell\ell'}$

Define:

(3) $b_n^{(\nu)}(k,r) = \frac{1}{\sqrt{N}} \sum_\ell e^{ik\cdot R_\ell} a_n^{(\nu)}(r-R_\ell)$

with:

(4) $a_n(r) = \sum_\nu \alpha_\nu a_n^{(\nu)}(r)$

(5) $b_n(k,r) = \sum_\nu \alpha_\nu b_n^{(\nu)}(k,r)$

(6) $\int b_{n'}^{(\nu')*}(k',r)\, b_n^{(\nu)}(k,r)\, d^3r = \frac{1}{N} \sum_{\ell\ell'} e^{i(k\cdot R_\ell - k'\cdot R_{\ell'})}$

$\cdot \int a_{n'}^{(\nu')*}(r-R_{\ell'})\, a_n^{(\nu)}(r-R_\ell)\, d^3r = \delta_{\nu\nu'}\delta_{kk'}\delta_{\ell\ell'}\delta_{nn'}$

(7) $\int |b_n(k,r)|^2\, d^3r = \sum_\nu |\alpha_\nu|^2 = 1$

Thus we have established some relations to work with. Now:

(8) $H\, b_n(k,r) = E_n(k)\, b_n(k,r)$

(9) $H \frac{1}{\sqrt{N}} \sum_\ell e^{ik\cdot R_\ell} \sum_\nu \alpha_\nu a_n^{(\nu)}(r-R_\ell)$

$= E_n(k) \frac{1}{\sqrt{N}} \sum_\ell e^{ik\cdot R_\ell} \sum_\nu \alpha_\nu a_n^{(\nu)}(r-R_\ell)$

We multiply by $\int a_{n'}^{(\nu')*}(r-R_{\ell'})\,d^3r$ and get:

(10) $E_n(k)\frac{1}{\sqrt{N'}}\sum_{\ell\nu}\alpha_{\nu'}e^{ik\cdot R_\ell}\delta_{\ell\ell'}\delta_{\nu\nu'}\delta_{nn'}$

$= E_{n'}(k)\,e^{ik\cdot R_{\ell'}}\frac{1}{\sqrt{N'}}\alpha_{\nu'}$ ($n\to n'$ because we want diagonal)

$= \frac{1}{\sqrt{N'}}\sum_{\ell}e^{ik\cdot R_\ell}\sum_{\nu}\alpha_\nu\underbrace{\int a_{n'}^{(\nu)*}(r-R_{\ell'})\,H\,a_{n'}^{(\nu)}(r-R_\ell)\,d^3r}_{H_{n'}^{(\nu\nu')}(\ell'-\ell)}$

Then, letting $n'\to n$:

(11) $\alpha_{\nu'}E_n(k) = \sum_{\nu}\alpha_\nu\sum_{\ell}e^{ik\cdot(R_\ell-R_{\ell'})}H_n^{(\nu\nu')}(\ell'-\ell)$

Finally, letting $R_{\ell'}-R_\ell\to R_\ell$:

(12) $$\boxed{E_n(k)\,\alpha_{\nu'} = \sum_{\nu}\left\{\sum_{\ell}e^{-ik\cdot R_\ell}H_n^{(\nu\nu')}(\ell)\right\}\alpha_\nu}$$

which is perfectly general for all degenerate states.

Now, following exactly the same procedure as before:

(13) $H_n^{(\nu\nu')}(\ell) = \int a_n^{(\nu)*}(r-R_\ell)\left[\frac{p^2}{2m}+V_a(r)+\delta V\right]a_n^{(\nu')}(r)\,d^3r$

$= E_n^a\,\delta_{\ell 0}\,\delta_{\nu\nu'} + \int a_n^{(\nu')*}(r-R_\ell)\,\delta V\,a_n^{(\nu)}(r)\,d^3r$

Define:

(14) $\alpha_n^{(\nu\nu')} = -\int a_n^{(\nu)*}(r)\,\delta V\,a_n^{(\nu')}(r)\,d^3r$

(15) $\beta_n^{(\nu\nu')}(\ell) = -\int a_n^{(\nu)*}(r-R_\ell)\,\delta V\,a_n^{(\nu')}(r)\,d^3r$

We get:

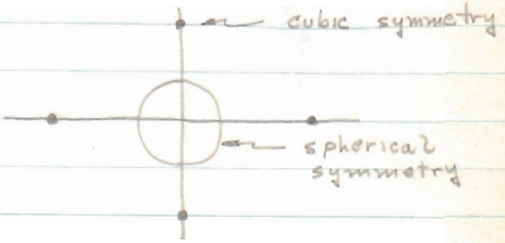
$$(16)\qquad \sum_{l} e^{-i k\cdot R_l} H_n^{(\nu\nu')}(l) = E_n^a \delta_{\nu\nu'} - \alpha_n^{(\nu\nu')} - \sum_{l}{}' e^{-i k\cdot R_l} \beta_n^{(\nu\nu')}(l)$$

Example: Simple cubic with nn interaction:

We first consider the symmetry of δV as this will be used in evaluating the integrals (14) and (15):

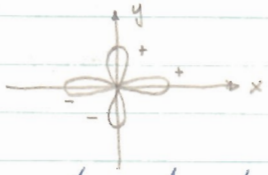
$$\delta V = \sum_{l} V_a(r - R_l) - V_a(r)$$

cubic symmetry — spherical symmetry



Since spherical symmetry is of higher order than cubic symmetry, we can consider spherical symmetry as containing cubic symmetry. We then examine the behaviour of the α_n's:

$$\alpha_n^{12} = \int x y\, f^2(r)\, \delta V\, d^3r$$



As $y \to -y$, the sign of the integrand changes. The same occurs for $x \to -x$. Therefore $\alpha_n^{12} = 0$. Another way of looking at this is to think of the integral as a joint moment of a spherically symmetric function of r which of course vanishes. It is apparent that such is the case for all $\nu \neq \nu'$. For $\nu = \nu'$, we have:

$$\int x^2 f^2(r)\, \delta V\, d^3r = \int y^2 f^2(r)\, \delta V\, d^3r = \int z^2 f^2(r)\, \delta V\, d^3r$$

These integrals do not vanish because there is no sign change in the integrand when $y \to -y$, $x \to -x$, $z \to -z$ or that the second moment of a spherically symmetric function is not zero and is equal in all directions. Thus,

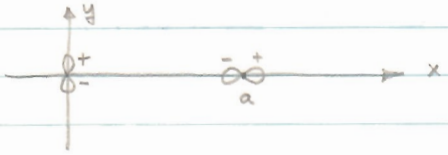
$$\alpha_n^{\nu\nu'} = \alpha_n^{\nu\nu} \delta_{\nu\nu'}$$

We now consider the behaviour of the β_n's:

$$\beta_n^{12}(100) = -\int a_n'^{*}(r-\bar{\imath}a)\,\delta V\, a_n^{2}(r)\,d^3r$$

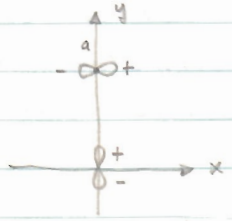
$$= -\int xy\, f(r-\bar{\imath}a)\delta V f(r)\,d^3r$$

Upon letting $x \to -x$ or $y \to -y$, the integral vanishes for the same reason as before.



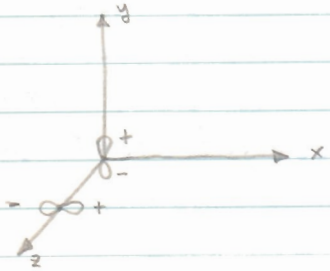
Reflect about the x-z plane. Sign changes.
Thus $\beta^{12}(100) = 0$

$$\beta_n^{12}(010) = -\int xy\, f(r-\bar{\jmath}a)\,\delta V\, f(r)\,d^3r$$



Reflect about the y-z plane. Sign of wave function changes. Or let $x \to -x$ and integrand changes sign.
Therefore $\beta_n^{12}(010) = 0$

$$\beta_n^{12}(001) = -\int xy\, f(r-\bar{k}a)\,\delta V\, f(r)\,d^3r$$



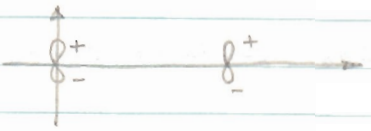
Reflect about the x-z plane. Sign changes, therefore $\beta_n^{12}(001) = 0$

It is now obvious that similar things happen when ever $\nu \neq \nu'$ in any direction. Therefore

$$\beta_n^{\nu\nu'}(l) = \beta_n^{\nu\nu}\,\delta_{\nu\nu'}$$

Two classes exist for non-vanishing β_n's corresponding to transverse and longitudinal polarizations:

1) polarization ∥ to R_ℓ

2)  polarization ⊥ to R_ℓ

1) $\beta_n^{11}(100) = -\int a^{(1)}(r-\bar{\imath}a)\,\delta V\, a^{(1)}(r)\,d^3r = -\beta < 0$

2) $\beta_n^{22}(100) = -\int a^{(2)}(r-\bar{\imath}a)\,\delta V\, a^{(2)}(r)\,d^3r = \beta' > 0$

$\beta_n^{33}(100) = -\int a^{(3)}(r-\bar{\imath}a)\,\delta V\, a^{(3)}(r)\,d^3r = \beta' > 0$

Similar operations occur for other directions giving in all only three independent parameters α_n, β_n, β_n'

Thus we have:

$$\sum_\ell e^{-\imath k\cdot R_\ell} H_n^{(\nu\nu')}(\ell) = E_n^a \delta_{\nu\nu'} - \alpha_n \delta_{\nu\nu''} + \beta_n\left(e^{-\imath k\cdot R_\nu} + e^{\imath k\cdot R_\nu}\right) - \beta_n'\left[\left(e^{-\imath k\cdot R_{\nu'}} + e^{\imath k\cdot R_{\nu'}}\right) + \left(e^{-\imath k\cdot R_{\nu''}} + e^{\imath k\cdot R_{\nu''}}\right)\right]\delta_{\nu\nu''}$$

where $R_{\nu'}$, $R_{\nu''}$ are nn distances not R_ν. ν is used as subscript x, y, z corresponding to $1, 2, 3$.

Now we have:

$$E_n(k)\alpha_{\nu'} = \sum_\nu \left\{ \sum_\ell e^{-\imath k\cdot R_\ell} H_n^{(\nu\nu')}(\ell)\, \delta_{\nu\nu'} \right\} \alpha_\nu$$

or $$E_n^{(\nu)}(k) = \sum_\ell e^{-\imath k\cdot R_\ell} H_n^{\nu\nu}(\ell)$$

The only reason we do not have to solve a secular equation is because of the high symmetry of the simple cubic.

We get a splitting into branches as follows:

$$E_n^{(x)}(k) = E_n^a - \alpha_n + 2\beta_n \cos k_x a - 2\beta_n' (\cos k_y a + \cos k_z a)$$

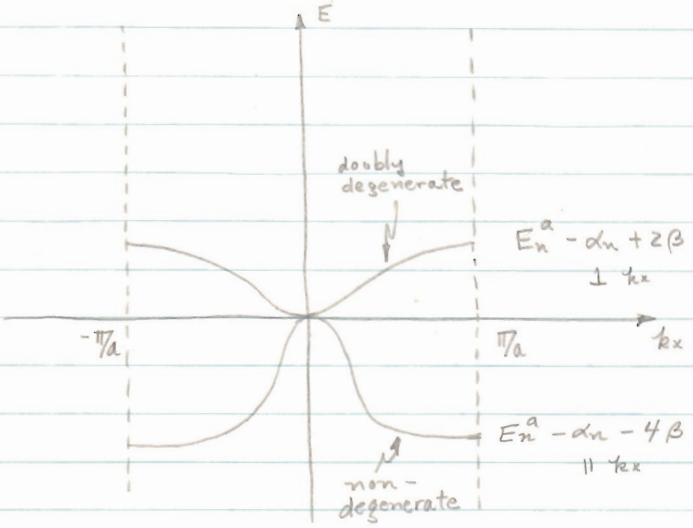
$$E_n^{(y)}(k) = E_n^a - \alpha_n + 2\beta_n \cos k_y a - 2\beta_n' (\cos k_z a + \cos k_x a)$$

$$E_n^{(z)}(k) = E_n^a - \alpha_n + 2\beta_n \cos k_z a - 2\beta_n' (\cos k_x a + \cos k_y a)$$

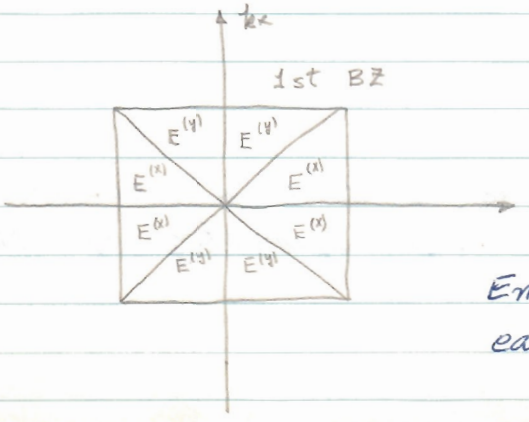
In the k_x direction: Choose $\beta' = \frac{1}{2}\beta$, because from the diagram one might think that there would be a greater chance of overlap and $\beta' < \beta$ consequently. For simplicity, take $\beta' = \frac{1}{2}\beta$. Now $k_y = k_z = 0$:

$$E_n^{(x)}(k) = E_n^a - \alpha_n + 2\beta \cos k_x a - 2\beta = E_n^a - \alpha_n - 2\beta(1 - \cos k_x a)$$

$$E_n^{(y)}(k) = E_n^{(z)}(k) = E_n^a - \alpha_n + 2\beta_n - \beta_n - \beta_n \cos k_x a$$
$$= E_n^a - \alpha_n + \beta_n (1 - \cos k_x a)$$



Note that minima occur at the zone faces.



In the x-y plane, $E_n^{(x)} \to E_n^{(y)}$ when $E_n^{(x)} = E_n^{(y)}$, that is, when $k_x = \pm k_y$

Energies change continuously into each other

Let us look at E vs. k near the (100) face.
Define: $\kappa_x = \pi/a - k_x$, $\kappa_y = k_y$, $\kappa_z = k_z$
Then:

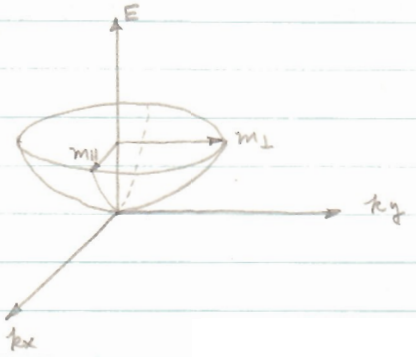
$$E_n^{(x)}(k) = E_n^a - \alpha_n - 2\beta \cos \kappa_x a - 2\beta' (\cos \kappa_y a + \cos \kappa_z a)$$

Now for $\kappa a \ll 1$:

$$E_n^{(x)}(k) \simeq E_n^{(a)} - \alpha_n - 2\beta - 2\beta' + \beta \kappa_x^2 a + \beta' (\kappa_y^2 + \kappa_z^2) a^2$$

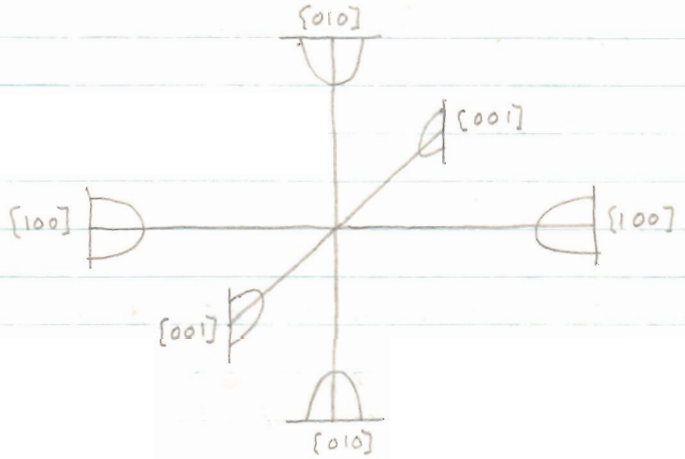
$$= E_{reference} + \frac{\hbar^2 \kappa_x^2}{2 m_{\parallel}} + \frac{\hbar^2}{2} \left(\frac{\kappa_y^2}{m_\perp} + \frac{\kappa_z^2}{m_\perp} \right)$$

Thus the contours of constant E are not spherical but are ellipsoids of revolution about the x-axis.



$\beta' < \beta$ implies $m_\perp > m_\parallel$.

This is E plotted as a variable versus the x-y plane.



Thus we have three ellipsoids per BZ

LECTURE XXI 11-16-60

$\bar{k}\cdot\bar{p}$ Perturbation Method:

Recall:

(1) $\left[\frac{1}{2m}(p+\hbar k)^2 + V(r)\right] u_n(k,r) = E_n(k)\, u_n(k,r)$

Define: $\epsilon_n(k) = E_n(k) - \frac{\hbar^2 k^2}{2m}$; then

(2) $\left[\frac{1}{2m}p^2 + V(r) + \frac{\hbar\, k\cdot p}{m}\right] u_n(k,r) = \epsilon_n(k)\, u_n(k,r)$

Consider $\epsilon_n(k+q)$ where q is a small distance from k:
In the Schroedinger equation, $k \to k+q$, $\hbar k\cdot p \to \hbar k\cdot p + \hbar q\cdot p$

(3) $\left[\frac{1}{2m}p^2 + V(r) + \frac{\hbar}{m}(k+q)\cdot p\right] u_n(k+q,r) = \epsilon_n(k+q)\, u_n(k+q,r)$

Using Perturbation methods:

(4) $H^{(0)} = \frac{1}{2m}p^2 + V(r) + \frac{\hbar\, k\cdot p}{m}$

$H^{(1)} = \frac{\hbar}{m}\, q\cdot p$

$u_n(k+q,r) = u_n^{(0)}(k,r) + u_n^{(1)}(k,r) + u_n^{(2)}(k,r)$

$\epsilon_n(k+q) = \epsilon_n^{(0)}(k) + \epsilon_n^{(1)}(k) + \epsilon_n^{(2)}(k)$

(5) $H^{(0)}\, u_n^{(0)}(k,r) = \epsilon_n^{(0)}(k)\, u_n^{(0)}(k,r)$

Important: The u_n's form a complete orthonormal set with k as a parameter. Now, with q in the μ direction, we have for the matrix element of $H^{(1)}$:

(6) $\langle n'|H^{(1)}|n\rangle = \frac{1}{\Omega}\int u_{n'}^{*}(k,r)\, \frac{\hbar q}{m}\, p^{\mu}\, u_n(k,r)\, d^3r$

$\equiv \frac{\hbar q}{m} P_{n'n}^{\mu}$

We now apply the second order perturbation theory given in Schiff, ch. 7.

$$(7)\quad \epsilon_n(k+q) = \epsilon_n^{(0)}(k) + \langle n|H^{(1)}|n\rangle + \sum_{n'}{}' \frac{\langle n|H^{(1)}|n'\rangle\langle n'|H^{(1)}|n\rangle}{\epsilon_n(k)-\epsilon_{n'}(k)}$$

$$= \epsilon_n^{(0)}(k) + \frac{\hbar}{m} q\, P_{nn}^{\mu} + \left(\frac{\hbar q}{m}\right)^2 \sum_{n'}{}' \frac{|P_{nn'}^{\mu}|^2}{\epsilon_n - \epsilon_{n'}}$$

$$(8)\quad u_n(k+q,r) = u(k,r) + \sum_{n'}{}' \frac{\langle n'|H^{(1)}|n\rangle\, u_{n'}(k,r)}{\epsilon_n(k)-\epsilon_{n'}(k)}$$

$$= u_n(k,r) + \frac{\hbar q}{m} \sum_{n'}{}' \frac{P_{n'n}^{\mu}}{\epsilon_n - \epsilon_{n'}}\, u_{n'}(k,r)$$

Let us consider:

$$(9)\quad f_{nn'}^{\mu} \equiv \frac{2}{m} \frac{|P_{nn'}^{\mu}|^2}{E_{n'} - E_n} = \frac{2}{m} \frac{|P_{nn'}^{\mu}|^2}{\epsilon_{n'}(k) - \epsilon_n(k)}$$

which looks like the oscillator strength in optics. Plugging in:

$$(10)\quad \epsilon_n(k+q) = \epsilon_n^{(0)}(k) + \frac{\hbar q}{m} P_{nn}^{\mu} - \frac{\hbar^2 q^2}{2m} \sum_{n'}{}' f_{n'n}^{\mu}$$

where the sum extends over all bands, filled or unfilled. Also,

$$(11)\quad \epsilon_n(k+q) = \epsilon_n(k) + q\frac{\partial \epsilon_n}{\partial k_\mu} + \frac{1}{2} q^2 \frac{\partial^2 \epsilon_n}{\partial k_\mu^2} + \cdots$$

expanding in a Taylor series and next equating coefficients.

$$(12)\quad \frac{\partial \epsilon_n}{\partial k_\mu} = \frac{\hbar}{m} P_{nn}^{\mu} \quad ;$$

$$\frac{\partial^2 \epsilon_n}{\partial k_\mu^2} = -\frac{\hbar^2}{m} \sum_{n'}{}' f_{n'n}^{\mu} = \frac{\partial^2 E_n}{\partial k_\mu^2} - \frac{\hbar^2}{m}$$

recalling $\epsilon_n(k) = E_n(k) - \frac{\hbar^2 k^2}{2m}$

Finally:

(13) $$\boxed{\sum_{n'}{}' f^{\mu}_{nn'} = 1 - \frac{m}{\hbar^2}\frac{\partial^2 E_n}{\partial k_\mu^2}}$$

This is called the f-sum rule. Leads to inverse of m^* and is very important.

In general; with vectors:

(14) $$\langle n'|H^{(1)}|n\rangle = \frac{1}{\Omega}\int u_{n'}^* \frac{\hbar q\cdot p}{m} u_n \, d^3r = \frac{\hbar q}{m}\cdot P_{nn'}$$

(15) $$\epsilon_n(k+q) = \epsilon_n(k) + \frac{\hbar}{m} q\cdot P_{nn} + \frac{\hbar^2}{m^2}\sum_{n'}{}' \frac{q\cdot P_{nn'}P_{n'n}\cdot q}{E_n - E_{n'}}$$

$$= \epsilon_n(k) + q\cdot\nabla_k \epsilon_n(k) + \frac{1}{2}\left(q\cdot\nabla_k\nabla_k \epsilon_n(k)\cdot q\right)$$

and fmd; for the f sum rule:

(16) $$\frac{m}{\hbar^2}\nabla_k\nabla_k E_n(k) = \mathbb{I} - \frac{2}{m}\sum_{n'}{}' \frac{P_{nn'}P_{n'n}}{E_{n'} - E_n}$$

$P_{nn'}P_{n'n}$ is called a dyadic.

Special Case:

Consider a simple band edge, with minimum at $k=0$, and assuming a simple cubic lattice with constant energy surfaces being spheres. Then $\left(\frac{\partial E_n}{\partial k_\mu}\right)_{k=0} = 0$ in all directions, thus $P^{\mu}_{n'n} = 0$ and the diagonal elements vanish for a simple band edge. We see that as $k \to 0$, q takes the place of k in the Schroedinger equation which is then taken as the perturbation term, and the unperturbed Schroedinger equation is:

(17) $$\left[\frac{p^2}{2m} + V(r)\right] u_n(0,r) = \epsilon_n(0)\, u_n(0,r)$$

Side Remarks: $P^{\mu}_{nn} \sim \int u_n(0,r) \frac{\hbar}{i} \frac{\partial}{\partial x_\mu} u_n(0,r) = 0$ does not hold for spin orbit splitting or non-inversion symmetry. All u's are real and energy is real.

Continuing:

(18) $$E_n(k) = E_n(0) + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 k^2}{2m} \sum_{n'}{}' \frac{|P_{nn'}|^2}{E_n - E_{n'}}$$

$$= E_n(0) + \frac{\hbar^2 k^2}{2 m_n^*}, \text{ thus:}$$

(19) $$\frac{m}{m_n^*} = 1 + \frac{2}{m} \sum_{n'}{}' \frac{|P_{nn}|^2}{E_n - E_{n'}} = 1 - \sum_{n'}{}' f^{\mu}_{n'n}$$

Expanding in a Taylor series again, this time about $k=0$,

(20) $$E_n(k) \rightleftharpoons E_n(0) + \frac{1}{2} k^2 \frac{\partial^2 E}{\partial k^2} = E_n(0) + \frac{\hbar^2 k^2}{2 m_n^*}$$

with the result that:

(21) $$\sum_{n'}{}' f^{\mu}_{n'n} = 1 - \frac{m}{m_n^*} = 1 - \frac{m}{\hbar^2} \frac{\partial^2 E}{\partial k^2}; \quad \frac{1}{m_n^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$$

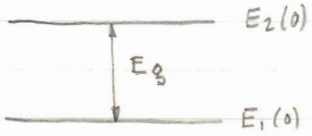
Vectorwise:

(22) $$E_n(k) = E_n(0) + \frac{1}{2} k \cdot \nabla_k \nabla_k E_n(k) \cdot k \equiv E_n(0) + \frac{1}{2} \hbar^2 \left[k \cdot |M^{-1}| \cdot k \right]$$

(23) $$|M^{-1}| = \frac{1}{\hbar^2} \nabla_k \nabla_k E = \frac{1}{m} \left[\mathbb{1} - \frac{2}{m} \sum_{n'}{}' \frac{P_{nn'} P_{n'n}}{E_{n'} - E_n} \right]$$

Therefore $|M^{-1}|$ is determined by the curvature of the band and the distance of the neighboring bands at the same point in k space.

Example: Consider only two bands and the point in k space at $k=0$, assuming cubic symmetry.



$$|P^{\mu}_{12}|^2 = |P^{\mu}_{21}|^2 = P^2$$

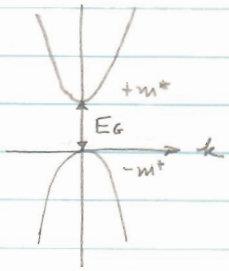
For $n=1$: $\sum_{n'}{}' f_{n'1} = f_{21} = \frac{2}{m}\frac{p^2}{E_G}$

$= 1 - \frac{m}{m_1^*}$

For $n=2$: $\sum_{n'}{}' f_{n'2} = f_{12} = \frac{2}{m}\frac{p^2}{(-E_G)} = 1 - \frac{m}{m_2^*}$

We then immediately get:

$$\frac{m}{m_1^*} = 1 - \frac{2}{m}\frac{p^2}{E_G} \quad ; \quad \frac{m}{m_2^*} = 1 + \frac{2}{m}\frac{p^2}{E_G}$$



If $\frac{2}{m}\frac{p^2}{E_G} \gg 1$ (E_G very small),

then $\frac{m}{m_1^*} \approx -\frac{m}{m_2^*} = -\frac{2}{m}\frac{p^2}{E_G}$

so that the effective mass at the top of band 1 is negative and that of the bottom of band 2 is positive and the effective mass goes as the energy gap, viz, $m_1, m_2 \sim E_G$

LECTURE XXII 11-18-60

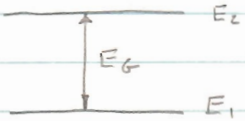
Summary of last Lecture:

$$|M^{-1}| = \frac{1}{\hbar^2}\nabla_k \nabla_k E_n(k) = \frac{1}{m}\left[\mathbb{1} - \sum_{n'}{}' f_{nn'}\right]$$

$$f_{nn'} = \frac{2}{m}\frac{P_{nn'}P_{n'n}}{E_n(k) - E_{n'}(k)} \quad ; \quad P_{n'n} = \frac{1}{\Omega}\int u_{n'}^*(k,r)\, p\, u_n(k,r)\, d^3r$$

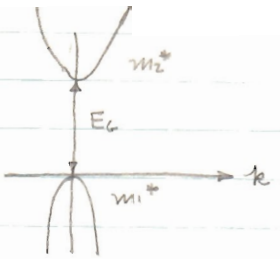
$$\nabla_k E_n(k) = \frac{\hbar}{m} P_{nn}$$

Two Band Example:



$$\frac{m}{m_1^*} = 1 - \frac{2}{m}\frac{p^2}{E_G}$$

$$\frac{m}{m_1^*} = 1 + \frac{2}{m}\frac{p^2}{E_G}$$



$$\epsilon_n(k) = E_n(k) - \frac{\hbar^2 k^2}{2m}$$

$$P_{nn}^{\mu} = \frac{m}{\hbar} \frac{\partial E(k)}{\partial k_\mu} - \hbar k_\mu$$

Points:

1) Holes are formed when electrons are excited from the valence to the conduction band; are not necessarily the same mass as electrons.
2) Under conditions where one of the bands is formed from s, p states, $P_{nn} \sim \int \underbrace{f(r)}_{s} \frac{\partial}{\partial x} \times \underbrace{g(r)}_{p} \, d^3r \neq 0$,

so that the first derivative at the band edge at $k = 0$ does not vanish and there is not a minimum there.

Optical Absorption

(1) $H_{op} = A \cdot p$, $A \sim A_0 e^{i(q \cdot r - \omega t)}$

The transition probability is:

(2) $\int b_2^*(k', r) \, A \cdot p \, b_1(k, r) \, d^3r$

or $A_0 e^{i\omega t} \int u_2^*(k', r) \, e^{-ik' \cdot r} \, p \, e^{iqr} \, e^{ik \cdot r} \, u_1(k, r) \, d^3r$

$$= \sum_R e^{i(k+q-k') \cdot R} \int [\;] \, d^3r \quad \propto \quad \delta_{k', k+q}$$

Points:

1) $P_{n'n}$ is the relevant matrix element
2) For $q \ll k$, that is, the wavelength of the incident photon longer than that of the electron in the band, we have the transition probability $\propto \delta_{k,k'}$, that is the transition will be vertical in the going from one band to the next. These results are similar to previous results. We can calculate the optical properties from a knowledge of m^*.

Group Velocity:

(3) $\langle v_g \rangle = \langle n k | \dot{r}_\alpha | n k \rangle$

(4) $i\hbar \dot{r}_\alpha = [r_\alpha, H]$, with $H = \frac{p^2}{2m} + V(r)$

then $i\hbar \dot{r}_\alpha = \left[r_\alpha, \frac{p_\alpha^2}{2m}\right] = \frac{1}{2m} 2i\hbar p_\alpha = \frac{i\hbar}{m} p_\alpha$

(5) Thus, $\langle n k | \dot{r}_\alpha | n k \rangle = \frac{1}{m} \langle n k | p_\alpha | n k \rangle$

with $\langle n k | p_\alpha | n' k' \rangle = \int u_n^*(k,r)\, e^{-ik\cdot r} \underbrace{p_\alpha\, e^{ik\cdot r}}_{e^{ik\cdot r}(p_\alpha + \hbar k_\alpha)} u_n(k,r)\, d^3r$

$= \hbar k_\alpha + \frac{1}{\Omega} \int u_n^*(k,r)\, p_\alpha\, u_n(k,r)\, d^3r$

$= \hbar k_\alpha + P_{nn}^\alpha = \frac{m}{\hbar} \frac{\partial E_n}{\partial k_\alpha} = m \langle v_g \rangle$, or:

(6) $\boxed{\langle v_g \rangle = \frac{1}{\hbar} \nabla_k E_n(k)}$

For the free particle, $\langle v_g \rangle = \frac{1}{\hbar} \frac{\hbar^2 k}{m} = \frac{\hbar k}{m}$

Another way to find $\langle v_g \rangle$ from crystal momentum and co-ordinates:

$i\hbar \frac{\partial}{\partial t} \hat{R} = [\hat{R}, E_n(k)] = i \nabla_k E_n(k)$

($\hat{R} \to i\nabla_k$)

why $\hat{R}$? $\quad r = \hat{R} + \hat{r}$

($\hat{R}$: intra band matrix element; $\hat{r}$: inter band matrix element)

Return to the Two Band Problem:

We can actually solve the Schroedinger equation exactly for this case. Before we examined around $k=0$. Again we assume the extrema at $k=0$ and that the u_n's form a complete set (important). Do the bands stay parabolic?

(7) $$\left[\frac{p^2}{2m} + V(r) + \frac{\hbar}{m} k\cdot p\right] u_n(k,r) = \epsilon_n(k)\, u_n(k,r)$$

↑ band coupling perturbation

(8) $k=0$: $$\left[\frac{p^2}{2m} + V(r)\right] u_n(0,r) = E_n(0)\, u_n(0,r)$$

with $u_n(k,r) = \alpha_n u_1(0,r) + \beta_n u_2(0,r)$

and $\int u_n^* u_n \, d^3r = |\alpha_n|^2 + |\beta_n|^2 = 1$, then:

(9) $$\left[\frac{p^2}{2m} + V(r) + \frac{\hbar}{m} k\cdot p\right]\left[\alpha_n u_1 + \beta_n u_2\right] = \epsilon_n(k)\left[\alpha_n u_1 + \beta_n u_2\right]$$

(We assume that the energies of the two bands at $k=0$ are known). Continuing, we want to find $\alpha_n, \beta_n, \epsilon_n(k)$. Multiply (9) by $\frac{1}{\Omega}\int u_1^*$, integrate to get one solution, then multiply by $\frac{1}{\Omega}\int u_2^*$, integrate, to get the other solution. We also write:

(10) $$P_{21}^{\mu} = \frac{1}{\Omega}\int u_2^* p^{\mu} u_1 \, d^3r = P_{12}^{*\mu} = P$$

which we can assume real without loss of generality and independent of μ from the cubic symmetry.

We then get:

(11) $$E_1(0)\,\alpha_n + \frac{\hbar}{m} k P \beta_n = \epsilon_n(k)\,\alpha_n$$

$$\frac{\hbar}{m} k P \alpha_n + E_2(0)\,\beta_n = \epsilon_n(k)\,\beta_n$$

This leads to the following secular equation:

(12) $$\begin{vmatrix} E_1(0) - \epsilon_n(k) & \frac{\hbar}{m} kP \\ \frac{\hbar}{m} kP & E_2(0) - \epsilon_n(k) \end{vmatrix} = 0$$

(13) Then: $\epsilon_n(k) = \frac{1}{2}\left[(E_1 + E_2) \pm \eta\right]$

where $\eta = \left\{ E_G^2 + 4\frac{\hbar^2 k^2}{m^2} P^2 \right\}^{1/2}$

For $k = 0$: $\eta = E_2 - E_1$

\+ solution: $\epsilon_n(0) = E_2$

\- solution: $\epsilon_n(0) = E_1$

We would like to check with the perturbation results, so let's look near $k = 0$:

(14) $$\eta \approx E_G\left[1 + \frac{2\hbar^2 k^2}{m^2 E_G^2} P^2\right]$$

$$\epsilon_2(k) \approx \frac{1}{2}\left[(E_2 + E_1) + (E_2 - E_1) + \frac{2\hbar^2 k^2}{m^2 E_G^2} P^2\right]$$

$$= E_2(0) + \frac{\hbar^2 k^2}{m^2 E_G^2} P^2$$

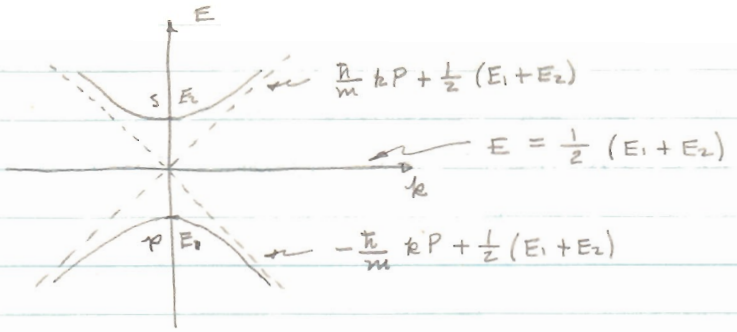
$$E_2(k) = E_2(0) + \frac{\hbar^2 k^2}{2m}\left[1 + \frac{2}{m E_G} P^2\right] = E_2(0) + \frac{\hbar^2 k^2}{2 m_2^*}$$

which is just the perturbation result. Similar results will hold for $E_1(k)$.

Now, for k large, $\frac{4\hbar^2 k^2 P^2}{m^2} \gg E_G^2$, $\eta = \frac{2\hbar k}{m} P$, and

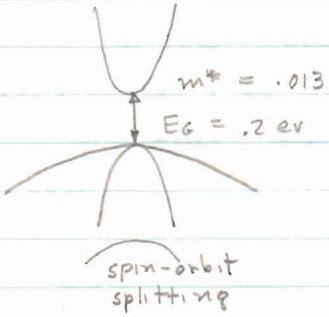
$$E_n(k) = \frac{\hbar^2 k^2}{2m} + \frac{1}{2}(E_1 + E_2) \pm^{n=1}_{n=2} \frac{\hbar k}{m} P$$

Thus we see that if the matrix element of momentum P is very large, the behaviour of E goes from quadratic to linear.



As we move away from $k=0$, we mix p and s functions.

This model we have just discussed where the gap is small, could apply to InSb or the III-V compounds.



LECTURE XXIII 11-21-60

From the secular equation of the last lecture, it is possible to find $\alpha_1, \alpha_2, \beta_1, \beta_2$ and thus obtain the wave functions $u_1(k,x)$ and $u_2(k,x)$:

$$(1)\quad u_1(k,x) = \frac{1}{\sqrt{2\eta}}\left[-\sqrt{\eta + E_G}\, u_1(0,x) + \sqrt{\eta - E_G}\, u_2(0,x)\right]$$

$$u_2(k,x) = \frac{1}{\sqrt{2\eta}}\left[\sqrt{\eta - E_G}\, u_1(0,x) + \sqrt{\eta + E_G}\, u_2(0,x)\right]$$

where $\eta = \left[E_G^2 + \frac{4\hbar^2 k^2}{m^2} P^2\right]^{1/2}$

In this course, we will not discuss the actual computation of energy bands. Refer to Reitz and Ziman.

Influence of External Fields:

We write for the Hamiltonian of an electron in a crystal under the influence of an external field the following:

$$(2)\quad H = \underbrace{\frac{p^2}{2m} + V(r)}_{\text{unperturbed part}} + \underbrace{\mathcal{U}(r,p,t)}_{\mathcal{U}(r)} = H_0 + \mathcal{U}(r)$$

It is seen that we consider the external field as a perturbation on the usual periodic crystalline potential. At this time, we consider the potential to be only dependent on position, for simplicity.

We now wish to find the effect of this perturbation on the Schroedinger equation, $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$. There are two ways to do this; that is, of representing Ψ.

Crystal Momentum Representation (CMR): $\Psi(r,t) = \sum_{nk} \varphi(k,t)\, b_n(k,r)$

Crystal Coordinate Representation (CCR): $\Psi(r,t) = \sum_{nl} \varphi_n(R_l,t)\, a_n(r-R_l)$

We shall not use operator methods, but proceed in a more pedestrian manner.

Uniform Electric Field: (CMR):

$$(3)\quad \mathcal{U}(e) = -e\,\bar{\mathcal{E}}\cdot\bar{r} = -e\,\mathcal{E}_x = -Fx,$$

Taking $\bar{\mathcal{E}} = (\mathcal{E},0,0)$

Our Schroedinger equation then becomes:

$$(4)\quad (H_0 - Fx)\,\Psi = i\hbar \frac{\partial \Psi}{\partial t} \rightarrow E\,\Psi$$

as the Hamiltonian is time-independent.

Now substitute for Ψ, the expansion in terms of Bloch functions:

$$(5)\quad \sum_{n'k'} \varphi_{n'}(k')\left[H_0 - F_x\right] b_{n'}(k',r) = \imath\hbar \sum_{n'k'} \frac{\partial \varphi_{n'}(k')}{\partial t} b_{n'}(k',r)$$

Multiply by $\int b_n^*(k,r)\, d^3r$, recalling $H_0\, b_{n'}(k',r) = E_{n'}(k')\, b_{n'}(k',r)$. Then:

$$(6)\quad E_n(k)\,\varphi_n(k) - F \sum_{n'k'} \varphi_{n'}(k') \langle nk|x|n'k'\rangle - \imath\hbar \frac{\partial \varphi_n(k)}{\partial t} = 0$$

Now, the matrix element $\langle nk|x|n'k'\rangle$ is non-quadratically integrable, that is, it diverges at the boundaries. Therefore, we normalize or evaluate by writing:

$$(7)\quad x = \lim_{q\to 0} \frac{\sin qx}{q}$$

Then we have $\left\langle nk \left| \frac{\sin qx}{q} \right| n'k' \right\rangle$.

$$(8)\quad \left\langle nk \left| \frac{\sin qx}{q} \right| n'k' \right\rangle = \frac{1}{2\imath q} \frac{1}{\Omega} \int u_n^*(k,r)\, u_{n'}(k',r) \cdot \left[e^{\imath(k'-k+q)\cdot r} - e^{\imath(k'-k-q)\cdot r} \right] d^3r$$

Consider:

$$(9)\quad \frac{1}{\Omega} \int u_n^*(k,r)\, u_{n'}(k',r)\, e^{\imath(k'-k\pm q)\cdot r}\, d^3r$$

Because of the periodicity of the lattice, we can replace the $\int d^3r$ over all space with a sum of integrals over a unit cell.

$$(10)\quad (9) = \underbrace{\frac{1}{\Omega} \sum_R e^{\imath(k'-k\pm q)\cdot R}}_{G^3\,\delta_{k',\,k\mp q}} \int_0 u_n^*(k,r)\, u_{n'}(k',r)\, e^{\imath(k'-k\pm q)\cdot r}\, d^3r$$

$$= \delta_{k',\,k\mp q}\, \frac{1}{V_a} \int_0 u_n^*(k,r)\, u_{n'}(k\mp q, r)\, d^3r \qquad \text{for } k' = k \mp q$$

Expanding in a Taylor Series:

$$(11)\quad \delta_{k',k\mp q}\,\frac{1}{Va}\int_0 u_{n'}^*(k,r)\,u_{n'}(k\mp q,r)\,d^3r$$

$$= \delta_{k',k\mp q}\,\frac{1}{Va}\int u_{n'}^*(k,r)\left[u_{n'}(k,r) \mp q\,\frac{\partial u_{n'}(k,r)}{\partial k_x}\right]d^3r$$

$$= \delta_{k',k\mp q}\left[\delta_{nn'} \mp \frac{q}{Va}\int_0 u_n^*\,\frac{\partial}{\partial k_x}\,u_{n'}\,d^3r\right]$$

Thus:

$$(12)\quad \langle nk|\,\frac{\sin qx}{q}\,|n'k'\rangle = \delta_{nn'}\,\frac{1}{2iq}\left[\delta_{k',k-q} - \delta_{k',k+q}\right]$$

$$-\frac{1}{2iq}\left[\delta_{k',k-q} + \delta_{k',k+q}\right]\cdot\frac{q}{Va}\int u_n^*\,\frac{\partial}{\partial k_x}\,u_{n'}\,d^3r$$

We now define:

$$(13)\quad \chi_{nn'}(k) = i\,\frac{1}{Va}\int u_n^*(k,r)\,\frac{\partial}{\partial k_x}\,u_{n'}(k,r)\,d^3r$$

Thus giving:

$$(14)\quad \langle nk|\,\frac{\sin qx}{q}\,|n'k'\rangle = \delta_{nn'}\,\frac{1}{2iq}\left[\delta_{k',k-q} - \delta_{k',k+q}\right] + \chi_{nn'}(k)\,\delta_{k'k}$$

and finally:

$$(15)\quad F\sum_{n'k'}\varphi_{n'}(k')\,\langle nk|x|n'k'\rangle = \lim_{q\to 0} F\,\frac{1}{2iq}\left[\varphi_n(k-q) - \varphi_n(k+q)\right]$$

$$+ F\sum_{n'}\chi_{nn'}\,\varphi_{n'}(k)$$

$$= i\,F\,\frac{\partial}{\partial k_x}\,\varphi_n(k) + F\sum_{n'}\chi_{nn'}\,\varphi_{n'}(k)$$

as $\lim_{q\to 0}\dfrac{\varphi_n(k-q) - \varphi_n(k+q)}{q} = -2\lim_{q\to 0}\dfrac{\varphi_n(k+2q) - \varphi_n(k)}{2q}$

$$\equiv -2\,\frac{\partial\,\varphi_n(k)}{\partial k_x}$$

Substituting in equation (6):

$$(16)\quad \underbrace{\left[E_n(k) - iF\frac{\partial}{\partial k_x} - i\hbar\frac{\partial}{\partial t}\right]\varphi_n(k)}_{\text{intra band terms}} - \underbrace{F\sum_{n'} \chi_{nn'}(k)\,\varphi_{n'}(k)}_{\text{inter band coupling}} = 0$$

One can show that $\chi_{nn}(k)$ vanishes for inversion symmetry. If not, it creates a first order Stark effect. If such is the case, we will consider it contained in $E_n(k) \to E_n(k) + F\chi_{nn}$

Consider, for the moment, motion within one band (time dependent)

$$(17)\quad \left[E_n(k) - iF\frac{\partial}{\partial k_x} - i\hbar\frac{\partial}{\partial t}\right]\varphi_n(k) = 0$$

$$\left[E_n(k) + iF\frac{\partial}{\partial k_x} + i\hbar\frac{\partial}{\partial t}\right]\varphi_n^*(k) = 0$$

Multiply by $\varphi_n^*(1)$ and $\varphi_n(2)$ respectively and subtract:

$$(18)\quad -iF\left[\varphi^*\frac{\partial}{\partial k_x}\varphi + \varphi\frac{\partial}{\partial k_x}\varphi^*\right] - i\hbar\left[\varphi^*\frac{\partial}{\partial t}\varphi + \varphi\frac{\partial}{\partial t}\varphi^*\right] = 0$$

$$\text{or}\quad \left(\hbar\frac{\partial}{\partial t} + F\frac{\partial}{\partial k_x}\right)\left|\varphi_n(k,t)\right|^2 = 0$$

This is an ordinary partial differential equation whose solution is of the form:

$$(19)\quad \left|\varphi_n(k,t)\right|^2 = \left|\varphi_n\left(k_x - \frac{1}{\hbar}Ft, 0\right)\right|^2 = f\left(k_x - \frac{1}{\hbar}Ft\right)$$

Proof: Let $\pi = k_x - \frac{1}{\hbar}Ft$

Then: $\hbar\frac{\partial f}{\partial t} = \hbar\frac{\partial f}{\partial \pi}\left(-\frac{1}{\hbar}F\right) = -F\frac{\partial f}{\partial \pi}$

and the equation is satisfied.

See Sokolnikoff on partial differential equations with constant coefficients.

Also, the solution to the equation (19), $f(k_x - \frac{1}{\hbar} F t)$, has the property that $\frac{1}{\hbar} F$ is the velocity of the wave in k space, that is:

(20) $$\boxed{\frac{dk_x}{dt} = \frac{1}{\hbar} F}$$

Upon integrating (20), we have $k_x = k_0 + \frac{1}{\hbar} F t$, so that the position in k space is linearly dependent on time.

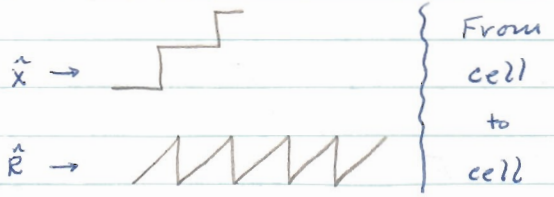
Recall: previously we stated $\dot{x} \to \dot{R}_x$ neglecting interband term, with $\langle n'k' | \dot{R}_x | n'k' \rangle = \imath \frac{\partial}{\partial k_x} \delta_{nn'} \delta_{kk'}$

Now we have

(21) $$\langle nk | x | n'k' \rangle = \imath \frac{\partial}{\partial k_x} \delta_{nn'} \delta_{kk'} + \chi_{nn'}(k) \delta_{kk'}$$

$$= \langle nk | \hat{R} | n'k' \rangle + \langle nk | \hat{x} | n'k' \rangle$$

with $x = \hat{R} + \hat{x}$ (intra band, inter band)



It is seen that the sum goes to a straight line, as would be usually expected.

Under the conditions observed here, that is, neglecting interband coupling, we can now replace $x \to \hat{R}_x$, and $H = E_n(k) - F \hat{R}_x$. First write:

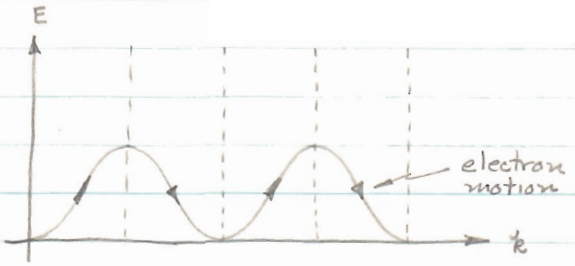
(22) $$\imath \hbar \frac{d}{dt} \hat{k} = [\hat{k}, H] = [\hat{k}_\alpha, -F R_x] = \imath F \delta_{\alpha x}$$

From $[\hat{R}_\alpha, k_\beta] = \imath \delta_{\alpha\beta}$

Thus we have a more general relation for the velocity in k space:

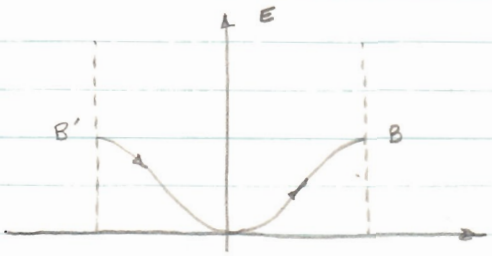
(23) $$\frac{\partial}{\partial t} k_\alpha = \frac{F}{\hbar} \delta_{\alpha x}$$

Look at Repeated Zone Scheme:



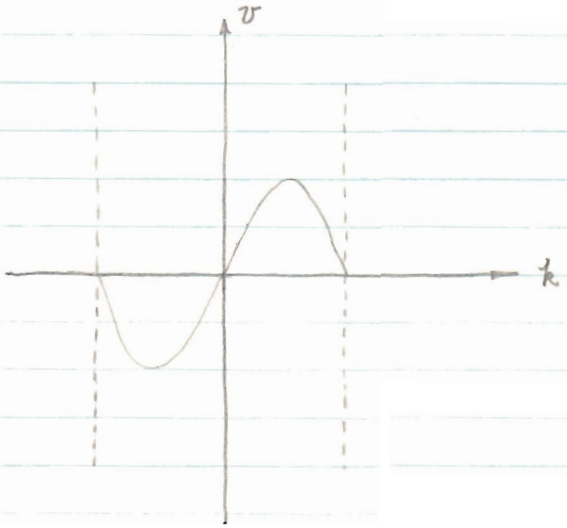
Since $\dot{k} = \frac{1}{\hbar} F$, the electron is moving at constant velocity and is meandering from zone to zone within the same band.

In the Reduced Zone Scheme:



In this scheme, the electron packet moves to B and then undergoes Bragg reflection, immediately reappearing at B'.

Recall the group velocity in real space: $v = \frac{1}{\hbar} \frac{\partial E_n(k)}{\partial k_x}$



One of the interesting things that has happened is that the external field has only entered the E vs k relation through the possible Stark splitting if inversion symmetry does not exist.

LECTURE XXIV 11-23-60

Continuation of Uniform Electric Field:

Consider the velocity in one dimension:

(1) $\dot{x} = \hbar^{-1} \frac{\partial E_n}{\partial k_x}$ and,

(2) $x(t) = x(0) + \frac{1}{\hbar} \int_0^t \frac{\partial E_n}{\partial k_x} dt$

(3) Now, from the previous lecture,

$k_x - \hbar^{-1} F t = k_0$; $\frac{1}{\hbar} dt = \frac{1}{F} dk_x$, then:

(4) $x(t) = x(0) + \frac{1}{F} \int_{k_0}^{k_x} \frac{\partial E_n}{\partial k'} dk'$

$= x(0) + \frac{1}{F} \left[E_n(k_x k_y k_z) - E_n(k_0, k_y, k_z) \right]$

If at $t = T$, $k_x = k_0 + K$, assuming $F \parallel K$, then:

(5) $x(T) = x(0) + \frac{1}{F} \underbrace{\left[E_n(k_0 + K) - E_n(k_0) \right]}_{0, \text{ by periodicity}} = x(0)$

What is T? $(k_0 + K) - \frac{1}{\hbar} F T = k_0$

(6) $\therefore \quad T = \frac{\hbar K}{F}$ where $K = 2\pi b = \frac{2\pi}{a}$

with the result that:

(7) $$\boxed{T = \frac{2\pi \hbar}{aF}}$$

Thus it is seen that the electrons apparently execute periodic motion in the real space as well as reciprocal space. It is seen that as $F \to 0$, $T \to \infty$ and the electrons are free to drift about the lattice.

Another Point of Interpretation, the Acceleration Approach:

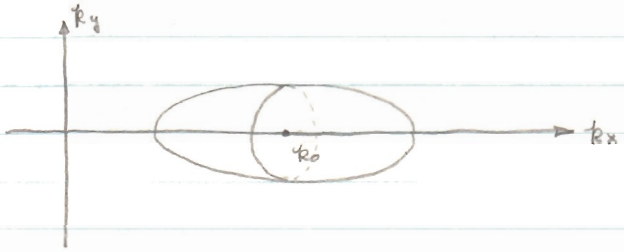
$$(8)\quad a = \frac{d}{dt} v = \frac{d}{dt}\left(\frac{1}{\hbar}\nabla_k E_n(k)\right) = \frac{1}{\hbar}\nabla_k \nabla_k E_n(k) \cdot \frac{dk}{dt}$$

$$= \frac{1}{\hbar}\nabla_k \nabla_k E_n(k) \cdot F = 1M^{-1} F$$

We see that in general a does not have to be $\parallel$ to F, and is only when M^{-1} is diagonal.

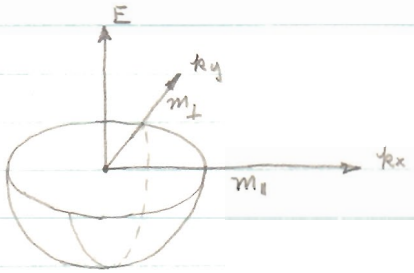
Example: Consider an ellipsoidal surface of constant energy whose equation we write as:

$$(9)\quad E = \frac{\hbar^2}{2}\left[\frac{(k_x - k_0)^2}{m_\parallel} + \frac{1}{m_\perp}(k_y^2 + k_z^2)\right]$$



Now draw E vs k_x, k_y. For $k_x = 0$, $E = \frac{\hbar^2 k_y^2}{2m_\perp} + \frac{\hbar^2 k_0^2}{2m_\parallel}$ which is a parabola.
For $k_y = 0$, $E = \frac{\hbar^2}{2m_\parallel}(k_x - k_0)^2$, another parabola.

For E = constant we have ellipses.



Usually $m_\parallel > m_\perp$

Now suppose that the field is applied in the x-y plane, that is, $F = (F_x, F_y, 0)$.

$$(10)\quad \therefore\ v = \frac{1}{\hbar}\nabla_k E = \frac{\hbar}{m_\parallel}(k_x - k_0)\bar{i} + \frac{\hbar}{m_\perp} k_y \bar{j}$$

and:

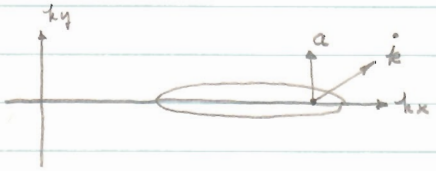
$$(11)\quad \dot{v} = \begin{bmatrix} m_{\parallel}^{-1} & 0 & \\ 0 & m_{\perp}^{-1} & 0 \\ & & m_{\perp}^{-1} \end{bmatrix} \begin{bmatrix} F_x \\ F_y \\ 0 \end{bmatrix} = \frac{1}{m_{\parallel}} F_x \bar{\imath} + \frac{1}{m_{\perp}} F_y \bar{\jmath}$$

Now: $k = k_x \bar{\imath} + k_y \bar{\jmath}$, then:

$$(12)\quad \dot{k} = \frac{1}{\hbar} F = \frac{1}{\hbar} \left[F_x \bar{\imath} + F_y \bar{\jmath} \right]$$

Thus the acceleration is not in the same direction as the force. However, the velocity in k space is.

Case of Extreme Ellipticity: $m_{\parallel} >> m_{\perp}$

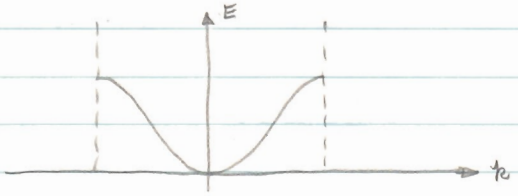


neglecting the x terms ($m_{\parallel} >> m_{\perp}$)

$$\dot{v} = \frac{1}{m_{\perp}} F_y \bar{\jmath}, \quad v = \frac{\hbar}{m_{\perp}} k_y \bar{\jmath}$$

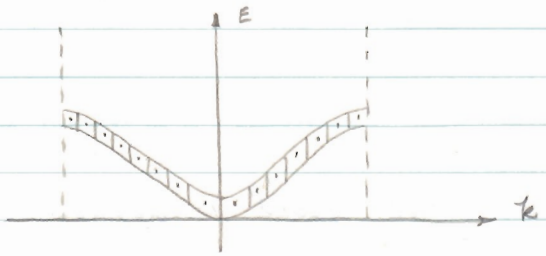
Band Occupation Effects:

1) one electron (empty):



2) Full Band:

a)



We depict schematically the occupation by splitting the E vs k up into k states with two electrons per k state because of spin

b) under full band conditions, there is no motion of electrons and no current:

$k \longleftrightarrow -k$

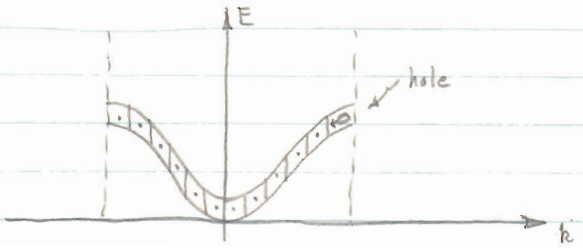
e^{ikx} $\quad$ e^{-ikx}

right traveling wave $\quad$ left traveling wave

$\searrow$ standing wave $\swarrow$

standing waves carry no current.

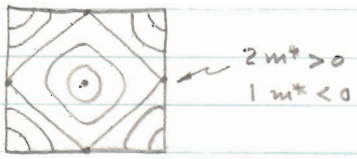
3) Almost Filled Band



When the field is turned on, electrons are decelerated and holes are accelerated.

This is consistent with $\dot{v} = (-M^{-1})(e\mathcal{E}) = (M^{-1})(-e\mathcal{E})$ for holes.

In Three dimensions, we cannot assign the name hole or electron uniquely. For tight binding:



We will now consider the constant field case as a problem in stationary states:

(13) $\quad i\hbar \frac{\partial}{\partial t} \rightarrow E$

(14) $\quad \left[E_n(k) - iF \frac{\partial}{\partial k_x} - E \right] \varphi_n(k) - F \sum_{n'} \chi_{nn'} \varphi_{n'}(k) = 0$

$\chi_{nn'} = 0$ when considering single band.

We then get:

(15) $\quad \frac{\partial \varphi_n(k)}{\partial k_x} = \frac{i}{F} \left[E - E_n(k) \right] \varphi_n(k)$

The solution is obviously:

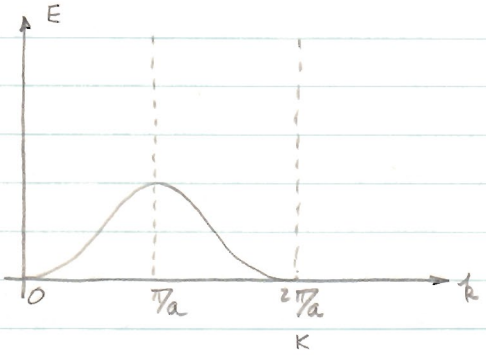
(16) $\varphi_n(k) = \mathcal{N}\, e^{\frac{i}{F}\int_0^{k_x}[E - E_n(k)]\,dk'_x}\, \delta_{k_{oy},k_y}\, \delta_{k_{oz},k_z}$

Since $\Psi = \sum_{nk} \varphi_n(k)\, b_n(k,\epsilon)$, we must have

$\sum_k' |\varphi_n(k)|^2 = 1$ for normality

$$\sum_k' |\varphi_n(k)|^2 = \mathcal{N}^2 \sum_{k_x k_y k_z} \delta_{k_y,k_{oy}}\, \delta_{k_z,k_{oz}} = \mathcal{N}^2 \sum_{k_x}' = \mathcal{N}^2 G$$

and $\mathcal{N} = \frac{1}{\sqrt{G}}$



Take $K \parallel F$.

Since $E(k) = E(k+K)$, we have $\varphi_n(k) = \varphi_n(k+K)$ which leads to the condition:

(17) $e^{\frac{i}{F}\int_0^K [E - E_n(k')]\,dk'_x} = 1 = e^{2\pi i \lambda}$, $\lambda =$ an integer

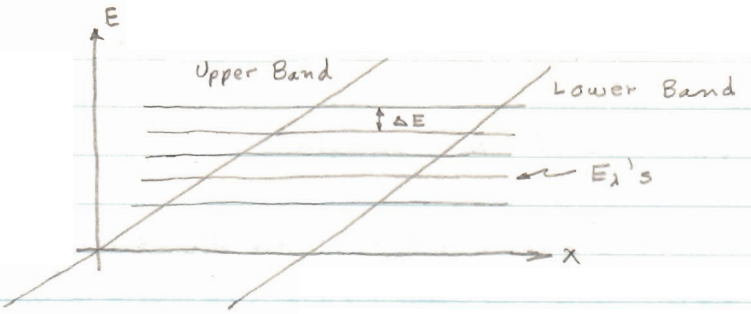
(18) $\therefore \int_0^K [E_\lambda - E_n(k')]\,dk'_x = 2\pi\lambda F$

or $E_\lambda K - \int_0^K E_n(k')\,dk'_x = 2\pi\lambda F$, and

(19) $\Delta E = E_{\lambda+1} - E_\lambda = \frac{2\pi F}{K}[(\lambda+1) - \lambda] = \frac{2\pi F}{K}$

so that the splitting is independent of λ.

To describe this splitting, and its effect on the band structure, we introduce the notion of tilting the bands to describe the effect of the constant field.



This diagram is called a stark ladder.

The problem of localization of an electron in a band is open. Considering the effects and presence of other bands under a constant field makes the electron seem to appear in all bands at once.

Let us now consider the spatial dependence of the wave functions expanded in Bloch functions:

(20) $$\Psi(r) = \sum_k \varphi_n(k)\, b_n(k,r)$$

Let:

(21) $$\sum_k \rightarrow \frac{\Omega^{1/3}}{2\pi} \int dk_x \sum_{k_y k_z}$$

Then:

(22) $$\Psi(r) = \frac{1}{\sqrt{\Omega}} \frac{\Omega^{1/3}}{2\pi} \sum_{k_y,k_z} \int dk_x\, \varphi_n(k)\, b_n(k,r)$$

$$= \frac{1}{\sqrt{\Omega}} \frac{\Omega^{1/3}}{2\pi} \frac{1}{\sqrt{G}} \int dk_x\, e^{\frac{1}{F}\int_0^{k_x} [E - E_n(k')]\, dk'_x}\, e^{ikr}\, M_n(k,r)$$

from equation (16). We can evaluate this integral by the method of least descents: See Morse and Feschbach, p. 437.

LECTURE XXV 11-25-60

From the previous lecture, we want to integrate:

(1) $$\int dk_x \exp\left\{\frac{1}{F}\int_0^{k_x}[E - E_x(k')]\,dk'_x + i\,k\cdot r + \ln M_x(k,r)\right\}$$

We choose F small and use the method of least descent:

(2) Write: $$J = \int_c e^{f(t)}\,dt = \int_c e^{\mathrm{Re}\,f(t)}\, e^{i\,\mathrm{Im}\,f(t)}\,dt$$

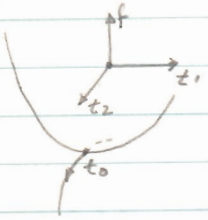
Choose the contour such that:

$$\left.\begin{aligned}\mathrm{Re}\,f(t) &= \text{maximum} = f(t_0)\\ \mathrm{Im}\,f(t) &= \text{constant} = \mathrm{Im}\,f(t_0)\end{aligned}\right\} \quad t \geq t_0$$

Then: $f'(t_0) = 0$

and, expanding: $f(t) = f(t_0) + \frac{1}{2}\underbrace{f''(t_0)(t-t_0)}_{-\tau^2}$

In the case of a saddle point, we take the contour which gives the decrease in $f(t)$.



We get for integral:

(3) $$J = \frac{e^{f(t_0)}}{\sqrt{-f''(t_0)}}\int_c e^{-\tau^2/2}\,d\tau$$

or: (4) $$\boxed{J \sim e^{f(t_0)}\sqrt{\frac{2\pi}{-f''(t_0)}}}$$

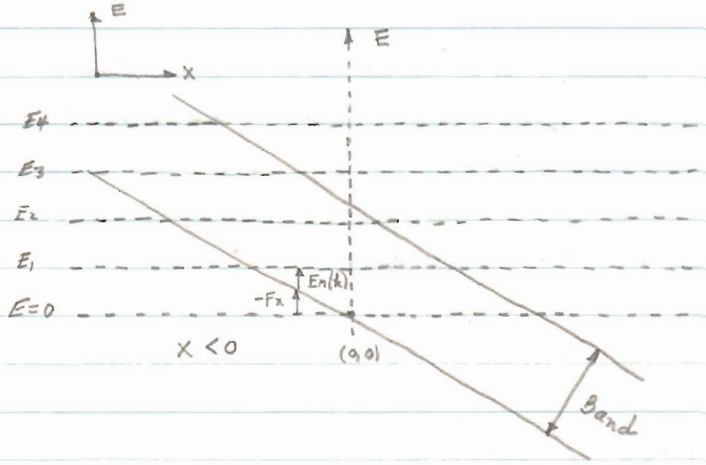
Now call the exponential integral of (1) $f(t)$ and and develop $f(t_0)$:

(5) $$\frac{d}{dk_x}\left[\frac{1}{F}\int_0^{k_x}[E - E_x(k')]\,dk'_x + i\,k\cdot r + \underbrace{\ln M_x(k,r)}_{\text{neglect}}\right] = 0$$

We get:

(6) $\frac{1}{F}\left[E - E_n(k_s, k_y, k_z)\right] + i x = 0$

or $E = E_n(k_s) - Fx$



Actually, the bands are not tilted very much so that $E_n(k)$ does not have to be $\perp$ to the band edge.

It is seen that a stark ladder develops and we will get discrete levels in the x direction and continuous bands in y and z.

Now:

(7) $f''(t) \Rightarrow -\frac{i}{F}\frac{\partial E_n}{\partial k_s}$, such that:

(8) $\Psi(r) \propto u_n(k_s, r)\, e^{i(k_{sx}x + k_{y0}y + k_{z0}z)}\, e^{\frac{i}{F}\int_0^{k_s}[E - E_n(k')]dk'} \sqrt{\frac{2\pi F}{i\left(\frac{\partial E_n}{\partial k_s}\right)}}$

(9) $\int_0^{k_s}[E - E_n(k')]\,dk' = -F\int_0^{k_s} x\,dk'$

$= \underbrace{-Fx\,k'\Big]_0^{k_s}}_{\text{depends only on } k_s} + F\int_{x_0}^{x} k_x\,dx$

We neglect $-Fx\,k'\Big]_0^{k_s}$ and $\sqrt{i}$ as they are only phase factors multiplying the Bloch functions and do not affect the shape of the wave functions. Then:

(10) $\Psi(r) \sim \sqrt{\frac{2\pi F}{\partial E/\partial k_s}}\, u_n(k_s, k_y, k_z, r)\, e^{i\int_{x_0}^{x} k_x\,dx}\, e^{i(k_y y + k_z z)}$

Inside the bands, we have Bloch-like waves: k_x, $-k_x$ are permitted.

In the band gap, we will integrate along $E = 0$ from 0 to x, in order to determine the behavior of the wave functions in this region.

(11) $E = E_n(k) - Fx = 0$, or $E_n(k) = Fx$

Since we are near the band edge, we will assume the constant energy surface to be spherical and we will make the equivalent mass approximation:

(12) $E_n(k) = \frac{\hbar^2 k_x^2}{2m^*}$ with $k_y, k_z = 0$, then:

(13) $k_x = -\frac{\sqrt{2m^* F}}{\hbar}\sqrt{x}$

↑ left traveling wave

↑ $x < 0$, as per diagram; $\therefore$ k_x will be imaginary

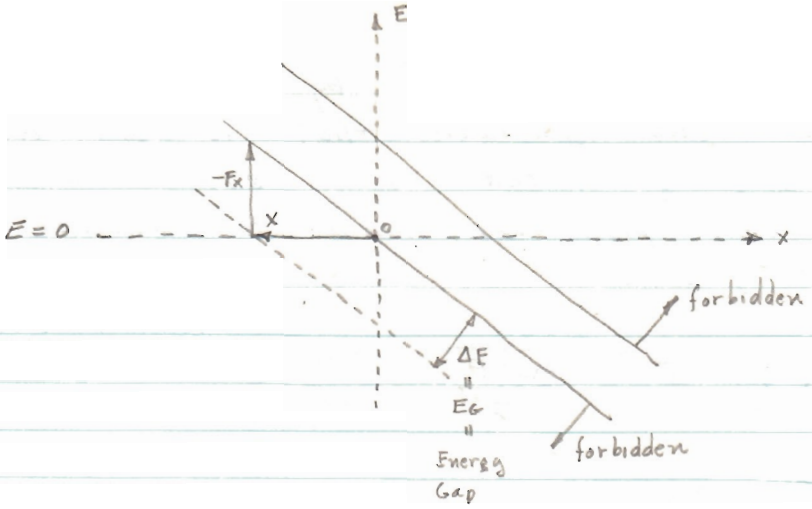
(14) $$\int_{x_0}^{x} k_x\,dx = -\frac{\sqrt{2m^* F}}{\hbar}\int_0^x \sqrt{x}\,dx = -\frac{\sqrt{2m^* F}}{\hbar}\,\frac{2}{3}\,x^{3/2}$$

$$= \frac{2}{3}\,i\,\frac{\sqrt{2m^* F}}{\hbar}\,|x|^{3/2}, \text{ since } x^{3/2} = -i\,|x|^{3/2};\ x < 0.$$

Finally:

(15) $$\Psi(x) \sim \frac{1}{\sqrt{\partial E/\partial k_x}}\,e^{-\frac{2}{3}\frac{1}{\hbar}\sqrt{2m^* F}\,|x|^{3/2}}$$

Thus we have a decaying exponential in the forbidden gap for a wave function. The effect is similar to the potential well problem where a slight tunneling takes place into the forbidden (classically) region. The result is a lessening in the definition, or blurring, of the band edges.



Define: X_a = the distance where the wave function has fallen off to 1/e of its original value.

$$\frac{2}{3}\frac{1}{\hbar}\sqrt{2m^*F}\,X_a^{3/2} = 1 \quad , \text{ or } \quad X_a = \left(\frac{\hbar^2}{2m^*F}\right)^{1/3}$$

Now, if the bands are not tilted too much, $\Delta E \approx Fx$ and $\Delta E = \left(\frac{\hbar^2 F^2}{m^*}\right)^{1/3}$

WKB Method:

(16) $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \quad ; \quad \frac{d^2\psi}{dx^2} + k^2(x)\psi = E\psi$$

where $k^2(x) = \frac{1}{\hbar}\sqrt{2m(E-V)}$

The WKB method provides a semiclassical approach. We take the wave functions to be of the form $\psi = \exp\left[\frac{1}{\hbar}S(x)\right]$. Upon expansion in powers of $\hbar$, the first order terms give:

(17) $$\psi(x) \cong \frac{1}{\sqrt{k(x)}}\, e^{\pm i\int_{x_0}^{x} k(x')\,dx'}$$

This equation shows the connection with the method of least desents. The band gap acts as a potential hill through which tunneling takes place. We have neglected inter band terms, which can give rise to a probability of electrons arriving across gap in other band. However we can

gain an appreciation of this effect by using result (15). It is clear from the diagram, that, for an untilted band or one slightly tilted, $x = E_G/F$. Now, the probability of leaking from one band to another is proportional to $|\Psi|^2$, with

(18) $$|\Psi|^2 \sim \exp\left\{ -\frac{4}{3}\sqrt{2} \frac{\sqrt{m^* F}}{\hbar} \frac{E_G^{3/2}}{F^{3/2}} \right\}$$

$$= \exp\left\{ -\frac{4\sqrt{2}}{3} \frac{m^* E_G^{3/2}}{\hbar F} \right\}$$ with the constant actually $\frac{\pi}{2\sqrt{2}}$ instead of $\frac{4\sqrt{2}}{3}$.

This concludes the examination of the constant electric field in the CMR.

LECTURE XXVI 11-28-60

We now consider the perturbation of a charged impurity in the lattice in the CCR. For example, As in Ge. Consider the Hamiltonian:

(1) $H = H_0 + U(r)$, where $U(r)$ is the perturbation in question and $H_0 = \frac{p^2}{2m} + V(r)$ satisfying $H\Psi = E\Psi$

In the CCR:

(2) $$\Psi(r) = \sum_{n'l'} \psi_{n'}(Re') a_{n'}(r - Re')$$

Multiply (2) by H and then $\int a_n^*(r-Re)\, d^3r$ and get:

(3) $$\int a_n^*(r-Re)\, H_0\, a_{n'}(r-Re')\, d^3r \equiv H_{nn'}(l-l')$$

$$\int a_n^*(r-Re)\, U(r)\, a_{n'}(r-Re')\, d^3r \equiv U_{nn'}(l,l')$$

with the result:

$$(4)\quad \sum_{n'l'} \left[H_{nn'}(l-l') + U_{nn'}(l,l') \right] \psi_{n'}(R_{l'}) = E\, \psi_n(R_l)$$

We evaluate $H_{nn'}(l-l')$ by expanding or expressing the Wannier functions, a_n, in terms of Bloch functions, b_n.

$$(5)\quad H_{nn'}(l-l') = \frac{1}{N} \sum_{kk'} e^{-ik'\cdot R_{l'}} e^{ik\cdot R_l} \int b_n^*(k,r)\, H_0\, b_{n'}(k',r)\, d^3r$$

$$= \frac{\delta_{nn'}}{N} \sum_{kk'} e^{-ik'\cdot R_{l'}} e^{ik\cdot R_l}\, \delta_{kk'}\, E_n(k)$$

$$= \frac{\delta_{nn'}}{N} \sum_{k} e^{ik\cdot(R_l - R_{l'})}\, E_n(k)$$

Notice that we have only intraband terms. Using our cosmological principle, setting $l' = 0$,

$$(6)\quad H_{nn'}(l) = \frac{\delta_{nn'}}{N} \sum_{k} e^{ik\cdot R_l}\, E_n(k)$$

We now take the inverse Fourier transform. Multiply by $\sum_l e^{-ik'\cdot R_l}$, use the usual identities, and get:

$$(7)\quad \boxed{E_n(k) = \sum_{l} H_{nn}(l)\, e^{-ik\cdot R_l}}$$

Returning then:

$$(8)\quad \sum_{n'l'} H_{nn'}\underbrace{(l-l')}_{l''} \psi_{n'}(R_{l'}) = \sum_{l''} H_{nn}(l'')\, \psi_n(R_l - R_{l''})$$

Recall that $T_l\, \psi_n(R) = \psi_n(R+R_l)$, $T_l = e^{ik\cdot R_l}$, $k = -i\nabla_r$.

Then:

$$(9)\quad (8) = \left[\sum_{l''} H_{nn}(l'')\, T_{-l''} \right] \psi_n(R_l) = \left[\sum_{l''} H_{nn}(l'')\, e^{-ik\cdot R_{l''}} \right] \psi_n(R_l)$$

$$= E_n(-i\nabla_r)\, \psi_n(R_l)$$

We would like to replace $\psi_n(R_\ell)$ by a continuous function of R such that it takes on $\psi_n(R_\ell)$ at the points R_ℓ, or so that we can then say $\psi_n(R_\ell) \to \psi_n(r)$. Thus let us look at the potential energy term. This cannot be handled explicitly. We therefore make the assumption that $\mathcal{U}(r)$ is slowly varying in distance, that is:

(10) $$a|\nabla \mathcal{U}| \ll \mathcal{U}(r)$$

We then expand $\mathcal{U}(r)$ about the center of cell R_ℓ:

(11) $$\mathcal{U}(r) = \mathcal{U}(R_\ell) + (r - R_\ell)\cdot \nabla \mathcal{U}(R_\ell) + \cdots$$

using the first term only. Then, substituting in (3):

(12) $$\mathcal{U}_{nn'}(\ell,\ell') = \mathcal{U}(R_\ell)\,\delta_{\ell\ell'}\,\delta_{nn'} + \nabla \mathcal{U}(R_\ell) \int a_n^*(r-R_\ell)(r-R_\ell)a_n(r-R_{\ell'})\,d^3R$$

Now, the integral is a maximum when $\ell = \ell'$ or when the Wannier functions apply to the same cell, and also when in the same band, $n = n'$.

(13) $$\int a_n^*(r-R_\ell)\,a_n\,d^3r \sim \int r\,|a_n(r)|^2 d^3r \sim a$$

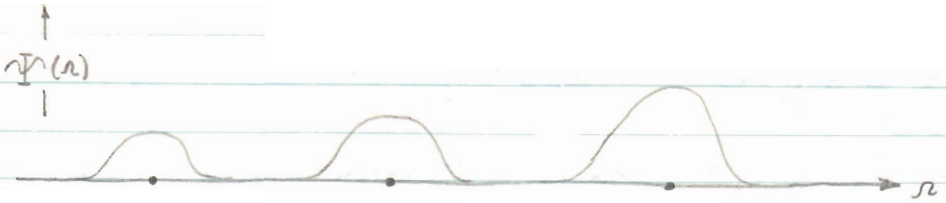
Therefore, the second term in the series goes as $a|\nabla \mathcal{U}| \ll \mathcal{U}(R_\ell)$ so what happens is that we can neglect the second term under the conditions of the approximation. Thus we arrive at:

(14) $$\left[E_n(-i\nabla_\ell) + \mathcal{U}(R_\ell)\right]\psi_n(R_\ell) = E\,\psi_n(R_\ell)$$

which we now want to examine continuously in terms of r which we can do if $\mathcal{U}(r)$ is a slowly varying function. We then write, making $R_\ell \to r$:

(15) $$\left[E_n(-i\nabla) + \mathcal{U}(r)\right]\psi_n(r) = E\,\psi_n(r)$$

Now $\psi_n(r)$ is an envelope because $\Psi(r) = \sum_n \psi_n(R_l)\, a_n(r - R_l)$ so that the Wannier functions are multiplied by a function which changes slowly from cell to cell.



Then:

$$(16)\quad \Psi(r) = \psi_n(r)\,\frac{1}{\sqrt{N}} \sum_k \underbrace{\left[\sum_l e^{i k \cdot R_l}\right]}_{N\,\delta_{k0}} b_n(k, r)$$

$$\propto \psi_n(r)\; b_n(0, r)$$

which means that under this approximation, we are dealing with a band (simple) with a minimum at $k = 0$. Note that we are neglecting interband terms in the matrix element of the perturbing potential. Thus, for a simple band we can say:

$$(17)\quad E_n(k) = E_n(0) + \frac{\hbar^2 k^2}{2 m^*}$$

or $E_n(-i\nabla) = E_n(0) - \frac{\hbar^2}{2m^*}\nabla^2$, then (15) becomes

$$(18)\quad \boxed{\left[-\frac{\hbar^2}{2m^*}\nabla^2 + \mathcal{U}(r)\right]\psi_n(r) = \left[E - E_n(0)\right]\psi_n(r)}$$

This is a very important result because it means that we can treat the bottom of simple bands with ordinary Schroedinger methods by making $m \to m^*$.

We shall take for the potential of an impurity center:

$$(19)\quad \mathcal{U}(r) = -\frac{e^2}{\epsilon r}$$

where ϵ is the dielectric constant.

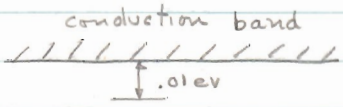
We assume that the electron does not come too close to $r=0$, as ϵ will change. We must also stay some lattice constants away so we will have a slowly varying potential. Thus, the Schroedinger equation becomes:

$$(20)\quad \left[\frac{-\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{\epsilon r}\right]\psi_n(r) = \left[E - E_n(0)\right]\psi_n(r)$$

which is analogous to the hydrogenic atom. In converting results from the solution to this case, we make $e \to e/\epsilon$, $m \to m^*$, $W_n \to E - E_n(0)$. See Pauling and Wilson. We can thus write for the Bohr orbit:

$$(21)\quad a_B^* = \frac{\epsilon\hbar^2}{m^* e^2} \sim 80\, a_B \sim 50\,\text{Å} \quad \text{(Germanium)}$$

Thus the electron is greatly removed from the nucleus even in its ground state. Of course, for s states there is probability of being at $r=0$, but this is removed when p states are considered. Continuing:



$$(22)\quad E = E_n(0) - \frac{e^4 m^*}{2\hbar^2\epsilon^2 n^2}$$

so that the states lie below the bottom of the conduction band by energies scaled down by about 1000 from ordinary hydrogenic energies.

In the ground state:

$$(23)\quad \psi_n(r) \doteq e^{-r/a_B^*}$$

so that we can write:

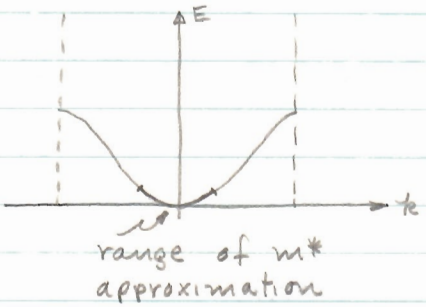
$$(24)\quad \Psi(r) = \sum_k \psi_n(R_k)\, a_n(r-R_k) \propto \sum_k \underbrace{\left[\int d^3r\, e^{-r/a_B^*} e^{-ik\cdot r}\right]}_{\propto \frac{1}{(1+k^2 a_B^{*2})^2}} b_n(k,r)$$

$$\propto \sum_k \frac{b_n(k,r)}{(1+k^2 a_B^{*2})^2}$$

The sum will be damped out when $k \sim \frac{1}{a_B^*}$

or $\frac{k}{K} \sim \frac{a}{a_B^*} \sim \frac{1}{50}$

↑ goes as interatomic distance



This means that if the orbit becomes smaller and smaller, E is more and more below the conduction band and we violate the convention of large distance from the nucleus. Thus, this method applies only to shallow impurities. Otherwise, so many Bloch functions are involved, that the m^* approximation is violated.

LECTURE XXVII 11-30-60

Recapitulation:

$$E_n(-i\nabla_{R_l})\,\psi_n(R_l) + \mathcal{U}(R_l)\,\psi_n(R_l) = E\,\psi_n(R_l)$$

$$\rightarrow \left[E_n(-i\nabla) + \mathcal{U}(r)\right]\psi_n(r) = E\,\psi_n(r)$$

with $$E_n(-i\nabla_{R_l})\,\psi_n(R_l) = \sum_l H_{nn}(l)\,\psi_n(R_l' - R_l)$$

This holds for slowly varying potential and is useful for a perturbation that confines the particle to a small region of k space.

We now consider the case of when the band edge is not at $k = 0$, but at $k = k_0$. Then:

$$(1) \quad E_n(k) = \frac{\hbar^2}{2}\left[\frac{(k_x - k_{x0})^2}{m_1} + \frac{(k_y - k_{y0})^2}{m_2} + \frac{(k_z - k_{z0})^2}{m_3}\right]$$

We want to get $E_n(k_0 - i\nabla)$ in the Schroedinger equation. Form:

$$(2) \quad \psi_n(r) = e^{i k_0 \cdot r} \; X_n(r)$$

($e^{i k_0 \cdot r}$: fast varying function; $X_n(r)$: slow varying function)

To get slowly varying wave function. Then:

$$(3) \quad E_n(-i\nabla)\,\psi_n(r) = E_n(-i\nabla)\, e^{i k_0 \cdot r} X_n(r)$$

and $E_n(-i\nabla)\, e^{i k_0 \cdot r} \sum_l H_{nn}(l)\, e^{-i R_l \cdot (-i\nabla)}\, e^{i k_0 \cdot r}$

which is in the form of two operators $e^A e^B$.

Theorem: (due to Schwinger)

$$e^A e^B = e^B e^A e^C, \quad \text{if } C = [A, B],\ [C, A] = 0,\ [C, B] = 0$$

For our case, $C = [-R_l \cdot \nabla,\ i k_0 \cdot r] = -i k_0 \cdot R_l$

Then:

$$(4) \quad E_n(-i\nabla)\, e^{i k_0 \cdot r} = \sum_l H_{nn}(l)\, e^{i k_0 \cdot r}\, e^{-i k_0 \cdot R_l}\, e^{-i R_l \cdot (-i\nabla)}$$

$$= e^{i k_0 \cdot r} \sum_l H_{nn}(l)\, e^{-i (k_0 - i\nabla) \cdot R_l} = e^{i k_0 \cdot r}\, E_n(k_0 - i\nabla)$$

Thus:

$$(5) \quad \boxed{\left[E_n(k_0 - i\nabla) + U(r)\right] X_n(r) = E\, X_n(r)}$$

In which we may have:

$$E_n(k_0 - i\nabla) = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m_3}\frac{\partial^2}{\partial z^2}$$

and $\mathcal{U}(r) = -\frac{e^2}{\epsilon r}$

Even so, this problem is not exactly solvable. We have for the total wave functions:

$$(6)\quad \Psi(r) = \sum_l \psi_n(R_l)\, a_n(r - R_l)$$

$$= \chi_n(r) \sum_l e^{i k_0 \cdot R_l} \sum_k \frac{1}{\sqrt{N}} e^{-i k \cdot R_l} b_n(k, r)$$

$$\simeq \chi_n(r)\, b_n(k, r)$$

This concludes the treatment of impurities.

Solid in a Magnetic Field

In this case, the perturbation is dependent on the momentum, that is:

$$(7)\quad \mathcal{U} = \mathcal{U}(r, p)$$

The only clear solvable case is near a band edge where the m^* approximation holds. We have for the Hamiltonian for motion in a magnetic field:

$$(8)\quad H = \frac{1}{2m}\left(p - \frac{e}{c}\underline{A}\right)^2 + V(r)$$

where $\mathcal{H} = \text{curl}\ \underline{A}$ and is constant for our purposes, and we have replaced p by $p - \frac{e}{c}\underline{A}$

Recall:

$$(9)\quad \left[\frac{1}{2m}(p + \hbar k)^2 + V(r)\right] u_n(k, r) = E_n(k)\, u_n(k, r)$$

For the Schroedinger equation $H\Psi = E\Psi$, we write $\Psi = u e^{ik\cdot r}$ and we have for (9) in the magnetic field case:

(10) $$\left[\frac{1}{2m}\left(p + \hbar k - \frac{e}{c}A\right)^2 + V(r)\right] u = E u$$

We hope that if we let $k \Rightarrow \pi = k - \frac{e}{c\hbar}A(r)$, we will get:

(11) CCR: $$E_n\left(-i\nabla - \frac{e}{c\hbar}A\right)\psi_n(r) = E\,\psi_n(r)$$

CMR: $$E_n\left(k - \frac{e}{c\hbar}A\{-i\nabla_k\}\right)\varphi_n(k) = E\,\varphi_n(k)$$

These equations have been shown to be true by:

Luttinger, PR 84, 814 (1951)
Harper, Proc Phys Soc. A68, 874 (1955)
Adams, PR 85, 41 (1952)

However, they all neglect interband terms. The magnetic field is not a small perturbation, so we will consider in the region about $k=0$ including interband terms. Before continuing we note:

(12) $$\pi \times \pi = \left(i\nabla + \frac{e}{\hbar c}A\right) \times \left(i\nabla + \frac{e}{\hbar c}A\right) = \frac{ie}{\hbar c}\left[\nabla \times A + A \times \nabla\right]$$

$$= \frac{ie}{\hbar c}(\nabla \times A) = \frac{ie}{\hbar c}\mathcal{H}$$

The treatment of this problem as we shall give it is that of Kohn and Luttinger, PR 97, 896 (1955) in which it is convenient to introduce the new basis functions:

(13) $$C_n(k, r) = u_n(0, r)\, e^{ik\cdot r}$$ (close to Block functions)

All thru the analysis, we will consider only simple band edges at $k=0$, sc lattice, etc.

We also introduce a new normalization scheme:

(14) $$\int b_n^*(k,r)\, b_{n'}(k',r)\, d^3r = \delta_{nn'}\,\delta(k'-k)$$

where $\delta(k'-k)$ is the Dirac delta function. To show this, we form:

$$\int e^{i(k'-k)\cdot r}\, u_n^*(k,r)\, u_{n'}(k'r)\, d^3r$$

We sum over all unit cells the integral over one unit cell and then change the sum into an integral thus:

$$\sum_R \rightarrow \frac{1}{v_a}\int d^3R$$

and we get:

$$\int e^{i(k'-k)\cdot r}\, u_n^*(k,r)\, u_{n'}(k',r)\, d^3r \rightarrow \frac{1}{v_a}\int d^3R\, e^{i(k'-k)\cdot R}$$

$$\cdot \int_0 e^{i(k'-k)\cdot r}\, u_n^*(k,r)\, u_{n'}(k,r)\, d^3r$$

$$= \frac{8\pi^3}{v_a}\,\delta(k'-k)\int_0 u_n^*(k,r)\, u_{n'}(k,r)\, d^3r = \delta_{nn'}\,\delta(k'-k)$$

Important Points:

A) Show that the $c_n(k,r)$ form a complete set if the $b_n(k,r)$ do: Expand:

$$f(r) = \int_{\text{1st BZ}} d^3k \sum_n g_n(k)\, b_n(k,r)$$

Now, the $u_n(0,r)$ are complete with respect to cell periodic functions.

$$u_n(k,r) = \sum_{n'} h_{nn'}(k)\, u_{n'}(0,r)$$

Then: $$f(r) = \sum_n \int d^3k\; g_n(k) \sum_{n'} h_{nn'}(k)\, c_{n'}(k,r)$$

$$= \sum_{n'} \int d^3k\; \bar{g}_{n'}(k)\, c_{n'}(k,r)$$

if $$\bar{g}_n(k) = \sum_n g_n(k)\, h_{nn'}(k)$$

B) Prove: $\int C_{nk}^*(k,r)\, C_{n'}(k',r)\, d^3r = \delta_{nn'}\,\delta(k'-k)$

$$\int C_{nk}^*\, C_{n'}\, d^3r = \int \underbrace{u_n^*(0,r)\, u_{n'}(0,r)}_{\text{periodic}}\, e^{i(k'-k)\cdot r}\, d^3r$$

$$= \sum_K U_K^{nn'}\, e^{-iK\cdot r}$$

This is possible as $u_n^*(0,r)\, u_{n'}(0,r)$ has the periodicity of the lattice. $U_K^{nn'}$ is usual numerical Fourier coefficient.

then: $\int C^*C\, d^3r \to 8\pi^3 \sum_K U_K^{nn'}\, \delta(k'-k-K)$

$\to 8\pi^3\, U_0^{nn'}\, \delta(k'-k)$

This operation is possible only because k and k' are in the first B.Z. and $K=0$.

We find that $U_K^{nn'}$ and $U_0^{nn'} = \frac{1}{8\pi^3}\delta_{nn'}$ found by using Fourier's Theorem.

We now write for the total wave function:

(15) $$\Psi(r) = \int d^3k' \sum_{n'} \chi_{n'}(k')\, C_{n'}(k',r)$$

with $H\Psi = E\Psi$

Following the well-known methods used many times before, we obtain for the Schroedinger equation

(16) $$\boxed{\sum_{n'} \int d^3k'' \langle nk|H|n'k'\rangle\, \chi_{n'}(k') = E\,\chi_n(k)}$$

where $|nk\rangle = C_{nk}(k,r)$

The Hamiltonian is:

(17) $$H = \frac{1}{2m}\left(p - \frac{e}{c}A\right)^2 + V(r)$$

$$= H_0 - \frac{e}{mc}\, p\cdot A + \frac{e^2}{2mc^2}A^2 \quad ; \quad p \to \hbar k + p$$

Introduce:

(18) $$s = \frac{e\cdot \text{Af}}{\hbar\, c} \doteq \frac{1}{L^2} \quad \text{(dimension-wise)}$$

The fact $L \gg a$ will be found to be true.

Choose the gauge such that $A = (-Hy, 0, 0)$, then the magnetic field will be in the z direction, viz:

$$\mathcal{H} = \nabla \times A = (0, 0, \mathcal{H})$$

Since the field is to be constant, we have $A_y = \mathcal{H} y$, and then $A = (-\mathcal{H} y, 0, 0)$. We therefore have for the Hamiltonian:

(19) $$H = H_0 + \frac{\hbar s}{m} p_x y + \frac{\hbar^2 s^2}{2m} y^2$$

LECTURE XXVIII 12-2-60

Magnetic Fields: Recapitulation

$$H = \frac{1}{2m}\left(p - \frac{e}{c} A\right)^2 + V(r)$$

$$A = (\mathcal{H} y, 0, 0), \quad \mathcal{H} = \nabla \times A = (0, 0, \mathcal{H})$$

$$H\Psi = E\Psi, \quad \Psi(r) = \int d^3k' \sum_{n'} \chi_{n'}(k') C_{n'}(k', r), \quad C_n(k, r) = e^{ik\cdot r} u_n(0, r)$$

$$H = H_0 + \frac{\hbar s}{m} p_x y + \frac{\hbar^2 s^2}{2m} y^2$$

$$\sum_{n'} \int d^3k' \langle nk | H | n'k' \rangle \chi_{n'}(k') = E \chi_n(k)$$

Continuum normalization: $\langle nk | n'k' \rangle = \delta_{nn'} \delta(k' - k)$

Example of use: $\langle nk | x | n'k' \rangle = \int u_n^*(0, r)\, u_{n'}(0, r)\, x\, e^{i(k'-k)\cdot r} d^3r$

$$= -i \frac{\partial}{\partial k_x'} \delta(k' - k)\, \delta_{nn'}$$

Consider the following in which the time derivative has been taken of the crystal momentum:

(i) $$\dot{k} = \frac{e}{\hbar c} v \times \mathcal{H}$$

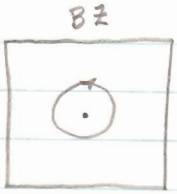
Using $v = \frac{1}{\hbar} \nabla_k E$, we have; as canonically conjugate variables:

(2) $\dot{k}_x = \frac{s}{\hbar} \frac{\partial E_n}{\partial k_y}$; $\dot{k}_y = -\frac{s}{\hbar} \frac{\partial E_n}{\partial k_x}$; $\dot{k}_z = 0$

We then find for the total time derivative of the energy:

(3) $\frac{d E_n(\vec{k})}{dt} = \frac{\partial E_n}{\partial k_x} \dot{k}_x + \frac{\partial E_n}{\partial k_y} \dot{k}_y = 0$

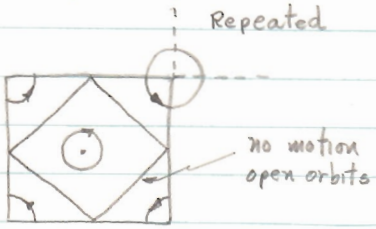
In other words, the electron moves on a constant energy surface in the Brillouin zone.



Thus the Larmour orbits are localized with frequency:

$$\omega_H = \frac{e H}{m^* c}$$

More completely, we have for a simple cubic in the tight binding approximation:



In the reduced zone scheme, one can think of the orbits being dividing among the four corners of the zone. When the electron completes a quarter-orbit in one corner, it immediately reappears in another.

In the extended (repeated) zone scheme, the electrons execute their usual circular orbits. The open orbits are important in magneto-resistance in high fields when saturation occurs as then the electrons of this energy are not tied up in orbits, and they could contribute to the conductivity.

We now proceed to the calculation of matrix elements.

Calculation of $\langle nk|H|n'k'\rangle$:

A) $\langle nk|y\,p_x|n'k'\rangle = \int e^{i(k'-k)\cdot r}\, u_n^*\, y\,(\hbar k_x + p_x)\, u_{n'}\, d^3r$

Aside: one of the matrix elements that will appear is:

$$\int e^{i(k'-k)\cdot r}\, u_n^*\, p_x\, u_{n'}\, d^3r$$

$$= \frac{1}{v_a}\int d^3R\, e^{i(k'-k)\cdot R}\int u_n^*\, p_x\, u_{n'}\, e^{i(k'-k)\cdot r}\, d^3r$$

$$= \frac{8\pi^3}{v_a}\int_0 u_n^*\, p_x\, u_{n'}\, d^3r\;\; \delta(k'-k) \equiv \delta(k'-k)\, P^x_{nn'}$$

Returning:

$$\langle nk|y\,p_x|n'k'\rangle = \left(-i\frac{\partial}{\partial k_y}\right)\left[\hbar k_x\,\delta_{nn'} + P^x_{nn'}\right]\delta(k'-k)$$

$$= \left[\hbar k_x\,\delta_{nn'} + P^x_{nn'}\right]\left(-i\frac{\partial}{\partial k_y}\right)\delta(k'-k)$$

($\hbar k_x\,\delta_{nn'}$: intraband; $P^x_{nn'}$: interband)

This was evaluated using the product rule for matrix elements, as will some of the following.

B) $\langle nk|y^2|n'k'\rangle = -\frac{\partial^2}{\partial k_y^2}\,\delta(k'-k)\,\delta_{nn'}$

C) $\langle nk|H_0|n'k'\rangle = \int e^{i(k'-k)\cdot r}\, u_n^*\left[\frac{1}{2m}(p+\hbar k|+V(r)\right] u_{n'}\, d^3r$

$$= \int u_n^*\, e^{i(k'-k)\cdot r}\left[E_{n'}(0) + \frac{\hbar k}{m}\cdot p + \frac{\hbar^2 k^2}{2m}\right] u_{n'}\, d^3r$$

$$= \left[E_{n'}(0) + \frac{\hbar^2 k^2}{2m}\right]\delta_{nn'}\,\delta(k'-k) + \frac{\hbar}{m}\,k\cdot P_{nn'}\,\delta(k'-k)$$

Finally:

(4) $\langle nk|H|n'k'\rangle = \left\{\left[E_n(0) + \frac{\hbar^2 k^2}{2m}\right]\delta(k'-k) + \frac{\hbar^2 s\,k_x}{m}\left(-i\frac{\partial}{\partial k_y}\right)\delta(k'-k)\right.$

$\left. - \frac{\hbar^2 s^2}{2m}\frac{\partial^2}{\partial k_y^2}\,\delta(k'-k)\right\}\delta_{nn'}$ (intraband terms)

$+ \frac{\hbar}{m}\left[k\cdot P_{nn'}\,\delta(k'-k) + s\,P^x_{nn'}\left(-i\frac{\partial}{\partial k_y}\right)\delta(k'-k)\right]$. (interband terms)

For a simple band, we would have $P_{nn} = 0$. As we are going to work in the m^* approximation, we want to be correct to k^2 and also we want to get rid of interband terms. Also, we will take s to be small, like k, subject to later verification. We then will transform away interband terms to lowest index. First, we simplify notation:

$$(5)\quad \left[E_n(0) + \frac{\hbar^2 k^2}{2m}\right] \delta(k'-k)\,\delta_{nn'} \equiv \langle n'k' | H_0 | n'k' \rangle$$

$$\frac{\hbar^2 s\, k_x}{m}\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k)\,\delta_{nn'} \equiv \langle n'k' | H_a | n'k' \rangle$$

$$-\frac{\hbar^2 s^2}{2m}\frac{\partial^2}{\partial k_y'^2}\,\delta(k'-k)\,\delta_{nn'} \equiv \langle n'k' | H_b | n'k' \rangle$$

$$\frac{\hbar}{m}\left\{k \cdot P_{nn'}\,\delta(k'-k) + s\,\hat{P}_{nn'}\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k)\right\} \equiv \langle n'k' | H' | n'k' \rangle$$

Then:

$$(6)\quad H = H_0 + H_a + H_b + H'$$

Now rewrite Schroedinger equation as:

$$(7)\quad H X = E X$$

Introduce the unitary transformation T, $T^{-1}T = \mathbb{I}$ and define the new wave function $X = T\bar{X}$. Thus:

$$(8)\quad H T \bar{X} = E T \bar{X}$$

$$(9)\quad \bar{H}\bar{X} = E\bar{X} \quad \text{with} \quad \bar{H} = T^{-1} H T$$

Now one writes $T = e^S$; then:

$$(10)\quad \bar{H} = \left(1 - S + \tfrac{1}{2}S^2 - \cdots\right) H \left(1 + S + \tfrac{1}{2}S^2 + \cdots\right)$$

$$= H + [H,S] + \frac{1}{2}\left[[H,S],S\right] + \cdots$$

Since intraband terms are to be kept, $S \sim k, s$ + higher powers. Keep only terms in k^n, s^n, $n \leq 2$. Then:

(11) $\bar{H} = H_0 + H_a + H_b + H' + [H_0 + H_a + H', S] + \frac{1}{2}[[H_0, S], S]$

$+ \{[H_b, S]$ of higher order$\}$

We can remove interband terms to lowest order by choosing S such that:

(12) $H' + [H_0, S] = 0$, then:

(13) $\bar{H} = H_0 + H_a + H_b + [H_a, S] + \frac{1}{2}[H', S]$

Find the proper S by taking matrix elements of (12):

(14) $\langle n'k'|H'|n'k'\rangle = \int d^3k'' \sum_{n''} \{\langle nk|S|n''k''\rangle \langle n''k''|H_0|n'k'\rangle$ ($n' \to k'$, $n' \to k'$)

$- \langle nk|H_0|n''k''\rangle \langle n''k''|S|n'k'\rangle\}$ ($n \to k$, $n \to k$)

$= \langle nk|S|n'k'\rangle \{E_{n'}(0) + \frac{\hbar^2 k'^2}{2m} - E_n(0) - \frac{\hbar^2 k^2}{2m}\}$

drop since of high order

Define $\langle nk|S|nk'\rangle = 0$ as we want to get rid of interband terms. Thus:

(15) $\langle nk|S|n'k'\rangle = \begin{cases} \frac{\langle nk|H'|n'k'\rangle}{E_{n'}(0) - E_n(0)}, & n' \neq n \\ 0, & n' = n \end{cases}$

We shall need to keep only intraband elements of $\bar{H}$.

LECTURE XXIX 12-5-60

See equations of last lecture. We must now find $\langle nk|\bar{H}|nk'\rangle$. It is diagonal in n as we have already eliminated interband band terms and have only intraband terms remaining. First:

(1) $\langle nk|[H_a, S]|nk'\rangle = \sum_{k''} \langle nk|H_a|n'k''\rangle\langle n'k''|S|nk'\rangle - \ldots$

$\delta_{nn'}$ $\quad$ $1-\delta_{nn'}$

$= 0$

Now evaluate:

(2) $\frac{1}{2}\langle nk|[H', S]|nk'\rangle = \frac{1}{2}\sum_{n''}{}' \int d^3k'' \left\{ \frac{\langle nk|H'|n''k''\rangle\langle n''k''|H'|nk'\rangle}{E_n - E_{n''}} \right.$

$\left. - \frac{\langle nk|H'|n''k''\rangle\langle n''k''|H'|nk'\rangle}{E_{n''} - E_n} \right\}$

$= \sum_{n''}{}' \frac{1}{E_n - E_{n''}} \int d^3k'' \langle nk|H'|n''k''\rangle\langle n''k''|H'|nk'\rangle$

$= \frac{\hbar^2}{m^2} \sum_{n''}{}' \frac{1}{E_n - E_{n''}} \int d^3k'' \left\{ (k \cdot P_{nn''} P_{n''n} \cdot k')\, \delta(k''-k)\, \delta(k'-k'') \right.$ (1)

$+ s\, k \cdot P_{nn''} P^{x}_{n''n}\, \delta(k''-k)\left(-i\frac{\partial}{\partial k'_y}\right)\delta(k''-k')$ (2)

$+ s\, P^{x}_{nn''} P_{n''n} \cdot k'\, \delta(k''-k')\left(-\frac{\partial}{\partial k''_y}\right)\delta(k''-k)$ (3)

$\left. + s^2 P^{x}_{nn''} P^{x}_{n''n} \left[\left(-i\frac{\partial}{\partial k''_y}\right)\delta(k''-k)\right]\left[\left(-i\frac{\partial}{\partial k'_y}\right)\delta(k'-k'')\right] \right\}$ (4)

Recall the f sum rule:

(3) $M^{-1} = \hbar^{-2}\nabla_k\nabla_k E_n(k) = \frac{1}{m}\left[1 - \sum_{n'}{}' f_{n'n}\right]$

where $ff_{n'n} = \frac{2}{m} \frac{P_{nn'} P_{n'n}}{E_{n'} - E_n}$; $\sum_{n'}' ff_{n'n} = \mathbb{I} - m\,IM^{-1}$ at $k=0$.

Then for term ①:

(4) $\frac{\hbar^2}{m^2} \int d^3k''\, \delta(k''-k)\, \delta(k'-k'')\, k \cdot \frac{m}{2} \underbrace{\left[-\sum_{n''}' ff_{n'n} \right]}_{-\mathbb{I} + m\,IM^{-1}} \cdot k$

$= -\frac{\hbar^2 k^2}{2m} \delta(k'-k) + \frac{\hbar^2}{2} k \cdot IM^{-1} \cdot k\, \delta(k'-k)$

We can treat terms ② and ③ together since we can turn P's around as they are Hermitian.

(5) $\frac{\hbar^2}{m^2} s \int d^3k'' \left\{ k \cdot \delta(k''-k) \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k'-k'') + k' \cdot \delta(k''-k') \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k''-k) \right] \cdot \sum_{n''}' \frac{P_{nn''} P_{n''n}^{\dagger}}{E_n - E_{n''}}$

$= -\frac{\hbar^2}{2m} s \sum_{\mu} (k_\mu + k'_\mu) \sum_{n''}' f_{n''n}^{\mu x} \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k'-k)$

$= -\frac{\hbar^2}{2m} s \left[(k_x + k'_x) - m \sum_{\mu}' (k_\mu + k'_\mu)\, IM^{-1}_{\mu x} \right] \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k'-k)$

For term ④, the result is:

(6) $+ \frac{\hbar^2}{2m} s^2 \left(1 - m\, IM^{-1}_{xx}\right) \frac{\partial^2}{\partial k_y'^2} \delta(k'-k)$

We can now write:

(7) $\langle n k | \bar{H} | n k' \rangle = \left\{ E_n(0) + \frac{\hbar^2 k^2}{2m} \right\} \delta(k'-k)$

$+ \frac{\hbar^2 s\, k_x}{m} \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k'-k) - \frac{\hbar^2 s^2}{2m} \frac{\partial^2}{\partial k_y'^2} \delta(k'-k)$

$- \frac{\hbar^2 k^2}{2m} \delta(k'-k) + \frac{\hbar^2}{2} k \cdot IM^{-1} \cdot k\, \delta(k'-k) - \frac{\hbar^2}{2m} s \left[(k_x + k'_x) - m \sum_{\mu} (k_\mu + k'_\mu)\, IM^{-1}_{\mu x} \right] \left(-i \frac{\partial}{\partial k_y'}\right) \delta(k'-k)$

$+ \frac{\hbar^2}{2m} s^2 \left(1 - m\, IM^{-1}_{xx}\right) \frac{\partial^2}{\partial k_y'^2} \delta(k'-k)$

Recognize that $E_n(k) = E_n(0) + \frac{\hbar^2}{2} k \cdot |M^{-1}| \cdot k$ and get:

$$(8)\quad \langle nk|\bar{H}|nk'\rangle = E_n(k)\,\delta(k'-k) + \frac{\hbar^2}{2m} s\,(k_x - k_x')\cdot\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k) + \frac{\hbar^2}{2} s \sum_\mu (k_\mu + k_\mu')\,|M^{-1}_{\mu x}|\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k) - \frac{\hbar}{2} s^2\,|M^{-1}_{xx}|\,\frac{\partial^2}{\partial k_y'^2}\,\delta(k'-k)$$

Now, we can show that $(k_x - k_x')\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k) = 0$ by integrating by parts and also, $(k_y - k_y')\frac{\partial}{\partial k_y'}\,\delta(k'-k) = \delta(k'-k)$.

Use these relations to investigate the terms containing k_μ's.

$$(9)\quad \frac{\hbar^2}{2} s \sum_\mu \{(k'_\mu - k_\mu) + 2k_\mu\}\,|M^{-1}_{\mu x}|\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k) = i\frac{1}{2}\hbar^2 s\,|M^{-1}_{yx}|\,\delta(k'-k) + \hbar^2 s \sum_\mu k_\mu\,|M^{-1}_{\mu x}|\left(-i\frac{\partial}{\partial k_y'}\right)\delta(k'-k)$$

Then:

$$(10)\quad \langle nk|\bar{H}|nk'\rangle = E_n(k)\,\delta(k'-k) + \frac{1}{2}\hbar^2 s\,|M^{-1}_{yx}|\,\delta(k'-k) + \hbar^2 s \sum_\mu k_\mu\,|M^{-1}_{\mu x}|\left(-\frac{\partial}{\partial k_y'}\right)\delta(k'-k) - \frac{\hbar^2}{2} s^2\,|M^{-1}_{xx}|\,\frac{\partial^2}{\partial k_y'^2}\,\delta(k'-k)$$

Now plug this in the effective mass equation in momentum space which is:

$$(11)\quad \int d^3k'\,\langle nk|\bar{H}|nk'\rangle\,\bar{X}_n(k') = E\,\bar{X}_n(k)$$

We shall have to use the relation:

$$(12)\quad \int f(k')\frac{\partial}{\partial k_y'}\,\delta(k'-k)\,d^3k' = \frac{\partial}{\partial k_y'}\left\{\frac{f(k)f(k'-k)}{f(k)+f(k'-k)}\right\} - \int \delta(k'-k)\frac{\partial f}{\partial k_y'}\,d^3k' = \frac{\partial f}{\partial k_y}$$

Then:

$$(13)\quad \left[E_n(k) + \tfrac{1}{2}\imath\hbar^2 s\cdot M_{yx}^{-1}\right]\bar{\chi}_n(k) + \hbar^2 s\imath \sum_\mu k_\mu M_{\mu x}^{-1}\frac{\partial \bar{\chi}_n(k)}{\partial k_y} - \tfrac{1}{2}\hbar^2 s^2 M_{xx}^{-1}\frac{\partial^2 \bar{\chi}_n(k)}{\partial k_y^2} = E\,\bar{\chi}_n(k)$$

We now transform back, recalling:

$$(14)\quad \Psi(r) = \int d^3k \sum_n \chi_n(k)\, C_n(k,r)$$

$$(15)\quad \chi_n(k) = \sum_{n'}\int d^3k' \underbrace{\langle nk|T|n'k'\rangle}_{\text{since } T=e^S \text{ and } S \text{ is purely interband}} \bar{\chi}_{n'}(k')$$

$$\downarrow$$

$$\delta_{nn'}\,\delta(k'-k)$$

Then $\chi_n(k) \sim \bar{\chi}_n(k)$, and

$$(16)\quad \Psi(r) = \int d^3k\ \bar{\chi}_n(k)\, C_n(k,r) = \underbrace{u_n(0,r)}_{b_n(0,r)}\ \underbrace{\int d^3k\ \bar{\chi}_n(k)\, e^{\imath k\cdot r}}_{\equiv F_n(r)}$$

Thus we see that $\Psi(r) = F_n(r)\, b_n(0,r)$ which is an envelope $F_n(r)$ times the Bloch functions evaluated at $k=0$. Now multiply by $e^{\imath k\cdot r}$ and integrate over k:

$$(17)\quad E_n(k)\,\bar{\chi}_n(k) \longrightarrow \int E_n(k)\,\bar{\chi}_n(k)\, e^{\imath k\cdot r}\, d^3k$$

$$= E_n(-\imath\nabla)\int \bar{\chi}_n(k)\, e^{\imath k\cdot r}\, d^3k = E_n(-\imath\nabla)\, F_n(r)$$

Then:

$$(18)\quad \hbar^2 s\imath \sum_\mu k_\mu M_{\mu x}^{-1}\frac{\partial \chi_n(k)}{\partial k_y} \longrightarrow \hbar^2 s\imath \sum_\mu \int d^3k\, k_\mu M_{\mu x}^{-1}\frac{\partial \bar{\chi}_n(k)}{\partial k_y} e^{\imath k\cdot r}$$

$$= \hbar^2 s\imath \sum_\mu (-\imath\nabla_\mu) M_{\mu x}^{-1}\int d^3k\ \frac{\partial \bar{\chi}_n(k)}{\partial k_y} e^{\imath k\cdot r}$$

Integrate by parts: Define $\bar{\chi}_n(k) = \frac{\Omega a}{8\pi^3}\sum_R F(R)\, e^{-\imath k\cdot R}$

which is the inverse Fourier transform of above $F_n(r)$.

Then:

$$(19)\quad \int d^3k\, \frac{\partial \bar{\chi}_n(k)}{\partial k_y} e^{ik\cdot r} = \frac{v_a}{8\pi^3} \sum_R (-iR_y) F(R) \underbrace{\int e^{ik\cdot(r-R)} d^3k}_{\delta(r-R)}$$

$\int d^3R$

$$= -iy\, F(r)$$

and equation (18) becomes:

$$(20)\quad \hbar^2 s \sum_\mu (-i\nabla_\mu) M^{-1}_{\mu x}\, y\, F(r)$$

For the last term in equation (13) on the LHS, using the same procedure as above, we have:

$$(21)\quad \tfrac{1}{2}\hbar^2 s^2 y^2 M^{-1}_{xx} F(r)$$

We finally get:

$$(22)\quad \Big[E_n(-i\nabla) + \tfrac{1}{2} i\hbar^2 s\, M^{-1}_{yx} + \hbar^2 s \sum_\mu (-i\nabla_\mu) M^{-1}_{\mu x}\, y + \tfrac{1}{2}\hbar^2 s^2 y^2 M^{-1}_{xx} \Big] F_n(r) = E\, F_n(r)$$

LECTURE XXX 12-7-60

Recapitulation:

$$H = \left(p - \frac{e}{c}A\right)^2 + V(r)$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_n \int d^3k\, \chi_n(k)\, C_n(k, r)$$

$$\sum_{n'} \int d^3k' \langle nk|H|n'k'\rangle \chi_{n'}(k') = E\, \chi_n(k)$$

We made the following canonical transformation:

$$T = e^{S} \qquad \left.\begin{aligned} \bar{X} &= T^{-1} X \\ \bar{H} &= T^{-1} H T \end{aligned}\right\} \quad \bar{H}\bar{X} = E\bar{X}$$

Got rid of interband terms:

$$\int d^3k' \langle n k | \bar{H} | n k' \rangle \bar{X}_n(k') = E \bar{X}_n(k)$$

and found by transforming back:

$$\Psi = F_n(r)\, b_n(0,r) \; ; \quad F_n(r) = \int d^3k\, \bar{X}_n(k)\, e^{ik\cdot r}$$

We now commence with:

$$(1) \quad \Big[E_n(-i\nabla) + \underbrace{\tfrac{1}{2}\hbar^2 s_x |M^{-1}_{yx} + \hbar^2 s \sum_\mu (-i\nabla_\mu) |M^{-1}_{\mu x}\, y + \tfrac{1}{2}\hbar^2 s^2 y^2 |M^{-1}_{xx}}_{\hbar^2 s \sum_\mu \left\{ (-i\nabla_\mu)|M^{-1}_{\mu x}\, y - \frac{1}{2}\left[|M^{-1}_{\mu x} (-i\nabla_\mu)\, y \right] \right\}} \Big] F_n(r) = E F_n(r)$$

Schematically, the situation we have here is:

$$\nabla(yF) - \tfrac{1}{2}(\nabla y) F = \nabla(yF) - \tfrac{1}{2}\nabla(yF) + \tfrac{1}{2} y \nabla F$$

$$= \tfrac{1}{2}\nabla(yF) + \tfrac{1}{2} y \nabla F$$

We then get for (1):

$$(2) \quad \Big\{ E_n(-i\nabla) + \tfrac{1}{2}\hbar^2 s \sum_\mu \left[(-i\nabla_\mu) y + y (-i\nabla_\mu) \right] |M^{-1}_{\mu x} + \tfrac{1}{2}\hbar^2 s^2 |M^{-1}_{xx}\, y^2 \Big\} F_n(r) = E F_n(r)$$

Recall now the relation:

$$(3) \quad E_n(k) = E_n(0) + \frac{\hbar^2}{2} k \cdot |M^{-1}| \cdot k$$

We will let $k \to -i\nabla - \frac{e}{\hbar c} A$, with $A = (-Hy, 0, 0)$

Then:

(4) $E_n\left(-i\nabla - \frac{e}{\hbar c}A\right) = E_n\left(-i\nabla - \frac{s}{\hbar}A\right) = E_n(-i\nabla + sy)$

$= E_n(0) + \frac{\hbar^2}{2}\sum_{\mu\nu}(-i\nabla_\mu + sy\,\delta_{\mu x})\,|M^{-1}_{\mu\nu}\,(-i\nabla_\nu + sy\,\delta_{\nu x})$

Writing $E_n(-i\nabla) = E_n(0) - \frac{\hbar^2}{2}\sum_{\mu\nu}\nabla_\mu\,|M^{-1}_{\mu\nu}\,\nabla_\nu$

we easily see that:

(5) $$\boxed{E_n\left(-i\nabla - \frac{e}{\hbar c}A\right)F_n(r) = E\,F_n(r)}$$

which we had deduced at the beginning.

Discussion of Results:

Now for simple bands, $|M^{-1}_{\mu\nu} = \frac{1}{m^*}\delta_{\mu\nu}$
which gives in equation (4):

(6) $E_n\left(-i\nabla - \frac{e}{\hbar c}A\right) = E_n(0) - \frac{\hbar^2}{2m^*}\nabla^2 - i\frac{\hbar^2}{m^*}sy\frac{\partial}{\partial x}$

$+ \frac{\hbar^2}{2m^*}s^2y^2$, which leads to:

(7) $\left[-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{\hbar^2}{2m^*}\underbrace{\left(\frac{\partial^2}{\partial x^2} + 2isy\frac{\partial}{\partial x} + i^2s^2y^2\right)}_{\left(\frac{\partial}{\partial x} + isy\right)^2}\right]F_n(r)$

$= [E - E_n(0)]\,F_n(r)$

Choose as a solution $F_n(r) = f_n(y)\,e^{i(k_x x + k_z z)}$
which when substituted gives:

(8) $-\frac{\hbar^2}{2m^*}\left[\frac{\partial^2}{\partial y^2} - k_z^2 + (ik_x + isy)^2\right]f_n(y) = [E - E_n(0)]\,f_n(y)$

Define $E_z \equiv E_n(0) + \frac{\hbar^2 k_z^2}{2m^*}$ and get for (8):

(9) $$-\frac{\hbar^2}{2m^*}\left[\frac{d^2}{dy^2} - (sy + k_x)^2\right] f_n(y) = (E - E_z) f_n(y)$$

Now define $\xi \equiv y + \frac{k_x}{s}$, and then

$$\frac{\hbar^2}{2m^*}(sy + k_x)^2 = \frac{\hbar^2 m^*}{2m^{*2}} \frac{e^2 \mathcal{H}^2}{\hbar^2 c^2} \xi^2 = \frac{1}{2} m^* \omega^2 \xi^2$$

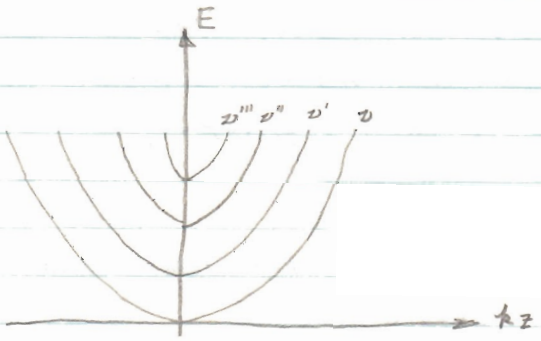
where $\omega = \frac{e\mathcal{H}}{m^* c}$, with the result:

(10) $$\left[-\frac{\hbar^2}{2m^*}\frac{d^2}{d\xi^2} + \frac{1}{2} m\omega^2 \xi^2\right] \varphi_n(\xi) = [E - E_z]\, \varphi_n(\xi)$$

where the $\varphi_n(y + \frac{k_x}{s})$ are the Hermite wave functions centered around $y_0 = -\frac{k_x}{s}$

and where $E - E_z = (n + \frac{1}{2})\hbar\omega$

or $$E = E_n(0) + \frac{\hbar^2 k_z^2}{2m^*} + (n + \frac{1}{2})\hbar\omega$$



We see that a family of parabolae are formed in the k_z direction.

We will now apply the Hamiltonian to the motion of the wave packets, using Ehrenfests' Theorem: Classically:

(11) $H = E_n\left(p - \frac{e}{c}A\right) + e\varphi$ ← scalar potential field

(12) $\dot{r} = \nabla_p H$; $\dot{p} = -\nabla_r H$; define $\pi \equiv p - \frac{e}{c}A$

(13) $$v = \dot{r} = \nabla_p E_n\left(p - \frac{e}{c}A\right) = \nabla_\pi E_n(\pi)$$

For the x component:

(14) $\dot{p}_x = -\frac{\partial}{\partial x}\left[E_n(\pi) + e\varphi\right] = -e\frac{\partial \varphi}{\partial x} - \nabla_\pi E_n(\pi)\cdot\frac{\partial \pi}{\partial x}$

$\frac{\partial \pi}{\partial x} = -\frac{e}{c}\frac{\partial}{\partial x}A$, then

$\dot{p}_x = -e\frac{\partial \varphi}{\partial x} + \frac{e}{c}v\cdot\frac{\partial}{\partial x}A$

(15) $\dot{\pi}_x = \dot{p}_x - \frac{e}{c}\dot{A}_x = -e\frac{\partial \varphi}{\partial x} + \underbrace{\frac{e}{c}v\frac{\partial}{\partial x}A - \frac{e}{c}\frac{\partial A_x}{\partial t} - \frac{e}{c}v\cdot\nabla A_x}$

$(v\times\nabla\times A)_x$
$= (v\times\mathcal{H})_x$

or $\dot{\pi}_x = -e\frac{\partial \varphi}{\partial x} - \frac{e}{c}\frac{\partial A_x}{\partial t} + \frac{e}{c}(v\times\mathcal{H})_x$

Now we make use of $\mathcal{E} = -\nabla\varphi - \frac{e}{c}\frac{\partial A}{\partial t}$:

(16) $\dot{\pi} = e\left[\mathcal{E} + \frac{1}{c}(v\times\mathcal{H})\right]$

What we want is $\dot{k} = \frac{1}{\hbar}e\left[\mathcal{E} + \frac{1}{c}(v\times\mathcal{H})\right]$

which cannot be shown from $\dot{\pi}$. However, this relation is needed for further work in metals and semiconductors and will be used without proof.

Onsager's Theorem:

This is a heuristic extension of the Bohr-Sommerfeld quantitization condition: Recall from before:

(17) $\kappa\times\kappa = \frac{ie}{\hbar c}\mathcal{H}$, $\mathcal{H} = (0,0,\mathcal{H})$, $\pi = i\nabla + \frac{e}{\hbar c}A$

then $[\kappa_x, \kappa_y] = \frac{ie}{\hbar c}\mathcal{H} = is$

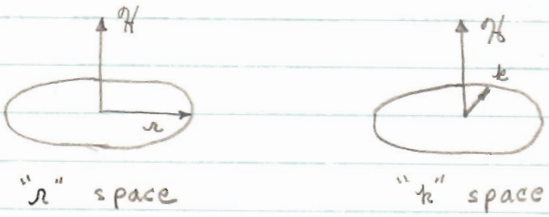
$[\kappa_x, \kappa_z] = [\kappa_y, \kappa_z] = 0$

Now the Bohr-Sommerfeld condition is:

(18) $\oint p\,dq = (n+\varphi)h$; $[q,p] = i\hbar$

$$(\text{Area})_k = \oint k_y \, dk_x = 2\pi s (n + \varphi), \text{ where } \varphi = 1/2$$

This is Onsager's Theorem.



The orbits are 90° out of phase between k and r space.

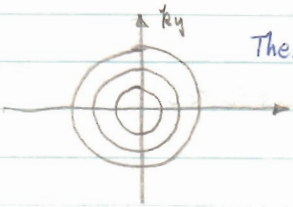
$$|r| = \frac{1}{s}|k|$$

If r orbit is big, k orbit small when $s \ll 1$.

Then near a band edge:

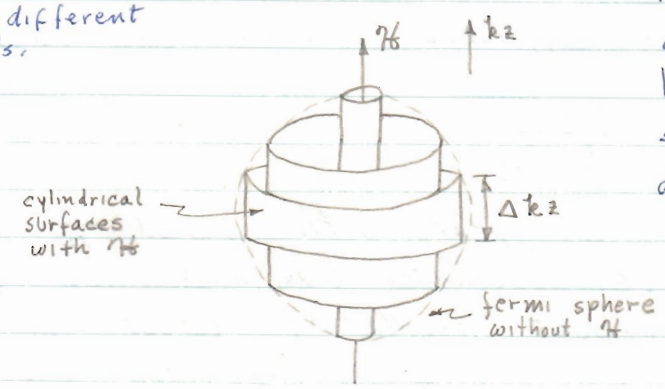
we have small orbits in k space, which is what one would expect from the Kohn-Luttinger functions.

The constant energy surfaces are in the x-y plane. In the z direction, we have free particle behaviour.

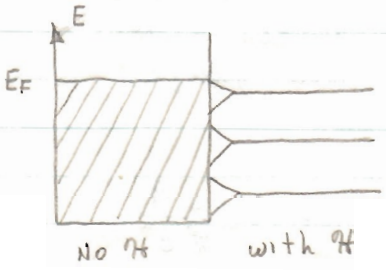


These circles correspond to different A_z's.

In 3-D:



There is a tremendous degeneracy introduced because electrons have same eigenstates in different parts of k space.

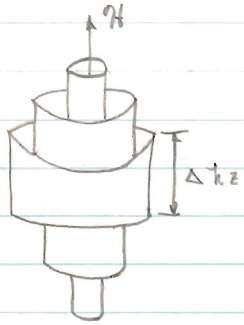


orbital degeneracy

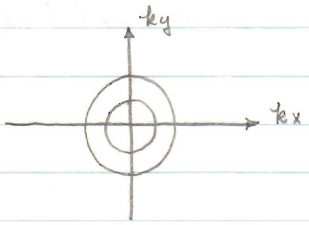
It is seen how the continuum of states collapses into discreet states upon the application of the magnetic field.

LECTURE XXXI 12-9-60

Recapitulation:



The application of a magnetic field quantizes the electrons in the x-y plane, but leaves them free in the k_z direction.



Electrons now fill up concentric cylinders inscribed inside original fermi sphere.

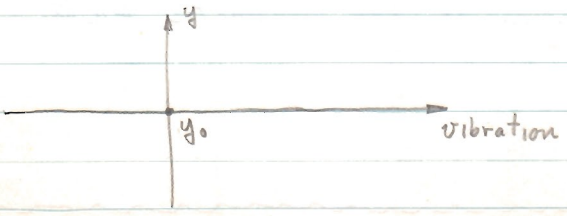
What happens for high $\mathcal{H}$? The area A_k becomes proportional to $\mathcal{H}$. $\Delta k_z \to 0$, $A_k \to A_{kF}$ where A_{kF} is the cross-sectional area of the fermi sphere. We get; from Onsager's Theorem:

(1) $$\frac{1}{\mathcal{H}} = \frac{2\pi e}{\hbar c A_{kF}} (n + \tfrac{1}{2})$$

We take the difference between two adjacent states:

(2) $$\Delta\left(\frac{1}{\mathcal{H}}\right) = \frac{2\pi e}{\hbar c A_{kF}}$$

The cylinders disappear with period $\frac{1}{\mathcal{H}}$ and the susceptibility (χ) oscillates (de Haas - van Alphen Effect). We would not expect oscillatory effect unless singularities occur. We will now prove that the density of states $\to \infty$ as $\Delta k_z \to 0$. When using an assymetric gauge, $A = (-\mathcal{H}y, 0, 0)$, we have:



$$y_0 = -\frac{k_x}{s}, \quad s = \frac{e\mathcal{H}}{\hbar c}$$

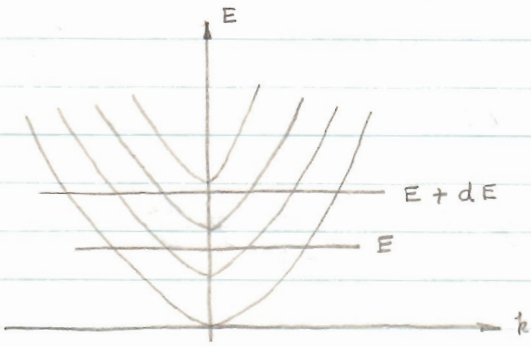
Density of States between $0 \le y_0 \le L_y$. The phase space under consideration is $\frac{L_x L_z}{4\pi^2}\, dk_x\, dk_z$ with $\Omega = L_x L_y L_z$

Now:

(3) $$\rho_E\, dE = \frac{L_x L_z}{4\pi^2}\, \frac{dk_z}{dE}\, dE \int_0^{sL_y} dk_x$$

Find $\frac{dk_z}{dE}$: $$E = E_n(0) + \frac{\hbar^2 k_z^2}{2m^*} + (\nu + \tfrac{1}{2})\hbar\omega$$

$$k_z = \frac{\sqrt{2m^*}}{\hbar}\left[E - E_n(0) - (\nu+\tfrac{1}{2})\hbar\omega\right]^{1/2}$$



Then:

$$\frac{dk_z}{dE} = \underbrace{2}_{\text{spin}} \cdot \frac{1}{2}\, \frac{\sqrt{2m^*}}{\hbar} \sum_{\nu=0}^{\nu_{max}} \frac{1}{\left[E - E_n(0) - (\nu+\frac{1}{2})\hbar\omega\right]^{1/2}}$$

with ν_{max} such that $[\ ]^{1/2} > 0$

(4) $$\rho_E\, dE = \frac{L_x L_z}{4\pi^2}\, \frac{\sqrt{2m^*}}{\hbar} \sum_{\nu} [\ ]^{-1/2}\, \frac{e\mathcal{H}}{\hbar c}\, L_y\, dE$$

$$= \frac{2\Omega}{4\pi^2} \cdot \frac{1}{2}\hbar\omega \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \sum_{\nu=0}^{\nu_{max}} \frac{1}{\left[E - E_n(0) - \hbar\omega(\nu+\frac{1}{2})\right]^{1/2}}$$

Now, when $k_z = 0$, $[\ ]^{1/2} = 0$, and $\rho_E = \infty$

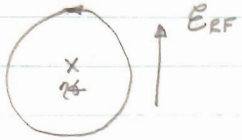
In a one dimensional band:

$$\rho_E\, dE = \frac{L}{2\pi}\, \frac{dk_z}{dE}\, dE$$

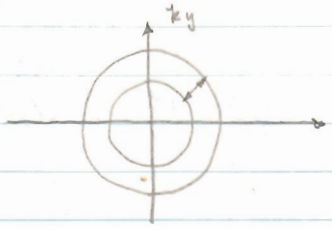
$$\rho \sim \frac{dk_z}{dE} \; ; \; E = \alpha k_z^2 \; ; \; \frac{dE}{dk_z} \sim k_z \sim \sqrt{E}$$

and $\rho \sim \frac{1}{\sqrt{E}}$ and we have an integrable singularity.

EM Wave in the direction of Cyclotron Resonance:



Consider closely adjacent orbits in k-space:



The distance of separation is

$$\frac{dE}{|\nabla_k E|} = \frac{dE}{\hbar v}$$ — velocity

The area of the annulus is: $dA = \frac{dE}{\hbar} \oint \frac{dk}{v}$

or $\frac{dA}{dE} = \frac{1}{\hbar} \oint \frac{dk}{v}$

Now $\dot{k} = \frac{e}{\hbar c} v \mathcal{H}$; $dt = \frac{\hbar c}{e v \mathcal{H}} dk$

Therefore, the orbit period is $T = \oint dt = \frac{\hbar c}{e\mathcal{H}} \oint \frac{dk}{v}$

$= \frac{\hbar c}{e\mathcal{H}} \hbar \frac{dA}{dE} = \frac{2\pi}{\omega_c}$

Then $\omega_c = \frac{2\pi e \mathcal{H}}{\hbar^2 c} \left(\frac{dA}{dE}\right)^{-1} = \frac{e\mathcal{H}}{m_c^* c}$

or $m_c^* = \frac{\hbar^2}{2\pi} \left(\frac{dA}{dE}\right)$

so that cyclotron resonance really measures $\frac{dA}{dE}$ and not m^*.

In the Kohn-Luttinger theory for a simple band;

$A_k = \pi k^2$, $E_k = \frac{\hbar^2}{2\pi m^*} A_k$; $\frac{dA}{dE} = \frac{2\pi m^*}{\hbar^2}$

and finally:

$$\boxed{m_c^* = m^*}$$

so that using the Kohn-Luttinger theory, we have cyclotron resonance giving the effective mass.

Many Electron Problem ÷ Hartree-Foch Approach

Recall:

$$(5)\quad \left\{ \frac{1}{2m} \sum_i p_i^2 + \sum_i V(X_i) + \sum_{i<j} \frac{e^2}{|X_i - X_j|} \right\} \Psi(X_1 \cdots X_n) = E\,\Psi(X_1 \cdots X_n)$$

where the X_n's are 3-D coordinate variables

We want to calculate $(\Psi, H\Psi)$. The Hartree-Foch (HF) approximation is that Ψ is the determinant of the individual wave functions:

$$(6)\quad \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(X_1) & \varphi_1(X_2) & \cdots \\ \varphi_2(X_1) & \varphi_2(X_2) & \cdots \\ \vdots & \vdots & \end{vmatrix}$$

In the electron gas, $1 \le k \le N$ states are occupied
$k > N$ states are empty
when the gas is in its ground state.

We take the X_i's to include the spin variable and also:

$$\int \varphi_{k'}^{*}(x)\, \varphi_k(x)\, dx = \delta_{k'k} \quad ; \quad (\Psi, \Psi) = 1$$

Returning to the Hamiltonian:

$$(7)\quad H = H_0 + \sum_i H_i + \frac{1}{2} \sum_{i \neq j}{}' H_{ij}$$

↑ because electrons counted twice

where $H_0 = \frac{1}{2} e^2 \sum_{s \neq k} \frac{Z_s Z_k}{|R_s - R_k|}$ and is the coulomb interaction between nuclei

$$H_i = \underbrace{\frac{p_i^2}{2m}}_{KE} - \underbrace{e^2 \sum_s \frac{Z_s}{|X_i - R_s|}}_{\text{interaction with nuclear cores.}}$$

and $H_{ij} = \dfrac{e^2}{|x_i - x_j|}$ which is the coulomb interaction between electrons.

We will now discuss density matrices before proceeding further:

References: Lowdin, Adv. in Phys. 5, 1 (1956)
Tolman, p. 327
Dirac, Camb. Phil. Soc. 76, 376 (1930)
Husimi, Fort. d. Phsik 6, 1 (1953) (English)

We define the n-particle density matrix as:

$$(8)\quad \Gamma(x_1' \cdots x_N' \mid x_1 \cdots x_N) = \Psi^*(1'2' \cdots N') \Psi(12 \cdots N) \Big|_{x_i'}$$

and the reduced density matrix as:

$$(9)\quad \Gamma(x_1' \mid x_1) = N \int \Psi^*(1'23 \cdots N) \Psi(123 \cdots N)\, dx_2 \cdots dx_N$$

$$\Gamma(x_1' x_2' \mid x_1 x_2) = \binom{N}{2} \int \Psi^*(1'2'3 \cdots N) \Psi(123 \cdots N)\, dx_3 \cdots dx_N$$

$$\Gamma(x_1' x_2' \cdots x_p' \mid x_1 x_2 \cdots x_p) = \binom{N}{p} \int \Psi^*(1'2' \cdots p' \cdots N) \Psi(12 \cdots p \cdots N)\, dx_{p+1} \cdots dx_N$$

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Recapitulation:

$$\Gamma(x_1' \cdots x_N' \mid x_1 \cdots x_N) = \Psi^*(1'2' \cdots N') \Psi(12 \cdots N)$$

$$\Gamma(x_1' \cdots x_p' \mid x_1 \cdots x_p) = \binom{N}{p} \int \Psi^*(1' \cdots p' \cdots N) \Psi(1 \cdots p \cdots N)\, dx_{p+1} \cdots dx_N$$

$\Gamma(x_1 \mid x_1)$ = # of particles × the probability of having $\{x_1, s_1\}$ with the rest arbitrary

$\Gamma(x_1 x_2 \mid x_1 x_2)$ = # of pairs × the probability of them having $\{x_1, s_1\}\{x_2, s_2\}$ with the rest arbitrary.

Determinential Wave Functions:

(1) $\Gamma(x_1' \cdots x_N' | x_1 \cdots x_N) = \frac{1}{N!} \det\{\varphi_k^*(x_i')\} \det\{\varphi_k(x_j)\}$

$= \frac{1}{N!} \det\left\{\sum_{k=1}^{N} \varphi_k^*(x_i')\, \varphi_k(x_j)\right\}$

Now define:

(2) $\rho(x_i', x_j) = \sum_{k=1}^{N} \varphi_k^*(x_i')\, \varphi_k(x_j)$

as an element of the density matrix.

A Dirac density matrix is defined as:

(3) $\rho(x_i', x_j) = \sum_k n_k\, \varphi_k^*(x_i')\, \varphi_k(x_j)$

(n_k: fermi factor)

where for the ground state $n_k = 1$, $k < k_F$

$n_k = 0$, $k > k_F$

Another density matrix is that of Von Neumann:

(4) $\rho(x_i', x_j | \beta) = \sum_k e^{-\beta E_k}\, \varphi_k^*(x_i')\, \varphi_k(x_j)$

where β is a Boltzmann factor

Properties of Density Matrix:

A. Trace $\{\rho\} = N$

Proof: $Tr\{\rho\} = \int \rho(x,x)\, dx = \sum_{k=1}^{N} \int \varphi_k^*(x)\, \varphi_k(x)\, dx$

$= N$

B. $\rho^2 = \rho$

Proof: $\rho^2(x,x') = \int dx_1\, \rho(x,x_1)\,\rho(x_1,x')$

$$= \sum_{kk'} \varphi_k^*(x) \underbrace{\left\{ \int dx_1\, \varphi_k(x_1)\, \varphi_{k'}^*(x_1) \right\}}_{\delta_{kk'}} \varphi_{k'}(x')$$

$$= \rho(x,x')$$

Key Statement and Theorem:

(5) $$\Gamma(x_1' \dots x_p' \,|\, x_1 \dots x_p) = \frac{1}{P!} \det{}_P \left\{ \rho(x_i', x_j) \right\}$$

(order P)

Proof by example:

$$\Gamma(x_1' x_2' x_3' \,|\, x_1 x_2 x_3) = \frac{1}{3!} \begin{vmatrix} \rho(x_1'x_1) & \rho(x_1'x_2) & \rho(x_1'x_3) \\ \rho(x_2'x_1) & \rho(x_2'x_2) & \rho(x_2'x_3) \\ \rho(x_3'x_1) & \rho(x_3'x_2) & \rho(x_3'x_3) \end{vmatrix}$$

Then $$\Gamma(x_1' x_2' \,|\, x_1 x_2) = \frac{1}{3!} \binom{3}{2} \int dx_3 \, \Big|\ \Big|_{x_3' = x_3}$$

$$= \frac{1}{3!} \frac{3!}{2!\,1!} \int dx_3 \left[\rho(x_3 x_3) \underbrace{\begin{vmatrix} \rho(x_1'x_1) & \rho(x_1'x_2) \\ \rho(x_2'x_1) & \rho(x_2'x_2) \end{vmatrix}}_{D} - \rho(x_2', x_3) \begin{vmatrix} \rho(x_1'x_1) & \rho(x_1'x_2) \\ \rho(x_3 x_1) & \rho(x_3 x_2) \end{vmatrix} \right.$$

$$\left. + \rho(x_1' x_3) \begin{vmatrix} \rho(x_2'x_1) & \rho(x_2'x_2) \\ \rho(x_3 x_1) & \rho(x_3 x_2) \end{vmatrix} \right]$$

$$= \frac{1}{2!} \left[3D - D - D \right] = \frac{1}{2!} \det{}_2 \left\{ \rho(x_i', x_j) \right\}$$

from $\int dx_3\, \rho(x_3 x_3) = 3$; $\int dx_3\, \rho(x_1' x_3)\rho(x_3 x_1) = \rho^2(x_1' x_1)$

$= \rho(x_1' x_1)$; $\int dx_3\, \rho(x_1' x_3)\,\rho(x_3 x_2) = \rho(x_1' x_2)$, etc.

Now $\Gamma(x_1'|x_1) = \frac{1}{3!}\binom{3}{1}\int dx_2\, dx_3 \Big|_{\substack{x_2'=x_2 \\ x_3'=x_3}}$

$$= \frac{1}{2!}\int dx_2 \begin{vmatrix} \rho(x_1'x_1) & \rho(x_1'x_2) \\ \rho(x_2x_1) & \rho(x_2x_2) \end{vmatrix}$$

$$= \frac{1}{2!}\left[3\rho(x_1'x_1) - \rho(x_1'x_1)\right] = \rho(x_1', x_1) \quad , \text{ QED.}$$

Continuing, Recall:

(6) $H = H_0 + \sum_i H_i + \frac{1}{2}\sum_{i\neq j} H_{ij}$

The program is to calculate $(\Psi, H\Psi)$ knowing $(\Psi, H_0\Psi) = H_0$
Now consider:

(7) $\left(\Psi, \sum_i H_i \Psi\right) = N(\Psi, H_1\Psi)$ (the particles are indistinguishable)

$$= N\int \Psi^*(1'2\cdots N)\, H_1\, \Psi(12\cdots N)\, dx_1\cdots dx_N$$

$$= \int H_1\, \Gamma(x_1'|x_1)\, dx_1$$

Notice the operator convention: keep $x_1' \neq x_1$ until after H_1 operates. We now proceed to the two particle case:

(8) $\left(\Psi, \frac{1}{2}\sum_{i\neq j} H_{ij}\Psi\right) = \frac{1}{2}N(N-1)\int \Psi^*(1'2'3\cdots N)\, H_{12}\, \Psi(12\cdots N)\, dx_1\cdots dx_N$

$$= \int H_{12}\, \Gamma(x_1'x_2'|x_1x_2)\, dx_1\, dx_2$$

Now, these are perfectly general results. To make the HF approximation, use the above theorem and write:

(9) $\Gamma(x_1'|x_1) = \rho(x_1'x_1)$

$$\Gamma(x_1'x_2'|x_1x_2) = \frac{1}{2}\begin{vmatrix} \rho(x_1'x_1) & \rho(x_1'x_2) \\ \rho(x_2'x_1) & \rho(x_2'x_2) \end{vmatrix}$$

Since the choice of x_1, x_2 is purely arbitrary, we can drop the primes in (9) and write:

$$x_1 \to x \quad , \quad x_2 \to x'$$

and introduce spin variables ξ, ξ' such that $\rho(xx') \to \rho_{\xi\xi'}(xx')$. Also make: $H_1 \to H(x)$. Then:

$$(10) \quad (\Psi, H\Psi) = H_0 + \sum_{\xi} \int dx\, H(x)\, \rho_{\xi\xi}(x'x)$$

$$+ \frac{1}{2} \sum_{\xi\xi'} \int dx \int dx' \frac{e^2}{|x-x'|} \left\{ \rho_{\xi\xi}(xx)\, \rho_{\xi'\xi'}(x'x') - \underbrace{\rho_{\xi\xi'}(xx')\, \rho_{\xi'\xi}(x'x)}_{\text{this term will vanish unless the electron spins are } \|.} \right\}$$

We could define the the charge density at x as:

$$(11) \quad \rho(x) = \sum_{\xi} \rho_{\xi\xi}(xx)$$

Consider, returning to the last term above:

$$(12) \quad \varphi_k(x) = \psi_k(x)\, \eta_k(\xi) \quad , \text{ then:}$$

$$(13) \quad \rho_{\xi\xi'}(xx') = \sum_{k} \psi_k^*(x)\, \psi_k(x')\, \eta_k^*(\xi)\, \eta_k(\xi') \quad , \text{ and}$$

$$(14) \quad \sum_{\xi\xi'} \rho_{\xi\xi'}(xx')\rho_{\xi'\xi}(x'x) = \sum_{\xi\xi'} \sum_{kk'} \psi_k^*(x)\, \psi_k(x')\, \eta_k^*(\xi)\, \eta_k(\xi')$$
$$\cdot \psi_{k'}^*(x')\, \psi_{k'}(x)\, \eta_{k'}^*(\xi')\, \eta_{k'}(\xi)$$

Now we require that $\sum_{\xi} \eta_k^*(\xi)\, \eta_{k'}(\xi) = \delta_{kk'}$, from which we deduce that the last term vanishes unless the spins are $\|$.

We now proceed to derive the HF equations by varying $(\Psi, H\Psi)$ subject to the condition $\int dx\, \varphi_k^*(x)\, \varphi_{k'}(x) = \delta_{kk'}$

We require that:

$$(15)\quad \delta\left[(\Psi, H\Psi) - \sum_{kk'} \lambda_{kk'} \int dx\, \varphi_k^*(x)\, \varphi_{k'}(x) \right] = 0$$

where $\lambda_{kk'}$ are the Lagrange multipliers.

Now:

$$(16)\quad (\Psi, H\Psi) = H_0 + \int dx \sum_k \varphi_k^*(x)\, H(x)\, \varphi_k(x)$$
$$+ \frac{1}{2} \sum_{kk'} \int dx\, dx' \frac{e^2}{|x-x'|} \varphi_k^*(x)\, \varphi_k(x)\, \varphi_{k'}^*(x')\, \varphi_{k'}(x')$$
$$- \frac{1}{2} \sum_{\substack{kk' \\ \text{ll spins}}} \int dx\, dx' \frac{e^2}{|x-x'|} \varphi_k^*(x)\, \varphi_{k'}(x')\, \varphi_{k'}^*(x')\, \varphi_k(x)$$

Perform the variation with respect to $\varphi_k^*(x)$

$$(17)\quad \delta(\Psi, H\Psi) = \int dx\, \delta\varphi_k^*(x) \left[H(x)\, \varphi_k(x) + \int dx' \frac{e^2}{|x-x'|} \rho(x')\, \varphi_k(x) \right.$$
$$\left. - \int dx' \frac{e^2}{|x-x'|} \rho(x'x)\, \varphi_k(x') \right]$$

Performing the variation on the second term:

$$(18)\quad \int dx\, \delta\varphi_k^*(x) \left[\sum_{k'} \lambda_{kk'}\, \varphi_{k'}(x) \right]$$
$$\downarrow$$
$$\epsilon\, \delta_{kk'} \text{ (by diagonalization)}$$

The result is:

$$(19)\quad H(x)\, \varphi_k(x,\xi) + \int dx' \frac{e^2}{|x-x'|} \rho(x')\, \varphi_k(x,\xi)$$
$$- \sum_{\xi'} \int dx' \frac{e^2}{|x-x'|} \rho_{\xi'\xi}(x'x)\, \varphi_k(x'\xi') = \epsilon_k\, \varphi_k(x\xi)$$

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We begin with the HF equations:

$$(1)\quad H(x)\,\varphi_k(x\xi) + \int dx' \frac{e^2}{|x-x'|}\rho(x')\,\varphi_k(x\xi) - \sum_{\xi'}\int dx' \frac{e^2}{|x-x'|}\rho_{\xi\xi'}(x'x)\,\varphi_k(x'\xi') = \epsilon_k\,\varphi_k(x\xi)$$

Now the exact solution for a free electron gas has been shown to be:

$$(2)\quad \psi_k(x) = \frac{1}{\sqrt{\Omega}}\,e^{ikx}$$

which gives for the elements of the density matrix:

$$(3)\quad \rho(xx') = \frac{1}{\Omega}\sum_{k<k_F} e^{-ik\cdot(x-x')} \to \frac{1}{4\pi^3}\int_{k<k_F} d^3k\, e^{-ik(x-x')}$$

$$= \frac{1}{2\pi^2}\int_0^{k_F} k^2\,dk \int_{-1}^{+1} d\mu\, e^{ik(x-x')\mu}$$

(μ: azimuthal variable)

$$(4)\quad \rho(xx') = \frac{1}{2\pi^3}\,\frac{1}{|x-x'|}\int_0^{k_F} k\,dk\,\sin k|x-x'| = \frac{k_F^2}{3\pi^2}\cdot 3\cdot\underbrace{\left\{\frac{\sin k_F|x-x'|}{k_F^3|x-x'|^3} - \frac{\cos k_F|x-x'|}{k_F^2|x-x'|^2}\right\}}_{Q(k_F|x-x'|)}$$

the integration being performed by the aid of the substitution $k|x-x'| = \kappa$

Now:

$$(5)\quad N = \frac{\Omega}{4\pi^3}\int_{k<k_F} d^3k = \frac{\Omega}{4\pi^3}\underbrace{\int_0^{k_F} k^2\,dk}_{\frac{4\pi}{3}k_F^3} = \frac{\Omega}{\pi^2}\,\frac{1}{3}\,k_F^3$$

with $n = \frac{N}{\Omega}$ as the density of states: Compare with (4).

Returning to equation (1):

$$(6) \quad -\int dx' \frac{e^2}{|x-x'|} \rho(x'x) \varphi_k(x') = -\frac{3ne^2}{\sqrt{\Omega}} e^{ikx} \int dx' \frac{Q(k_F|x-x'|)}{|x-x'|} e^{ik|x'-x|}$$

with:

$$\int dx' \frac{Q(k_F|x-x'|)}{|x-x'|} e^{ik(x'-x)} = \frac{2\pi}{k_F^2} \int_0^\infty y^2 dy \frac{Q(y)}{y} \int_{-1}^{+1} e^{i\alpha y \mu} d\mu$$

Substitute: $y = |x'-x| k_F$

$$\alpha = \frac{k}{k_F}$$

$$= \frac{4\pi}{k k_F} \int_0^\infty dy\, Q(y) \sin \alpha y = \frac{4\pi}{k k_F} \frac{1}{2} \left(\frac{k}{k_F}\right) \left[1 + \frac{1-\alpha^2}{2\alpha} \log \left|\frac{1+\alpha}{1-\alpha}\right|\right]$$

Then:

$$(7) \quad -\int dx' \frac{e^2}{|x-x'|} \rho(x'x) \varphi_k(x') = -3 \frac{k_F^3}{3\pi^2} e^2 \frac{e^{ikx}}{\sqrt{\Omega}} \frac{2\pi}{k_F^2} \cdot \left[1 + \frac{1-\alpha^2}{2\alpha} \log \left|\frac{1+\alpha}{1-\alpha}\right|\right]$$

$$= -\frac{2e^2 k_F}{\pi} \left[1 + \frac{1-\alpha^2}{2\alpha} \log \left|\frac{1+\alpha}{1-\alpha}\right|\right] \varphi_k(x)$$

Now for free-type electrons, $H(x) = \frac{\hbar^2 k^2}{2m^*}$ from $H(x) = \frac{p^2}{2m}$.

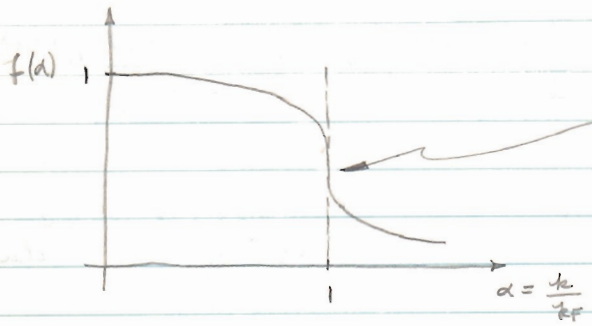
Thus the solution to equation (1) is:

$$(8) \quad \epsilon_k = \frac{\hbar^2 k^2}{2m^*} - \frac{2e^2 k_F}{\pi} \left[1 + \frac{1-\alpha^2}{2\alpha} \log \left|\frac{1+\alpha}{1-\alpha}\right|\right]$$

This is still a one particle solution but it takes into effect the correlation of the other particles.

To obtain an idea of the behaviour of this relation, we will plot $\frac{1}{2}\left[1 + \frac{1-\alpha^2}{2\alpha} \log \left|\frac{1+\alpha}{1-\alpha}\right|\right]$ vs. α.

$$f(\alpha) = \frac{1}{2}\left[1 + \frac{1-\alpha^2}{2\alpha}\log\left|\frac{1+\alpha}{1-\alpha}\right|\right] \quad \text{vs.} \quad \alpha = \frac{k}{k_F}$$



Recall: $\rho(E) \sim k^2 \frac{dk}{dE}$, with $\frac{dE}{dk} = \infty$ at fermi surface, so $\rho(E_F) = 0$.

However, the free electron approximation gives the right solution which is $\frac{\Omega}{\pi^2}\frac{1}{3}k_F^3$. The trouble is that we must take higher order terms.

Now calculate E_x – Total Exchange Energy.
For $\uparrow\uparrow$ spin electrons, we have, $\frac{1}{2}E_x$. Recall $(\Psi, H\Psi)$ and define $\eta_{\uparrow\uparrow} = \frac{1}{2}\eta$, then; from XXXII (10)

(9)
$$\frac{1}{2}E_x = -\frac{1}{2}e^2 \iint dx\,dx' \frac{1}{|x-x'|}\rho(x\,x')\rho(x'x)$$

$$= -\frac{1}{2}e^2 \cdot 9\,\eta_{\uparrow\uparrow}^2 \int dx\,dx' \frac{Q^2(k_F|x-x'|)}{|x-x'|}$$

$$= -\Omega\,\frac{1}{2}e^2\,9\,\eta_{\uparrow\uparrow}^2 \cdot \frac{4\pi}{k_F^2}\underbrace{\int_0^\infty dy\, y\, Q^2(y)}_{1/4}$$

$$\eta_{\uparrow\uparrow}^2 \to \frac{k_F^6}{36\pi^4}$$

$$= -\frac{\Omega}{8\pi^3}e^2 k_F^4$$

Recall now the ground state energy for a free particle (XII (10)):

(10)
$$E_0 = \frac{\Omega}{8\pi^3}\cdot\frac{4}{5}\pi\frac{\hbar^2 k_F^5}{m}$$

and Then:

(11)
$$E = E_0 + E_x = \frac{\Omega}{8\pi^3}\left[\frac{4}{5}\pi\frac{\hbar^2}{m}k_F^5 - e^2 k_F^4\right]$$

The minus sign in (11) indicates that the spins are kept apart and the total energy is lowered due to interaction. However we must show this. The correlation energy has been calculated for a high density electron gas exactly by Pines, Gell-mann and Bruckner (Phys Rev) and Sawada. We won't go into this.

Pair Correlation Function (|| spin electrons)

(12) $\Gamma(x_1 x_2 | x_1 x_2) = \#$ of pairs $\times P(x_1 x_2)$

$$= \frac{1}{2} \begin{vmatrix} \rho(x_1 x_1) & \rho(x_1 x_2) \\ \rho(x_2 x_1) & \rho(x_2 x_2) \end{vmatrix}$$

Now $\rho(x_1 x_1) = 3 n_{\uparrow} Q(0)$. $Q(0)$ is found by:

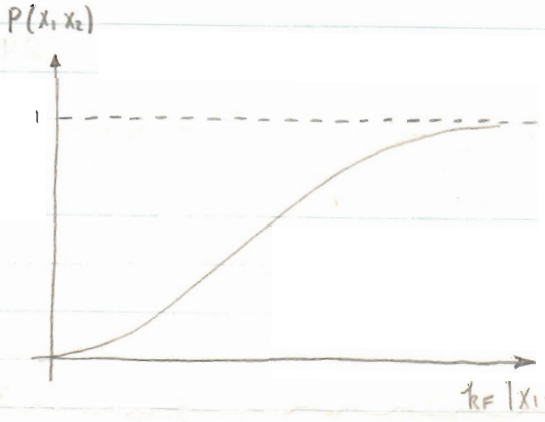
$$\lim_{\epsilon \to 0} Q(\epsilon) = \left[\frac{1}{\epsilon^3} \left(\epsilon - \frac{1}{6}\epsilon^3 \right) - \frac{1}{\epsilon^2} \left(1 - \frac{1}{2}\epsilon^2 \right) \right]$$

$$= 1/3$$

Then $\rho(x_1 x_1) = n_{\uparrow}$, and:

(13) $\Gamma(x_1 x_2 | x_1 x_2) = \underbrace{\frac{1}{2} n_{\uparrow}^2}_{\substack{\# \text{ of} \\ \text{pairs} \\ \approx \frac{1}{2} n_{\uparrow}(n_{\uparrow}-1)}} \underbrace{\left[1 - 9 Q^2 (k_F |x_1 - x_2|) \right]}_{P(x_1 x_2)}$

Notice that $P(x_1 x_1) = 0$, or two electrons cannot be in the same place at the same time. For a typical electron gas $k_F |x_1 - x_2| >> 1$, $|x_1 - x_2| >> a$ and $P(x_1 x_2) = 1$



This shows that || spin electrons are kept apart.

Exchange Hole (Slater):

See Slater, PR 81, 385 (1951)

Discussion of Slater's Article:

(14) $$-\int dx' \frac{e^2}{|x-x'|}\rho(x'x)\varphi_k(x') \rightarrow -\int dx' \frac{e^2}{|x-x'|}\left\{\frac{\rho(x'x)\varphi_k^*(x)\varphi_k(x')}{\varphi_k^*(x)\varphi_k(x)}\right\}\varphi_k(x)$$

multiply and divide by $\varphi_k^*(x)\varphi_k(x)$

Slater noticed that this is similar to interaction term. call $\rho_x(x'x)$

That is, it is an exchange density depending on x, x': $\rho_x(x';x)$ → depends on x, x'. Notice order of terms in RHS term above.

Results:

(A) Total exchange charge = 1 electronic charge

That is:

result = $\delta_{kk'}$

$$\int \rho_x(xx')\,dx' = \sum_{k'} \int dx' \frac{\varphi_{k'}^*(x')\varphi_{k'}(x)\varphi_k^*(x)\varphi_k(x')}{\varphi_k^*(x)\varphi_k(x)} = 1$$

(B) $\rho_x(xx) = \rho(xx)$, $V_0 = \int \frac{e^2}{|x-x'|}\rho(xx')\,dx'$

LECTURE XXXIV 12-16-60

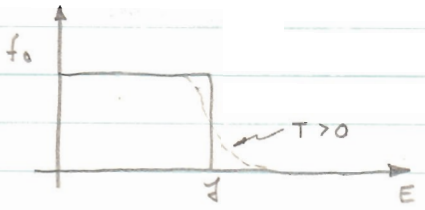
Fermi-Dirac Statistics

A Fermi gas obeys:

(1) $F_0(E) = \dfrac{1}{e^{(E-\mathcal{F})/kT}+1}$; $\mathcal{F} = E_F$

(A) n small, T large, $f_0(E) \rightarrow$ (Boltzmann) $= e^{(\mathcal{F}-E)/kT}$

(B) n large, T small, $E < \mathcal{F}$, $e^{E-\mathcal{F}/kT} << 1$, $f_0 = 1$
$E > \mathcal{F}$, $e^{E-\mathcal{F}/kT} >> 1$, $f_0 = 0$



We will show (A) for a free electron gas:

$$\rho(E)\,dE = \frac{d}{dE}\left(\frac{\Omega}{4\pi^3}\,d^3k\right)dE, \qquad E = \frac{\hbar^2k^2}{2m^*}$$

$$\therefore \rho(E) = \frac{\Omega}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E} \sim m^{*3/2}\sqrt{E}$$

$$N = \int_0^\infty f_0(E)\,\rho(E)\,dE = e^{\mathcal{F}/kT}\,\frac{\Omega}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\underbrace{\int_0^\infty e^{-E/kT}\sqrt{E}\,dE}_{(kT)^{3/2}\frac{\sqrt{\pi}}{2}}$$

($f_0(E)$: pick Boltzmann)

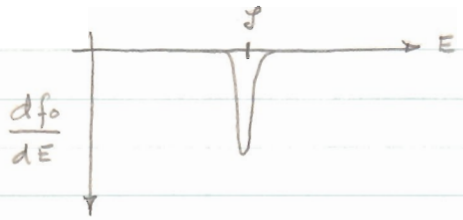
Now, $n = \frac{N}{\Omega}$, which gives:

$$e^{-\mathcal{F}/kT} = \frac{1}{4n}\left(\frac{2m^*kT}{\pi\hbar^2}\right)^{3/2} \sim \frac{T^{3/2}}{n} \quad \text{(large number)}$$

and which implies $\mathcal{F} < 0$.

Thus this implies that the distribution is indeed Boltzmann: $f_0(E) \approx e^{\mathcal{F}/kT}e^{-E/kT}$

Notice that the derivative of the Fermi function is:



We now want to calculate $\bar{E} = \int_0^\infty E\, f_0(E)\, \rho(E)\, dE$

Consider the integral:

(2) $I = \int_0^\infty f_0(E)\, \frac{\partial \varphi}{\partial E}\, dE = -\int_0^\infty \varphi(E)\, \frac{df_0}{dE}\, dE$, since $f_0(\infty) = \varphi(0) = 0$ we assume

Thus for $T = 0$:

(3) $I \to -\varphi(\zeta)\left[\underset{0}{f_0(\infty)} - \underset{1}{f_0(0)}\right] = \varphi(\zeta)$

or that the derivative of the Fermi function at $T=0$ is a negative delta-function.

For $T \neq 0$, expand $\varphi(E)$ in a Taylor series about ζ and integrate term by term. This is done in Wilson on p. 331.

Result:

(4) $\int_0^\infty f_0(E)\, \frac{d\varphi}{dE}\, dE = \varphi(\zeta) + 2\sum_{n=1}^{\infty} C_{2n}\, (kT)^{2n} \left(\frac{d^{2n}\varphi(E)}{dE^{2n}}\right)_{E=\zeta}$

where $C_2 = \frac{\pi^2}{12}$; $C_4 = \frac{7\pi^4}{720}$

Electronic Specific Heat:

We now calculate $\bar{E}$, then $C_V = \frac{d\bar{E}}{dT}$

We set $\frac{d\varphi}{dE} = E\rho(E)$; then $\varphi(E) = \int_0^E E'\rho(E')\, dE'$

Upon plugging into equation (4):

(5) $$\bar{E} = \int_0^{\mathcal{E}} E\,\rho(E)\,dE + 2\,\frac{\pi^2}{12}\,(kT)^2\left\{\rho(\mathcal{E}) + \mathcal{E}\,\frac{d\rho}{d\mathcal{E}}\right\} + \mathcal{O}(T^4)$$

(6) $$C_V = \frac{\partial \bar{E}}{\partial T} = \mathcal{E}\,\rho(\mathcal{E})\,\frac{d\mathcal{E}}{dT} + \frac{\pi^2}{3}\,k^2 T\left\{\rho(\mathcal{E}) + \mathcal{E}\,\frac{d\rho}{d\mathcal{E}}\right\}$$

What is the temperature dependence of the Fermi energy $\mathcal{E}$? Consider:

(7) $$N = \int_0^{\infty} f_0(E)\,\rho(E)\,dE \;;\quad \frac{d\varphi}{dE} = \rho(E)$$

$$= \int_0^{\mathcal{E}} \rho(E)\,dE + \frac{2\pi^2}{12}\,(kT)^2\,\frac{d\rho}{d\mathcal{E}}$$

We see that $\int_0^{\mathcal{E}} \rho(E)\,dE = N(\mathcal{E})$ = number of the particles in the gas, if it is at $T=0$ and the fermi level were at $\mathcal{E}$. Or we can say that:

(8) $$N(\mathcal{E}) = \underbrace{N(\mathcal{E}_0)}_{\substack{\text{number}\\ \text{of particles}\\ \text{''}\\ N}} + (\mathcal{E}-\mathcal{E}_0)\,\rho(\mathcal{E}_0)\,, \qquad \mathcal{E}_0 = \text{fermi level at } T=0.$$

Resubstituting in (7), we arrive at:

(9) $$\mathcal{E} = \mathcal{E}_0 - \frac{\pi^2}{6}\,(kT)^2\,\frac{1}{\rho(\mathcal{E}_0)}\,\frac{d\rho}{d\mathcal{E}_0}$$

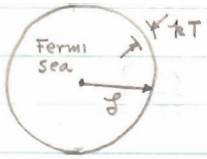
and $$\frac{d\mathcal{E}}{dT} = -\frac{\pi^2}{3}\,k^2 T\,\frac{1}{\rho(\mathcal{E}_0)}\,\frac{d\rho}{d\mathcal{E}_0}$$

Finally, on substituting in (6):

(10) $$C_V = -\frac{\pi^2}{3}\,k^2 T\,\mathcal{E}_0\,\frac{d\rho}{d\mathcal{E}_0} + \frac{\pi^2}{3}\,k^2 T\left[\rho(\mathcal{E}_0) + \mathcal{E}_0\,\frac{d\rho}{d\mathcal{E}_0}\right]$$

$$\therefore \quad C_V = \frac{1}{3}\,\pi^2 k^2 T\,\rho(\mathcal{E}_0)$$

Physical Interpretation:



Only a small group of electrons participate in C_v (important), that is:

$$kT\,\rho(\mathcal{E}_0)\cdot 3k \rightarrow 3k^2T\,\rho(\mathcal{E}_0)$$

Thus, only electrons around the fermi surface contribute to the specific heat and not all as expected classically.

Note That: electrons: $C_v \propto T$; lattice: $C_v \propto T^3$ } Thus the electronic C_v can be measured at low temperatures.

Also we can obtain $\rho(\mathcal{E}_0)$ from C_v measurements.
Under exchange conditions, $\rho(\mathcal{E}) = 0$, $C_v \sim \frac{T}{|\log T|}$

Fini to electronic specific heats.

Plasma Oscillations in Solids:

Conduction electrons are coupled by long range coolomb forces and tend to move cooperatively. There are two important effects:

Screening: perturbation of adding electrons
Oscillations: displacement of plasma, unbalances occur, and oscillations occur in attempt to restore equilibrium in charge density.

Hueristic Proof of Boltzmann Equation:

Introduce a classical distribution function $f(k,r,t)$.
Now $\frac{\Omega}{4\pi^3} f(k,r,t)\, d^3k\, d^3r$ = # of particles in $d^3k\, d^3r$

Looking at time $t+dt$:

(III) $$f(k+\dot{k}\,dt,\ r+v\,dt,\ t+dt) - f(k,r,t) = \left(\frac{\partial f}{\partial t}\right)_{\text{collision}} dt$$

By Liouville's Theorem which we have yet to show. Expanding in Taylor Series; and keeping only first order terms:

$$(12)\quad \frac{\partial f}{\partial t} + \dot{k} \cdot \nabla_k f + v \cdot \nabla_r f = \left(\frac{\partial f}{\partial t}\right)_{coll.}$$

This is the Boltzmann equation.

Screening Effects:

Introduce a point charge q into the plasma. The resulting potential is given by Poisson's equation:

$$\nabla^2 \varphi = 4\pi q - \underbrace{4\pi e\, \delta p}_{\text{induced change in charge density.}}$$

The other electrons tend to cluster around the point charge

For the free particle, $v = \frac{\hbar k}{m}$, and the Boltzmann equation becomes:

$$\dot{v}\, \nabla_v f + v \cdot \nabla_r f = 0 \qquad \text{(stationary State)}$$

We linearize our distribution function: $f = f_0 + f_1$, then:

$$\dot{v} = a = \frac{-e\mathcal{E}}{m} = \frac{e}{m} \nabla \varphi$$

considering the external fields to be small. Then: in the first order:

$$a \cdot \nabla_v f_0 + v \cdot \nabla_r f_1 = 0 \quad , \quad \text{as } \nabla_r f_0 = 0$$

$$a \cdot \nabla_v f_0 = m a \cdot v \frac{df_0}{dE} = e v \cdot \nabla \varphi \frac{df_0}{dE}$$

Thus the Boltzmann equation can be written:

$$v \cdot \nabla \left(e\varphi \frac{df_0}{dE} + f_1 \right) = 0 \quad , \quad f_1 = -e\varphi \frac{df_0}{dE}$$

Assuming a Boltzmann distribution function, $f_0 \sim e^{-E/kT}$, then, $\frac{df_0}{dE} = \frac{-f_0}{kT}$

and we have $f_1 = \frac{e\varphi}{kT} f_0$; $f = f_0 (1 + \frac{e\varphi}{kT})$.

Integrate over velocities and get:

$$n(x) = n_0 \left(1 + \frac{e\varphi}{kT}\right) \simeq n_0 e^{e\varphi/kT}$$

Now notice that $\delta\rho = n - n_0 = \frac{n_0 e \varphi}{kT}$

and make the substitution in Poisson's equation.

$\left[\nabla^2 + \frac{4\pi n_0 e^2}{kT}\right] \varphi = 4\pi q$, with the solution:

$\varphi(r) = \frac{q}{r} e^{-r/\lambda_D}$ (well-known relation)

where λ_D = Debye length $= \sqrt{\frac{kT}{4\pi n_0 e^2}}$

For $T \to \infty$, $\lambda_D \to \infty$ and the screening effect disappears.

LECTURE XXXV 12-19-60

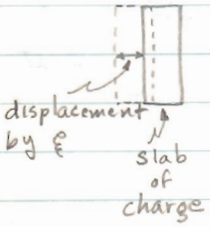
Recapitulation:

Screening effects:

Boltzmann equation: $\frac{\partial f}{\partial t} + a \cdot \frac{\partial f}{\partial v} + v \cdot \frac{\partial f}{\partial x} = 0$

a is related to $\mathcal{E}$ which is related to $\nabla\varphi$ which comes from $\nabla^2\varphi = 4\pi q - 4\pi e\, \delta n$.
This is called the self consistent field method.

Plasma Oscillations:



Background is + charge

Now: $\sigma = ne\xi$

$\mathcal{E} = 4\pi\sigma = 4\pi n e \xi$

$m\ddot{\xi} = -e\mathcal{E} = -4\pi n e^2 \xi$

or $\ddot{\xi} + \frac{4\pi n e^2}{m} \xi = 0$;

This is the equation of a harmonic oscillator with frequency $\omega_p = \sqrt{\frac{4\pi ne^2}{m}}$, and is called the plasma frequency.

For metals: $\omega_p \sim 10\text{-}20$ ev
semiconductors: $\omega_p \sim .02$ ev

Means of experimental observation: shoot electrons at foils, ejected electrons differ in energy by ω_p

Some figures on Screening Length:

$$\lambda_D = \sqrt{\frac{kT}{4\pi ne^2}} \quad \text{(Boltzmann)}$$

$$\lambda_{TF} = \sqrt{\frac{E_F}{6\pi ne^2}} \quad \text{(Fermi)}$$

} About 50 Å in semiconductors.

Liouville Equation:

Density Matrix:
Recall:

$$(1) \quad \rho(xx') = \sum_k n_k \varphi_k^*(x) \varphi_k(x')$$

n_k: 1 up to fermi surface, 0 beyond } for $T=0$

Now a more general density matrix can be defined as:

$$(2) \quad \rho(xx') = \Psi^*(x,t)\,\Psi(x',t)$$

where Ψ satisfies $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$. How does this reduce to the above definition? Suppose we develop Ψ in a series of basis functions:

$$(3) \quad \Psi(x,t) = \sum_k a_k(t)\,\varphi(k,x)$$

where φ satisfies $H_0\,\varphi(k,x) = E(k)\,\varphi(k,x)$

Then:

$$(4)\quad \rho(xx') = \sum_{kk'} \underbrace{a_{k_1}^*(t)\, a_{k}(t)}_{\| \rho(kk')} \varphi^*(k',x')\,\varphi(k,x)$$

$$= \sum_{kk'} \rho(kk')\, \varphi^*(k'x')\,\varphi(kx)$$

where $\rho(kk')$ is the density matrix in the momentum representation. We can consider $\rho(xx')$ as a matrix element operator:

$$(5)\quad \rho(xx') = \langle x|\rho|x'\rangle = \int d^3x\ \delta(x-x_1)\,\rho(H(x_1))\,\delta(x_1-x')$$

($\rho(H(x_1))$: operates only on x_1)

Recall Closure Formula (Schiff, p. 52):

$$(6)\quad \delta(x-x_1) = \sum_k \varphi(k,x)\,\varphi^*(k,x_1)\ ,\ \text{then:}$$

$$(7)\quad \rho(xx') = \sum_{kk'} \int d^3x_1\ \varphi(kx)\ \underbrace{\varphi^*(kx_1)\,\rho(H(x_1))\,\varphi(k'x_1)}_{\langle k|\rho|k'\rangle = \rho(kk')}\ \varphi^*(k'x')$$

$$= \sum_{kk'} \rho(kk')\,\varphi^*(k'x')\,\varphi(kx)$$

If $H = H_0$: $\langle k|\rho|k\rangle = \rho(E(k))\,\delta_{kk'}$

and: $\rho(xx') = \sum_k \rho(E(k))\,\varphi^*(kx')\,\varphi(kx)$

Now, using equation 1), we are able to make the identification:

$$(8)\quad \rho(E(k)) \longrightarrow n_k \quad \text{or} \quad f_0(E_k)$$

Crucial point: we can write ρ as a single particle operator that determines the distribution function such that:

(9) $f_0 = \dfrac{1}{e^{\beta(H_0 - \mu)} + 1}$; $\underline{\rho_0}\,|k\rangle = f_0(E_k)\,|k\rangle$

Now we want to find the equation of motion. We do this by the usual method of multiplying by the complex conjugate and integrating. We use the schroedinger equation and the wave functions of (3):

(10) $$i\hbar \frac{\partial}{\partial t} a_k = \sum_{k''} \langle k|H|k''\rangle a_{k''}$$

$$-i\hbar \frac{\partial}{\partial t} a_{k'}^* = \sum_{k''} a_{k''}^* \langle k''|H|k'\rangle$$

Now $\langle k|\rho|k'\rangle = \rho(kk') = a_{k'}^* a_k$, then:

(11) $$i\hbar \frac{\partial}{\partial t}(a_{k'}^* a_k) = i\hbar\left[a_k \frac{\partial}{\partial t} a_{k'}^* + a_{k'}^* \frac{\partial}{\partial t} a_k\right]$$

$$= -a_k \sum_{k''} a_{k''}^* \langle k''|H|k'\rangle + a_{k'}^* \sum_{k''} \langle k|H|k''\rangle a_{k''}$$

and, using the definition of the density matrix in the momentum representation, Then:

(12) $$i\hbar \frac{\partial}{\partial t}\langle k|\rho|k'\rangle = \sum_{k''}\left[\langle k|H|k''\rangle\langle k''|\rho|k'\rangle - \langle k|\rho|k''\rangle\langle k''|H|k'\rangle\right]$$

$$= \langle k|[H,\rho]|k'\rangle$$

or we have:

(13) $$\boxed{i\hbar \frac{\partial}{\partial t}\rho = [H,\rho]}$$

NB: for any other operator:
$i\hbar \frac{\partial}{\partial t} O = [O, H]$

This is the Liouville Equation

The Louville equation is nice for taking expectation values. Example of taking expectation values:

$$\langle O\rangle = \int \Psi^*(x)\, O\, \Psi(x)\, d^3x = \sum_{kk'} a_{k'}^* a_k \int \varphi^*(k'x)\, O\, \varphi(kx)\, d^3x$$

$$= \sum_{kk'} \langle k|\rho|k'\rangle\langle k'|O|k\rangle = \sum_k \langle k|\rho O|k\rangle = \mathrm{Tr}\{\rho O\} = \mathrm{Tr}\{O\rho\}$$

One of the operators we will be using in the work to follow is the charge density operator because of its use in Poisson's equation.

Example: Charge Density operator :- $\delta(x - x_e)$

(x: position; x_e: operator)

Then $Tr\{\rho\, \delta(x-x_e)\} = \sum_{k k'} a^*_{k'}\, \varphi^*(k'x)\, a_k\, \varphi(kx)$

$= \Psi^*(x)\, \Psi(x)$ which is the charge density.

The operator x_e is the variable of integration which picks off that part of the wave function at point x to form charge density.

Electron Gas in a Solid:

Consider the Liouville equation:

(14) $i\hbar \frac{\partial}{\partial t} \rho = [H, \rho]$ where $H = H_0 + V(x,t)$

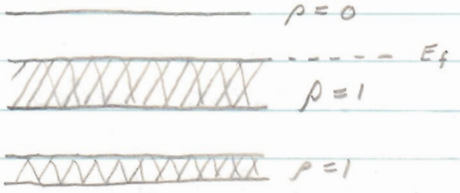
($V(x,t)$: perturbation)

and $H_0 = \frac{p^2}{2m} + V_p(x)$; $H_0 |nk\rangle = E_n(k) |nk\rangle$

($V_p(x)$: periodic)

$|nk\rangle = b_n(k, x)$

and also: $\rho^{(0)} |nk\rangle = f_0(E_n(k)) |nk\rangle$ which means that when operating on a state nk we get either 0 or 1 or Fermi distribution.



Now $V(x,t)$ is the perturbation, consequently small, such that ρ can be linearized:

(15) $\rho = \rho^{(0)} + \rho^{(1)}$ and

(16) $i\hbar \frac{\partial}{\partial t} \rho^{(1)} = [H_0, \rho^{(1)}] + [V, \rho^{(0)}]$

since $i\hbar \frac{\partial}{\partial t} \rho^{(0)} = [H_0, \rho^{(0)}] = 0$

Now take matrix elements $\langle nk | \; | k+q, n' \rangle$

(17) $i\hbar \frac{\partial}{\partial t} \langle kn | \rho^{(1)} | k+q, n' \rangle = \left[E_n(k) - E_{n'}(k+q) \right] \langle nk | \rho^{(1)} | k+q, n' \rangle$

$+ \left[f_0(E_{n'}(k+q)) - f_0(E_n(k)) \right] \langle kn | V | k+q, n' \rangle$

Next: Fourier analyze $V = V_0 + V_s$

(V_0: external; V_s: screening)

with:

$$V = \sum_q e^{iqx} V(q,t)$$

$$\nabla^2 V_s = 4\pi e^2 n(x)$$

$$n(x) = \mathrm{Tr} \left\{ \delta(x - x_e) \rho \right\}$$

LECTURE XXXVI 12-21-60

Recapitulation:

$$i\hbar \frac{\partial}{\partial t}\rho = [H, \rho]$$

$$H = H_0 + V(x,t)$$
$$\rho = \rho^{(0)} + \rho^{(1)}$$
$$\rho^{(0)} |nk\rangle = f_0(E_n(k)) |nk\rangle$$
$$H_0 |nk\rangle = E_n(k) |nk\rangle$$

$$i\hbar \frac{\partial}{\partial t}\rho^{(0)} = [H_0, \rho^{(0)}] = 0$$

and $$i\hbar \frac{\partial \rho^{(1)}}{\partial t} = [H_0, \rho^{(1)}] + [V, \rho^{(0)}]$$

or: $$i\hbar \frac{\partial}{\partial t}\langle kn|\rho^{(1)}|k+q, n'\rangle = [E_n(k) - E_{n'}(k+q)]\langle nk|\rho^{(1)}|n', k+q\rangle$$
$$+ [f_0(E_{n'}(k+q)) - f_0(E_n(k))]\langle nk|V|n', k+q\rangle$$

We now expand V in a Fourier series:

(1) $$V(x,t) = \sum_{q'} e^{-iq'\cdot x} V(q',t)$$, then:

(2) $$\langle nk|V|k+q, n'\rangle = \sum_{q'} V(q't)\langle nk|e^{-iq'\cdot x}|k+q, n'\rangle$$

Operate with:

(3) $$\frac{1}{\Omega}\int u_n^*(k,x)\, u_{n'}(k+q, x)\, e^{i(q-q')\cdot x}\, d^3x$$

$$= \frac{\delta_{qq'}}{v_a}\int_0 u_n^*(kx)\, u_{n'}(k+q, x)\, d^3x$$

$$= \delta_{qq'}\,(kn\,|\,k+q, n')$$

where the parentheses are taken to mean the matrix element with respect to the u's

Then:

(4) $\langle n'k' | V | k+q, n' \rangle = V(q,t) \; (kn / k+q, n')$

Now $V(q,t)$ is the sum of two terms, the external potential and the screening potential.

(5) $V(q,t) = V_0(q,t) + V_s(q,t)$

V_0: external; V_s: screening

where $\nabla^2 V_s(x,t) = -4\pi e^2 n(x,t)$

and: $n(x,t) = Tr \left\{ \delta(x - x_e) \rho^{(1)} \right\}$

Program:

evaluate $V_s(x,t)$ in terms of the density matrix $\rho^{(1)}$ and plug in Liouville's equation.

First calculate $n(xt)$:

(6) $n(xt) = \sum_{\substack{nk \\ n'k'}} \langle n'k' | \delta(x - x_e) | nk \rangle \langle nk | \rho^{(1)} | n'k' \rangle$

where $\langle n'k' | \delta(x - x_e) | nk \rangle = b^*_{n'}(k'x) \; b_n(kx)$

Now what we really want is the Fourier transform of $n(xt)$ as defined by:

(7) $n(xt) = \sum_{q'} e^{-iq' \cdot x} \; n(q't)$, then:

(8) $\langle n'k' | \delta(x - x_e) | nk \rangle = \sum_q e^{-iq \cdot x} \; \beta_{k'n', \, kn}(q)$

where $\beta_{k'n', \, kn}(q) = \frac{1}{\Omega} \int b^*_{n'}(k'x) \; b_n(k,x) \; e^{iq \cdot x} \, d^3x$

$= \frac{1}{\Omega} \delta_{k', \, k+q} \; (k'n' / kn)$

Substituting in (7):

$$(9)\quad n(xt) = \sum_q e^{-iq\cdot x} \underbrace{\sum_{\substack{nk\\ n'k'}} \frac{1}{\Omega}\, \delta_{k',k+q}\, (k'n'|kn)\, \langle nk|\rho^{(1)}|k+q,n'\rangle}_{n(q,t)}$$

To avoid confusion with the symbology used in the Liouville equation, make the change: $n \to l$, $n' \to l'$, $k \to k'$

$$(10)\quad n(qt) = \sum_{\substack{k'\\ ll'}} \frac{1}{\Omega}\, (k'+q, l'|k'l)\, \langle lk'|\rho^{(1)}|k'+q, l'\rangle$$

Poisson's equation, when transformed, becomes:

$$(11)\quad -q^2 V_s(q,t) = -4\pi e^2 n(qt), \text{ then:}$$

$$(12)\quad V_s(qt) = \underbrace{\frac{4\pi e^2}{\Omega q^2}}_{v_q} \sum_{\substack{k'\\ ll'}} (k'+q,l|k'l)\, \langle k'l|\rho^{(1)}|k'+q,l'\rangle$$

with $\frac{e^2}{x} = \sum_q v_q e^{-iq\cdot x}$, $v_q = \frac{4\pi e^2}{\Omega q^2}$, then:

$$(13)\quad \langle kn|V|k+q,n'\rangle = (kn|k+q,n')\left[v_q \sum_{k'll'} (k'+q,l'|k'l) \cdot \langle k'l|\rho^{(1)}|k'+q,l'\rangle + V_0(qt)\right]$$

from equations (4) and (12).

We now substitute this into the Liouville equation of which the matrix elements have been taken.

$$(14)\quad i\hbar \frac{\partial}{\partial t} \langle kn | \rho^{(1)} | k+q, n' \rangle = \left[E_n(k) - E_{n'}(k+q) \right] \langle kn | \rho^{(1)} | k+q, n' \rangle$$

$$+ \left[f_0 (E_{n'}(k+q)) - f_0 (E_n(k)) \right] (kn | k+q, n') \left[v_q \sum_{k'll'} \underbrace{(k'+q, l' | k'l) \langle k'l | \rho^{(1)} | k'+q, l' \rangle}_{V_s} + V_0(qt) \right]$$

Define:

$$(15)\quad \langle kn | \tilde{\rho} | k+q, n' \rangle = (k+q, n' | kn) \langle kn | \rho^{(1)} | k+q, n' \rangle$$

Multiply (14) by $(k+q, n' | kn)$, then

$$(16)\quad i\hbar \frac{\partial}{\partial t} \langle kn | \tilde{\rho} | q+k, n' \rangle = \left[E_n(k) - E_{n'}(q+k) \right] \langle kn | \tilde{\rho} | k+q, n' \rangle$$

$$+ \left[f_0 (E_{n'}(k+q)) - f_0 (E_n(k)) \right] | (kn | k+q, n') |^2$$

$$\cdot \left[v_q \sum_{l'll'} \langle k'l | \tilde{\rho} | k'+q, l' \rangle + V_0(qt) \right]$$

We will now obtain the Boltzmann equation for the free electron gas from this Liouville equation in the classical limit. At first, we merely drop the band index n:

$$(17)\quad i\hbar \frac{\partial}{\partial t} \langle k | \rho^{(1)} | k+q \rangle = (E_k - E_{k+q}) \langle k | \rho^{(1)} | k+q \rangle$$

$$+ \left[f_0 (E_{k+q}) - f_0 (E_k) \right] \langle k | V | k+q \rangle$$

The classical limit corresponds to $\hbar \to 0$ or in our case $q \to 0$ as then the matrix elements become classical mean values of the operators. We thus expand $E_k - E_{k+q}$ in a Taylor series:

$$(18)\quad E_k - E_{k+q} = -q \cdot \nabla_k E_k - \frac{1}{2} \underbrace{(q \cdot \nabla_k)^2 E_k}_{\frac{\hbar^2}{2m^*}} = \hbar q \cdot v + \mathcal{O}(\hbar^2)$$

and by the same token:

(19) $f_0(E_{k+q}) - f_0(E_k) \approx q \cdot \nabla_k f_0(E_k)$

Recall from equation (4) as $q \to 0$:

(20) $\langle k|V|k+q\rangle = V(q,t)$

and write:

(21) $\langle k|\rho^{(1)}|k+q\rangle = f_k^{(1)}(q)$, then

(22) $i\hbar \frac{\partial}{\partial t} f_k^{(1)}(q) = -\hbar q \cdot v\, f_k^{(1)}(q) + q \cdot \nabla_k f_0(E_k)\, V(q,t)$

or: $i\hbar \frac{\partial}{\partial t} f_k^{(1)}(q) + \hbar q \cdot v\, f_k^{(1)}(q) - ie\,\mathcal{E}(q,t) \cdot \nabla_k f_0(E_k) = 0$

since $ie\,\mathcal{E}(q,t) = q\,V(qt)$ from equation (1).

As we want our relations in real space, we make the following transformations:

(23) $f_k^{(1)}(x) = \sum_q f_k^{(1)}(q)\, e^{-iq\cdot x}$

$\mathcal{E}(x,t) = \sum_q \mathcal{E}(q,t)\, e^{-iq\cdot x}$

$i\nabla f_k^{(1)}(x) = \sum_q q\, f_k^{(1)}(q)\, e^{-iq\cdot x}$

with $\dot{k} = \frac{m\dot{v}}{\hbar} = \frac{F}{\hbar} = \frac{-e\,\mathcal{E}(x,t)}{\hbar}$

Now sum (22) over q after multiplying thru by $e^{-iq\cdot x}$ and get; after cancelling $i\hbar$:

(24) $\frac{\partial}{\partial t} f_k^{(1)}(x) + v \cdot \nabla f_k^{(1)}(x) + \dot{k} \cdot \nabla_k f_0(E_k) = 0$

which is the linearized Boltzmann equation.

Consider now an External Perturbation varying harmonically with time:

(25) $V_0(q,t) \cong \lim_{\alpha \to 0^+} e^{\alpha t} e^{i\omega t}$; $\alpha \to 0$ from + direction, then,

(26) $\langle kn | \tilde{\rho} | k+q, n' \rangle \sim e^{\alpha t} e^{i\omega t}$

$$i\hbar \frac{\partial}{\partial t} \langle kn | \tilde{\rho} | k+q, n' \rangle = (-\hbar\omega + i\hbar\alpha) \langle kn | \tilde{\rho} | k+q, n' \rangle$$

We then write:

(27) $V(q,t) = V(q,\omega)\, e^{i\omega t} e^{\alpha t}$

with the result that equation ~~XXXV~~ (17) gives:

(28) $$\langle kn | \rho^{(1)} | k+q, n' \rangle = \frac{f_0(E_{n'}(k+q)) - f_0(E_n(k))}{[E_{n'}(k+q) - E_n(k) - \hbar\omega] + i\hbar\alpha} |(kn | k+q, n')|^2 V(q,t)$$

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Recapitulation: (1) $i\hbar \frac{\partial \rho^{(1)}}{\partial t} = [H_0, \rho^{(1)}] + [V, \rho^{(0)}]$

(2) $H_0 | nk \rangle = E_n(k) | nk \rangle$

(3) $\rho^{(0)} | nk \rangle = f^{(0)}(E_n(k)) | nk \rangle$

(4) $V = \underbrace{V_0}_{\text{external}} + \underbrace{V_S}_{\text{screening}}$

(5) $\nabla^2 V_S = -4\pi e^2 n(x,t)$

(6) $n(x,t) = Tr\{ \delta(x - x_e)\, \rho^{(0)} \}$

We define:

(7) $V = \sum_q V(q,t)\, e^{i q \cdot x}$

We arrive at:

$$(8)\quad \frac{\partial}{\partial t}\left\{ i\hbar \langle n\mathbf{k}|\tilde{\rho}|\mathbf{k}+\mathbf{q},n'\rangle \right\}$$

$$= (E_{n\mathbf{k}} - E_{n',\mathbf{k}+\mathbf{q}})\langle n\mathbf{k}|\tilde{\rho}|\mathbf{k}+\mathbf{q},n'\rangle + (f_{n',\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}})\left|(n\mathbf{k}|\mathbf{k}+\mathbf{q},n')\right|^2 \left[V_{\mathbf{q}} \sum_{\mathbf{k}'ll'} \langle l\mathbf{k}'|\tilde{\rho}|\mathbf{k}+\mathbf{q},e'\rangle + V_0(\mathbf{q},t)\right]$$

where we have defined:

$$(9)\quad \langle n\mathbf{k}|\tilde{\rho}|\mathbf{k}+\mathbf{q},n'\rangle = (n\mathbf{k}|\mathbf{k}+\mathbf{q},n')\langle n\mathbf{k}|\rho^{(1)}|\mathbf{k}+\mathbf{q},n'\rangle$$

$$\text{and}\quad (n\mathbf{k}|\mathbf{k}+\mathbf{q},n') = \int_0 u_n^*(\mathbf{k},x)\, u_{n'}(\mathbf{k}+\mathbf{q},x)\, d^3x$$

We take the perturbation to be harmonic and turned on adiabatically:

$$(10)\quad V_0 = V_0(\omega,\mathbf{q})\, e^{i\omega t} e^{\alpha t} = V_0(\mathbf{q},t)$$

taking $\alpha \to 0^+$

Hence, we conclude that $\langle |\tilde{\rho}| \rangle \sim e^{i\omega t} e^{\alpha t}$ and get:

$$(11)\quad \langle n\mathbf{k}|\tilde{\rho}|n',\mathbf{k}+\mathbf{q}\rangle = F(n',\mathbf{k}+\mathbf{q};\, n\mathbf{k})\underbrace{\left|(\mathbf{k}n|\mathbf{k}+\mathbf{q},n')\right|^2}_{\text{contains all of solid state aspects of problem}} V(\omega,\mathbf{q})$$

where:

$$F(n',\mathbf{k}+\mathbf{q};\, n\mathbf{k}) \equiv \frac{f_{n',\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}}{E_{n',\mathbf{k}+\mathbf{q}} - E_{n\mathbf{k}} - \hbar\omega + i\hbar\alpha}$$

We tacitly assume a frequency and wave number dependence in the dielectric constant and proceed from a classical basis. Now Vo polarizes the system:

$$(12)\quad P(\omega,q) = \frac{1}{4\pi}\left\{\epsilon(\omega,q)-1\right\}\mathcal{E}(\omega,q)$$

The polarization is also related to the induced change in charge density:

$$(13)\quad \nabla\cdot P = e n$$

We Fourier analyze (13) according to the operation $\sum_q e^{-iq\cdot x}$ and get:

$$(14)\quad -iq\cdot P(\omega,q) = e\,n(\omega,q)$$

and from $e\mathcal{E} = \text{grad } V$

$$(15)\quad e\,\mathcal{E}(\omega,q) = -iq\,V(\omega,q)$$

If we consider transverse disturbances to be non-existant and condiser only longitudinal disturbances, we can divide (14) by q.

$$(16)\quad P(\omega,q) = \frac{ie}{q}n(\omega,q) = \frac{1}{4\pi}\left\{\epsilon(\omega,q)-1\right\}\left\{\frac{-iq}{e}V(\omega,q)\right\}$$

Hence:

$$(17)\quad \boxed{n(\omega,q) = \frac{-q^2}{4\pi e^2}\left\{\epsilon(\omega,q)-1\right\}V(\omega,q)}$$

What we now need is the relation between $n(\omega,q)$ and the potential: Recall:

$$(18)\quad n(\omega,q) = \frac{1}{\Omega}\sum_{k,nn'}\langle nk|\tilde{\rho}|k+q,n'\rangle$$

$$= \frac{1}{\Omega}V(\omega,q)\sum_{knn'}{}' F(n';k+q;nk)\left|(kn|k+q,n')\right|^2$$

Then by comparison:

$$(19)\qquad \boxed{\epsilon(\omega,q) = 1 - \lim_{\alpha\to 0^+} v_q \sum_{kn n'} \frac{(f_{n',k+q} - f_{n,k})\,|(nk|k+q,n')|^2}{E_{n'k+q} - E_{nk} - \hbar\omega + i\hbar\alpha}}$$

where $v_q = \dfrac{4\pi e^2}{\Omega q^2}$

This dielectric constant is the inverse of Schwinger's quantity $\pi(\omega,q) = \dfrac{1}{\epsilon(\omega,q)}$.

Properties: Relationship Between V and V_0.

We write the Fourier transformed Poisson equation:

$$(20)\qquad -q^2 V_s(\omega,q) = -4\pi e^2 n(\omega,q)$$

$$\text{or}\qquad n(\omega,q) = \frac{q^2}{4\pi e^2} V_s(\omega,q)$$

Now classically:

$$(21)\qquad V_s(\omega,q) = V(\omega,q) - V_0(\omega,q) = -(\epsilon - 1) V(\omega,q)$$

and

$$(22)\qquad \underbrace{V(\omega,q)}_{\substack{\text{not}\\ \text{internal}\\ \text{potential}}} = \frac{V_0(\omega,q)}{\epsilon(\omega,q)}$$

where the screening potential is contained in $\epsilon(\omega,q)$. Under the condition when $\epsilon(\omega,q)=0$ we obtain a tremendous internal field from any finite external field. This is the resonance condition, which gives rise to plasma oscillations.

We now assume that the external field is not present or that it is present but completely shielded:

$$(23)\quad (-\hbar\omega + \epsilon\hbar\alpha)\langle nk|\hat{\rho}|k+q,n'\rangle = (E_{nk} - E_{n',k+q})\langle nk|\hat{\rho}|k+q,n'\rangle + (f_{n';k+q} - f_{nk})\,|(kn|k+q,n')|^2 v_q \sum_{k'll'} \langle k'l|\hat{\rho}|k+q,n'\rangle$$

From whence we obtain:

$$(24)\quad \sum_{k,nn'} \frac{(f_{n';k+q} - f_{nk})}{E_{n';k+q} - E_{nk} - \hbar\omega + \epsilon\hbar\alpha}\,|(kn|k+q,n')|^2 v_q = 1$$

which from equation (9) means $\epsilon(\omega,q)=0$ or the oscillatory condition. This is the self-consistent method, and we can determine $\omega = f(q)$ called the plasma dispersion relation.

What is the meaning of the imaginary part of $\epsilon(\omega,q)$?

$$(25)\quad \epsilon(\omega,q) = \epsilon_1(\omega,q) \underbrace{- i\,\epsilon_2(\omega,q)}_{\text{left travelling wave}}$$

In or near the plasma oscillation condition: $\omega \sim \omega_p$ and:

$$(26)\quad \epsilon_1(\omega,q) = \underbrace{\epsilon_1(\omega_p,q)}_{0} + (\omega-\omega_p)\left(\frac{d\epsilon_1}{d\omega}\right)_{\omega_p}$$

Hence:

$$(27)\quad V(\omega,q) = \frac{V_0(\omega,q)}{\left(\frac{d\epsilon_1}{d\omega}\right)_{\omega_p}(\omega-\omega_p) - i\,\epsilon_2(\omega_p,q)}$$

$$(28)\qquad V(\omega,q) = \left(\frac{d\epsilon_1}{d\omega}\right)^{-1} \frac{V_0(\omega,q)}{(\omega-\omega_p) - \frac{1}{2}i\Gamma(\omega_p,q)}$$

$$\text{where}\quad \Gamma(\omega_p,q) = 2\epsilon_2(\omega_p,q)\left(\frac{d\epsilon_1}{d\omega}\right)^{-1}_{\omega_p}$$

This is a Lorentzian system with damping effects. The damping is due to the imaginary part of $\epsilon(\omega,q)$ and damps the plasma oscillations. ϵ_2 is finite so damping is always present, except at $T=0$.

EXAMPLE: Free Electron Gas:

Here $|(k\alpha|k+q,\alpha')|^2 = \left|\int_0 u_\alpha(k,r)\, u_{\alpha'}(k+q,r)\, d^3r\right|^2 = 1$

from whence (19):

$$(29)\qquad \epsilon(\omega,q) = 1 + v_q \sum_k \frac{f_k - f_{k+q}}{E_{k+q} - E_k - \hbar\omega + i\hbar\alpha}$$

Do the following: Let $\sum_k \to \frac{\Omega}{4\pi^3}\int d^3k$ and let $k+q \to k$ in second term of (29):

$$(30)\qquad \epsilon(\omega,q) = 1 + v_q \frac{\Omega}{4\pi^3}\int d^3k\, f_k \left\{\frac{1}{E_{k+q} - E_k - \hbar\omega + i\hbar\alpha}\right.$$

$$\left. + \frac{1}{E_{k-q} - E_k + \hbar\omega - i\hbar\alpha}\right\}$$

Take $\lim_{\alpha\to 0^+}$ using theorem in Heitler, 3rd ed., pp. 69-70 (also Dirac):

$$\lim_{\alpha\to 0}\frac{1}{x - i\alpha} = P\left(\frac{1}{x}\right) + i\pi\,\delta(x)$$

We get then:

$$(31)\qquad \boxed{\epsilon_1 = 1 + \frac{e^2}{\pi^2 q^2} P\int d^3k\, f_k \left\{\frac{1}{E_{k+q} - E_k - \hbar\omega} + \frac{1}{E_{k-q} - E_k + \hbar\omega}\right\}}$$

(32) $$\epsilon_2 = \frac{e^2}{\pi q^2} \int d^3k \; \underbrace{(f_k - f_{k+q})}_{\text{occupation term}} \; \underbrace{\delta(E_{k+q} - E_k - \hbar\omega)}_{\text{conservation of energy}}$$

Under conditions of plasma oscillations, $\epsilon_1 = 0$. Examine this condition near $q=0$. See (31):

(33) $$\{\;\} \to -\frac{1}{\hbar^2\omega_p^2}\left\{(E_{k-q} - E_k) + (E_{k+q} - E_k)\right\}$$

with $$E_{k+q} = E_k + (q\cdot\nabla_k)E_k + \frac{1}{2}(q\cdot\nabla_k)^2 E_k$$

or $$\{\;\} \to -\frac{1}{\hbar^2\omega_p^2}(q\cdot\nabla_k)^2 E_k = -\frac{q^2}{\hbar^2\omega_p^2}\frac{\hbar^2}{m} = -\frac{q^2}{m\omega_p^2}$$

Now: $$\int d^3k\, f_k = \frac{4\pi^2}{\Omega} N = 4\pi^3 n$$

Then:

(34) $$\epsilon_1 = 1 - \frac{e^2}{\pi^2 q^2}\cdot 4\pi^3 n \frac{q^2}{\omega_p^2 m} = 1 - \frac{4\pi n e^2}{\omega_p^2 m} = 0$$

or

(35) $$\boxed{\omega_p^2 = \frac{4\pi n e^2}{m}}$$

This, of course, corresponds to the limit of long waves as $q \to 0$ which naturally gives the classical result.

LECTURE XXXVIII 1-9-61

Recapitulation:

$$\epsilon_1(\omega,q) = 1 + \frac{e^2}{\pi^2 q^2} P \int d^3k\, f_k \left\{ \frac{1}{E_{k+q} - E_k - \hbar\omega} + \frac{1}{E_{k-q} - E_k + \hbar\omega} \right\}$$

$$\epsilon_2(\omega,q) = \frac{e^2}{\pi q^2} \int d^3k\, (f_k - f_{k+q})\, \delta(E_{k+q} - E_k - \hbar\omega)$$

$\epsilon_1(\omega,0) = 0$ for plasma oscillations,

$$\epsilon_1(\omega,0) = 1 - \frac{\omega_p^2}{\omega^2} = 0\,; \quad \omega_p = \frac{4\pi n e^2}{m}$$

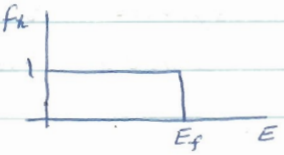
$\hbar\omega_p \sim 10$ ev for a typical metal.

Plasma Dispersion

We suspect $\omega_p^2(q) \sim \omega_p^2(0) + \alpha q^2 + \cdots$

How about higher q? $\epsilon_2 = 0$ or at least $\epsilon_2 \ll 1$

Recall at 0°K:



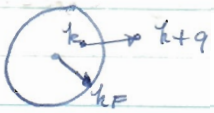
If we consider k_F to always lie between k and $k+q$, we can write:

$$f_k - f_{k+q} = f_k (1 - f_{k+q})$$

since $f_k = 1$ always. Then:

(1) $$\epsilon_2(\omega,q) = \frac{e^2}{\pi q^2} \int d^3k\, f_k (1 - f_{k+q})\, \delta(E_{k+q} - E_k - \hbar\omega)$$

Hence we see the meaning of ϵ_2 in that, it denotes excitation from the fermi sea and hence absorption, or damping.



Now find the minimum q such that energy is conserved; $E_{k+q} - E_k - \hbar\omega = 0$.

$$\frac{\hbar^2}{2m}\left\{(k+q)^2 - k^2\right\} = \hbar\omega$$

or $$\frac{\hbar^2}{2m}\left(2k\cdot q + q^2\right) = \hbar\omega$$

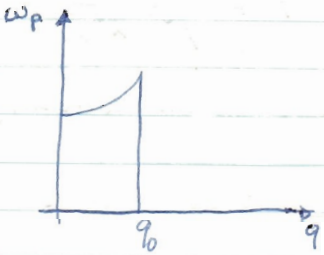
Since $k\cdot q = kq\mu$

(2) $$q = -k\mu + \sqrt{k^2\mu^2 + \frac{2m\omega}{\hbar}}$$

hence $k\mu$ must be max for q min.
For $k = k_F$, $\mu = 1$.

(3) $$2q_0 k_F + q^2 - \frac{2m\omega_p(q_0)}{\hbar} = 0$$

This defines the plasma cutoff, because oscillations are damped out. So plasma oscillations exist to q_0 and not beyond.



If not at $T=0$, q_0 can approach 0 so damping always occures.

We could do a normal mode analysis using density matrices and transforming:

$$i\hbar\frac{\partial}{\partial t}D_k = (E_k - E_{k+q})D_k + \{\ \}\sum_{k'} D_{k'}$$

to $$i\frac{\partial}{\partial t}G_k = \omega_k G_k$$

Screening Effects: Free Electron Gas:

Take $\omega \to 0$ means stationary charge
$q \to 0$ means classical screening effect.

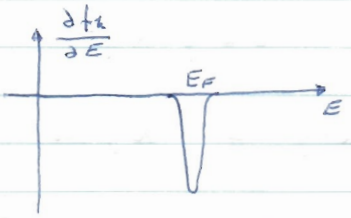
Then:

$$(4) \quad \epsilon_1(0,q) = 1 - v_q \frac{\Omega}{4\pi^3} \int d^3k \underbrace{\frac{f_{k+q} - f_k}{E_{k+q} - E_k}}_{\frac{\partial f_k}{\partial E} \text{ as } q \to 0}$$

Recall $\int d^3k \frac{\partial f_k}{\partial E}$:

$$= 4\pi \int k^2 \frac{dk}{dE} \frac{df_k}{dE} dE$$

$$= -4\pi k_F^2 \frac{dk_F}{dE_F}$$



$$(5) \quad \epsilon_1(0,q) = 1 + \frac{4\pi e^2}{\Omega q^2} \cdot \frac{\Omega}{4\pi^2} \cdot 4\pi k_F^2 \frac{dk_F}{dE_F}$$

$$k_F^2 \frac{dk_F}{dE_F} = k_F^2 \frac{m}{\hbar^2 k_F} = \frac{k_F m}{\hbar^2} \underbrace{\frac{3\pi^2 n}{k_F^3}}_{1} = \frac{1}{2} \frac{3\pi^2 n}{E_F}$$

Finally:

$$(6) \quad \epsilon_1(0,q) = 1 + \frac{1}{q^2} \cdot \frac{6\pi n e^2}{E_F} = 1 + \frac{1}{q^2 \lambda_{TF}^2}$$

where $\lambda_{TF}^2 = \frac{E_F}{6\pi n e^2}$ (Thomas-Fermi Screening Length)

Notice: $\frac{1}{\epsilon_1(0,q)} = \frac{q^2}{q^2 + \lambda_{TF}^{-2}}$

Recalling $v_q \sim \frac{1}{q^2}$

Hence $v_q \to \frac{v_q}{\epsilon} = \frac{1}{q^2} \cdot \frac{q^2}{q^2 + \lambda_{TF}^{-2}}$

$$= \frac{1}{q^2 + \lambda^{-2}}$$

which is a typical screening action.

Generally, $\epsilon(\omega, q)$ has the form:

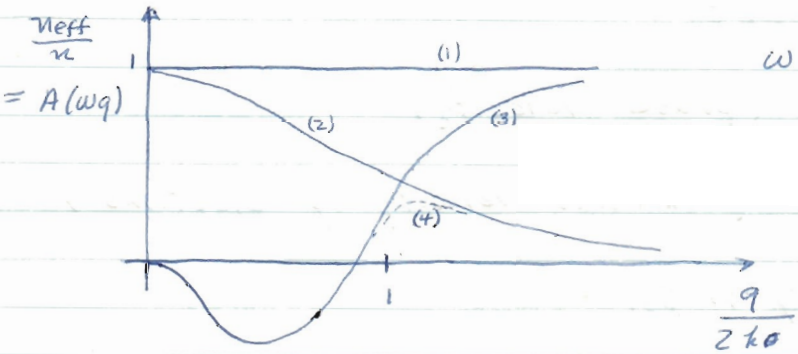
(7) $$\epsilon(\omega,q) = 1 + \frac{1}{q^2 \lambda^2} A(\omega,q)$$

If we did this for a Boltzmann gas, we would get the Debye screening length instead of TF.
$\lambda_D^2 = \frac{kT}{4\pi n e^2}$ or replace E_F by kT.

Anyway, since $\lambda^2 \sim \frac{1}{n}$

(8) $$\epsilon(\omega,q) = 1 + \frac{1}{q^2 \lambda_{eff}^2}$$

or $\lambda_{eff}^2 \cong \frac{1}{n_{eff}}$ where $n_{eff} = n\, A(\omega,q)$



ω fixed

where $k_0 = k_F$ (Fermi)
or $\frac{\hbar^2 k_0}{2m} = kT$ (M-B)

We consider 4 cases:

(1) Classical ($q=0$), Static ($\omega=0$) Case

(2) Quantum Mechanical, Static Case ($q \neq 0$, $\omega = 0$)

If k_0 represents electron ∿∿∿ and
q disturbance ~~~~~
we get (1).

If $q \sim k_0$, we have QM effects because we cannot localize, hence the number of effective screening electrons is reduced.

(3) Dynamical, Classical, ω fixed, q varies.
This is case of polar semiconductor, two atoms per unit cell.

If we have a longitudinal optical wave, then we get polarization:

$$P = \frac{e}{v_a}(u_+ - u_-)\, e^{i(q\cdot r - \omega t)}$$

$$4\pi \nabla\cdot P = \nabla^2 \varphi \quad , \quad \varphi(\omega, q) \sim \frac{1}{q}$$

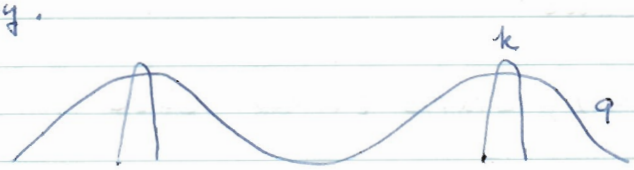
Electrons would like to collect in troughs of disturbing wave. For optical modes, dispersion is almost constant.

Now $v_\varphi = \frac{\omega}{q}$ (phase velocity)

$v_0 = \frac{\hbar k_0}{m}$ (thermal velocity of electrons)

As $q \to 0$, $v_\varphi \gg v_0$.

Consider q wave as standing still and electrons going by.

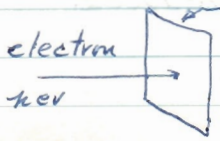


Get build-up or anti-screening.

When $v_\varphi \sim v_0$, electrons collect in valleys.

(4) QM, dynamical.

Characteristic Energy Losses (Experimental Observations)



loses energy in discreet amounts of E_k - 10 ev, 20 ev, 30 ev } due to plasmon excitation.

Classical Treatment:

$$\rho(r,t) = -e\,\delta(r - vt)$$

Electron going thru medium polarizes it which then acts on electron, so electron then loses energy. Make Fourier analysis.

(9) $$\rho(x,t) = \frac{1}{(2\pi)^4}\int d^3q \int d\omega\; e^{i(q\cdot x - \omega t)}\,\rho(\omega,q)$$

(10) $$\rho(\omega,q) = \int d^3x \int dt\; e^{-i(q\cdot x - \omega t)}\,\rho(x,t)$$

or:

(11) $$\rho(\omega,q) = -e\int_{-\infty}^{\infty} dt\, e^{-i(q\cdot v - \omega)t} = -2\pi e\,\delta(q\cdot v - \omega)$$

Now write the Fourier Transform of Poisson's equation:

(12) $$\varphi(\omega,q) = \frac{4\pi\rho(\omega,q)}{q^2\,\epsilon(\omega,q)} = \frac{-8\pi^2 e\,\delta(\omega - q\cdot v)}{q^2\,\epsilon(\omega,q)}$$

This is the potential created by the electron and which it also must overcome. Then the energy loss thru the foil / unit distance is:

(13) $$-\frac{dW}{dx} = -e\,\mathcal{E}_x(x,t)\Big|_{x=vt} = -\frac{e}{v}\,v\cdot\mathcal{E}\Big|_{r=vt}$$

Now $\mathcal{E} = -\nabla\varphi$, $\therefore$ $-\frac{dW}{dx} = \frac{e}{v}\,\vec{v}\cdot\nabla\varphi$

Then:

(14) $$-\frac{dW(\omega,q)}{dx} = -8\pi^2 e^2\,\frac{1}{q^2 v}\,q\cdot v\,\frac{1}{\epsilon(\omega,q)}\,\delta(\omega - q\cdot v)$$

The energy loss is the Fourier transform of this:

(15) $$-\frac{dW}{dx} = \frac{e}{2\pi^2 v}\int d^3q \int d\omega\; \underbrace{\mathrm{Im}\left\{\frac{1}{\epsilon(\omega,q)}\right\}}_{\text{from } \frac{1}{\epsilon} = R\frac{1}{\epsilon} + i\,\mathrm{Im}\frac{1}{\epsilon}}\,\frac{\omega}{q^2}\,\delta(\omega - q\cdot v)$$

LECTURE XXXIX 1-11-61

Recapitulation:

The Characteristic Energy Losses can be described classically because the plasma oscillations are excited by large values of energy.

$$\rho(r,t) = -e\,\delta(r-vt)$$

$$-\frac{dW}{dx} = \frac{e}{v}\, v\cdot\nabla\varphi$$

$$\boxed{-\frac{dW}{dx} = \frac{e^2}{2\pi^2 v}\int d^3q \int d\omega\ \mathrm{Im}\left\{\frac{1}{\epsilon}\right\}\frac{\omega}{q^2}\,\delta(\omega - q\cdot v)}$$

No exponential in Fourier Transform because $\mathcal{E}$ is evaluated at $r = vt$:

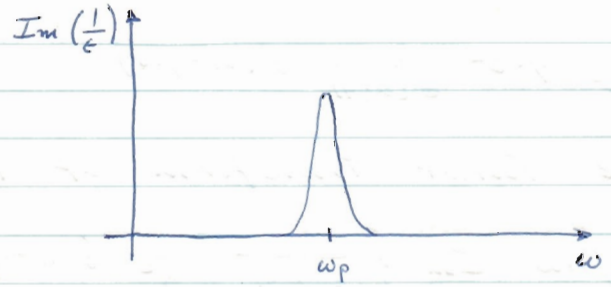
$e^{i(q\cdot r - \omega t)} = e^{iq\cdot(r-vt)} = 1$

How can energy losses be discreet and excite proper plasma oscillations? Recall:

(1) $$\epsilon(\omega,q) = \left(\frac{d\epsilon_1}{d\omega}\right)^{+1}_{\omega_p}\left[(\omega-\omega_p) - \frac{1}{2}i\Gamma\right]^{+1} = \epsilon_1 - i\epsilon_2$$

(2) $$\mathrm{Im}\left(\frac{1}{\epsilon}\right) = \frac{\epsilon_2}{\epsilon_1^2+\epsilon_2^2} \propto \frac{\frac{1}{2}\Gamma}{(\omega-\omega_p)^2 + \frac{1}{4}\Gamma^2}$$

$$\xrightarrow[\Gamma\to 0]{} \pi\,\delta(\omega-\omega_p)$$



Thus energy losses occur in region around ω_p, recognizing that energy losses are related to $\mathrm{Im}\left(\frac{1}{\epsilon}\right)$.

We now discuss plasma oscillations in solids:
Recall:

$$(3)\quad \varepsilon(\omega,q) = 1 - v_q \sum_{k,nn'}{}' \frac{f_{n'k+q} - f_{nk}}{E_{n'k+q} - E_{nk} - \hbar\omega + i\hbar\alpha} \left|(kn|k+q,n')\right|^2$$

where $(kn|k+q,n') = \frac{1}{v_a}\int_0 u_{n'}^*(k,x)\, u_{n'}(k+q,x)\, d^3x$

We are interested in the case when $q \to 0$. Use the results from k·p perturbation theory:

$$(4)\quad u_{n'}(k+q,x) = u_{n'}(k,x) + \frac{\hbar}{m} q \cdot \sum_{\substack{n'' \\ n''=n\neq n'}}{}' \frac{P_{n''n'}}{E_{n'} - E_{n''}} u_{n''}(k,x)$$

Form matrix elements, recalling:

$$\frac{1}{v_a}\int_0 u_{n'}^*(k,x)\, u_n(k,x)\, d^3x = \delta_{nn'}$$

We get the familiar intra- and inter-band terms:

$$(5)\quad (kn|k+q,n') = \delta_{nn'} + (1-\delta_{nn'})\frac{\hbar}{m}\frac{q\cdot P_{nn'}}{E_{n'} - E_n}$$

What we want is:

$$(6)\quad \left|(kn|k+q,n')\right|^2 = \delta_{nn'} + (1-\delta_{nn'})\left(\frac{q}{m\omega_{nn'}}\right)^2 \left|P^\mu_{n'n}\right|^2$$

where $\hbar\omega_{n'n} = E_{n'k} - E_{nk}$

Now, using oscillator strengths, viz:

$$f^\mu_{n'n} = \frac{2}{m}\frac{\left|P^\mu_{n'n}\right|^2}{E_{n'} - E_n}$$

Hence:

$$(7)\quad \left|(kn|k+q,n')\right|^2 = \underbrace{\delta_{nn'}}_{\substack{\text{intraband} \\ \text{(free electron)}}} + \underbrace{(1-\delta_{nn'})\frac{\hbar q^2}{2m}\frac{f^\mu_{n'n}}{\omega_{n'n}}}_{\substack{\text{interband} \\ \text{(due to solid)}}}$$

Then:

$$(8)\quad \epsilon_1(\omega, q\to 0) = 1 + v_q \frac{\Omega}{4\pi^3} P\int d^3k \sum_n{}' f_{nk}\left[\frac{1}{E_{n,k+q} - E_{nk} - \hbar\omega} + \frac{1}{E_{n,k+q} - E_{nk} + \hbar\omega}\right] + v_q \frac{\Omega}{4\pi^3} P\int d^3k \sum_{nn'}{}' f_{nk}$$

$$\left[\frac{1}{E_{n'k} - E_{nk} - \hbar\omega} + \frac{1}{E_{n'k} - E_{nk} + \hbar\omega}\right]\frac{\hbar q^2}{2m}\ \frac{f''_{n'n}}{\omega_{n'n}}$$

In the limit as $q\to 0$:

$$(9)\quad \text{First}\ [\ ] = \lim_{q\to 0}\left\{\frac{2\left(E_{n,k+q} - E_{nk}\right)}{\left(E_{n,k+q} - E_{nk}\right)^2 + (\hbar\omega)^2}\right\}$$

$$= -\frac{(q\cdot\nabla_k)^2 E_{nk}}{(\hbar\omega)^2} \quad \text{by Taylors Theorem}$$

$$(10)\quad \text{Second}\ [\ ] = \frac{2}{\hbar}\frac{\omega_{n'n}}{\omega_{n'n}^2 - \omega^2}$$

Then:

$$(11)\quad \epsilon_1(\omega, q\to 0) = 1 - \left(\frac{e}{\pi\hbar\omega}\right)^2 \sum_n{}' \int d^3k\ f_{nk}\ \frac{\partial^2 E_{nk}}{\partial k_\mu^2}$$

$$+ \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{nn'}{}' P\int d^3k\ f_{nk}\ \frac{f''_{n'n}}{\omega_{n'n}^2 - \omega^2}$$

Remember the difference between oscillator strengths and distribution functions.

To examine the above relation, examine insulators first. Would not expect plasma oscillations as the bands are either all full or all empty. Assume for the band indices on the distribution function:

$$n < n_{\text{valence}}: \quad f_{nk} = 1$$
$$n > n_{\text{valence}}: \quad f_{nk} = 0$$

$$\hbar\omega_{v+1,v} = E_G \quad (\text{Gap})$$

For a full band:

(12) $$\int_{BZ} d^3k \frac{\partial^2 E_{nk}}{\partial k_\mu^2} = \underbrace{\frac{1}{3}\int d^3k \, \nabla_k^2 E_n(k)}_{\text{cubic crystal, } q \text{ along principle axis.}}$$

$$= \frac{1}{3}\int d^3k \, \nabla_k E_n(k) \cdot dS' = 0$$

because opposite sides of a full BZ contribute equally, hence this term vanishes for insulators (also for $n > n_v$, $f_{nk} = 0$, so 0 there too).

We now show that the plasma frequency cannot fall in the band gap, that is, is there a solution such that $\omega < \omega_{v+1,v}$?

Define:

(13) $$g_{n'n} \equiv \frac{\omega^2}{\omega_{n'n}^2 - \omega^2} = g_{nn'}$$

For oscillation, set $\epsilon_1(\omega, 0) = 0$, multiply by ω^2 and get from (11):

(14) $$\omega^2 = -\frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{nn'}' P\int d^3k \, \underbrace{f_{nk} f^\mu_{n'n} g_{n'n}}_{\frac{1}{2}\sum_{nn'}' P\int d^3k \left\{ f_{nk} f^\mu_{n'n} g_{n'n} + f_{n'k} f^\mu_{nn'} g_{nn'} \right\}}$$

Now $f_{nn'} = -f_{n'n}$, $g_{n'n} = g_{nn'}$

Then:

$$\{\ \} = (f_{nk} - f_{n'k}) f^\mu_{n'n} g_{n'n}$$

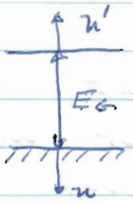
Now split up the sum:

$$\sum_{nn'}' = \underbrace{\sum_{\substack{n \le n_v \\ n' \le n_v}}'}_{\substack{\downarrow \\ 0 \\ f_n = f_{n'}}} + \underbrace{\sum_{\substack{n \le n_v \\ n' > n_v}} + \sum_{\substack{n > n_v \\ n' \le n_v}}}_{f_n = 1,\ f_{n'} = 0 \text{ or vice-versa; takes back factor of } \frac{1}{2}} + \underbrace{\sum_{\substack{n > n_v \\ n' > n_v}}'}_{\substack{\downarrow \\ 0}}$$

Then:

$$(15) \qquad \omega^2 = \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{\substack{n \le n_v \\ n' > n_v}}' P \int d^3k \, f^{\mu}_{n'n} \frac{\omega^2}{\omega^2 - \omega^2_{n'n}}$$

Thus we have divided the band notation such that:



$$|\omega_{n'n}| > |\omega_{v+1,v}|$$

Now: $f^{\mu}_{n'n}$ is always positive and

$$\frac{\omega^2}{\omega^2 - \omega^2_{n'n}} \quad \text{is negative if } \omega < \omega_{n'n}$$

hence there is no real solution for ω^2 if ω in band gap.

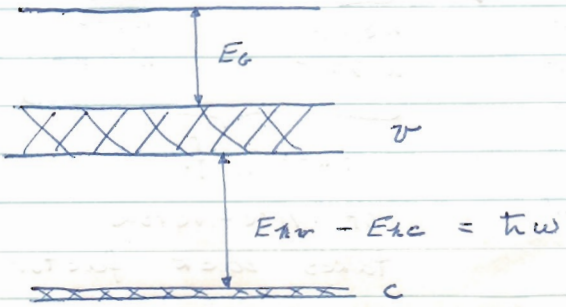
For large plasma oscillations, band gap plays a less important role. We can replace $n' > n_v$ by n' if $\sum_{\substack{n \le n_v \\ n' \le n_v}} = 0$

Proof:

$$\sum_{nn'} \frac{1}{2} \int d^3k \underbrace{\left[f^{\mu}_{n'n} \varrho_{n'n} + f^{\mu}_{nn'} \varrho_{nn'} \right]}_{(f_{n'n} - f_{n'n})\varrho_{n'n} = 0} \qquad \text{QED.}$$

We now go to actually find plasma frequencies. We take electrons to be divided thus:

(1) core electrons (2) valence electrons



(16) $$\omega^2 = -\frac{1}{m}\left(\frac{e}{\pi}\right)^2 \omega^2 \sum_{cn'}{}' P\int d^3k \; \frac{f^{\mu}_{n'c}}{\omega^2_{nc}}$$

$$+ \frac{1}{m}\left(\frac{e}{\pi}\right)^2 P \sum_{vn'}{}' \int d^3k \; f^{\mu}_{n'v} \frac{\omega^2}{\omega^2 - \omega^2_{n'v}}$$

The dielectric constant of the core which provides background for events to take place we take as:

(17) $$\epsilon_c = 1 + \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{cn'}{}' P\int d^3k \; \frac{f^{\mu}_{n'c}}{\omega_{n'c}}$$

which is static. For convenience, write:

$$\frac{\omega^2}{\omega^2 - \omega^2_{n'v}} = 1 + \frac{\omega^2_{n'v}}{\omega^2 - \omega^2_{n'v}}$$

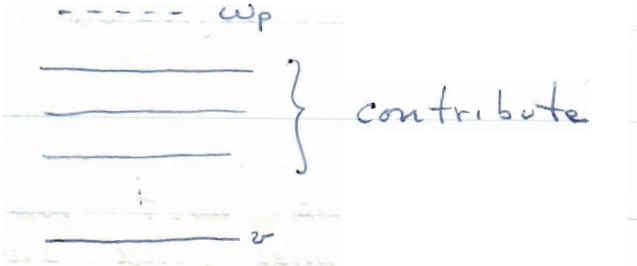
Finally:

(18) $$\epsilon_c \omega^2 = \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{vn'}{}' \int d^3k \underbrace{f^{\mu}_{n'v}}_{1 - \frac{m}{\pi^2}\frac{\partial^2 E}{\partial k^2_{\mu}}} + \sum_{n'v}{}' \int d^3k \; f^{\mu}_{n'v} \frac{\omega^2_{n'v}}{\omega^2 - \omega^2_{n'v}}$$

$$\underbrace{\qquad}_{4\pi^3 n_v} \qquad 0 \text{ (band full)}$$

(19) $$\omega^2 = \underbrace{\frac{4\pi n_v e^2}{\epsilon_c m}}_{\text{free electron modified by } \epsilon_c} + \underbrace{\sum_{n'v}{}' \frac{1}{\epsilon_c} \int d^3k \; f^{\mu}_{n'v} \frac{\omega^2_{n'v}}{\omega^2 - \omega^2_{n'v}}}_{\text{interband correction. small if } \omega >> |\omega_{n'v}| \text{ for all bands contributing to f-sum rule.}}$$

That is:



LECTURE XV 1-13-61

Recapitulation:

$$(1)\quad \epsilon_1(\omega, q\to 0) = 1 - \left(\frac{e}{\pi\hbar\omega}\right)^2 \sum_n \int d^3k\, f_{nk}\, \frac{\partial^2 E_{nk}}{\partial k_\mu^2} + \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{nn'}{}' P \int d^3k\, f_{nk}\, \frac{f^\mu_{n'n}}{\omega^2_{n'n} - \omega^2}$$

For free electron metals:

$$\frac{1}{\hbar^2}\,\frac{\partial^2 E_{nk}}{\partial k_\mu^2} = m^*_n$$

We get:

$$(2)\quad \omega_p^2 = \frac{4\pi n e^2}{\epsilon\, m^*_n} + \frac{1}{m}\left(\frac{e}{\pi}\right)^2 \sum_{nn'}{}' P \int d^3k\, f^\mu_{n'n}\, f_{nk} \cdot \frac{\omega^2}{\omega^2_{n'n} - \omega^2}$$

We see that we have interband perturbation. For Ag, free $\hbar\omega_p \sim 9$ ev, actually 3.6 ev. The only real free electron gas is in semiconductors. In this case, the plasma energy is much less than the band gap and we can take the valence band and below as forming the core.

In semiconductors, therefore, interband terms can be neglected.

We must now treat both holes and electrons.

From equation (18) of the last lecture:

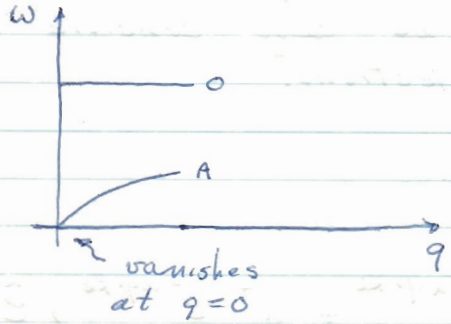
$$(3)\quad \epsilon\omega^2 \propto \int d^3k\, f_{kn}\, \frac{\partial^2 E_{kn}}{\partial k_\mu^2} + \int d^3k\, f_{kp}\, \frac{\partial^2 E_{kp}}{\partial k_\mu^2}$$

Now the hole distribution function is $f_{kp} = 1 - f_{kn}$ and also $\frac{1}{m_p} = -\frac{1}{\hbar^2}\frac{\partial^2 E_{kn}}{\partial k_\mu^2}$.

Thus $\epsilon\omega^2 \to 4\pi n e^2\left(\frac{1}{m_n} + \frac{1}{m_p}\right)$ and

$$(3)\quad \boxed{\omega_p^2 = \omega_{pn}^2 + \omega_{pp}^2}$$

Because there are two different particles, there are two normal modes, optical and acoustical. Acoustical $\rightrightarrows$; optical $\rightleftharpoons$. It takes more energy to excite the optical mode as charge is displaced. What we have found is the optical mode. This effect is analogous to lattice vibrations.



To get the acoustical mode, make assumption that
$m_n \ll m_p$ and
$E_{k+q,n} - E_{kn} \gg \hbar\omega_p$
$E_{k+q,p} - E_{kp} \ll \hbar\omega_p$

It can be shown by Fermi Statistics:

$$(4)\quad \omega_p^2 = \frac{1}{3}\frac{m_n}{m_p}\, v_n^2(E_F)\, q^2$$

Hence acoustical and optical plasmons possible in intrinsic semiconductors.

Now consider an alkalli metal. Forget lattice periodicity, consider as gas of ions and electrons. We get similar results to above which must be sound wave velocity. Error of only 20%. This is entirely different approach.

Here we assume only long-range forces acting where lattice vibration theory uses tight binding.

The Theory of plasma oscillations is as correct as random phase methods to the first degree.

ELECTRON - PHONON INTERACTION

Formerly we considered stationary lattice in electron theory. We now include lattice vibrations. We use the Born - Oppenheimer Approximation (Adiabatic). That is, we write the total system wave function as a product of lattice and electron wave functions. See Ziman, PP 5.1. We write:

(5) $\chi(R)\,\psi(r_e, R)$

Hence we can get back to one-electron picture in metals. Recall lattice displacement in terms of lattice creation and annihilation operators. Phonons are a good concept because we can conciere of a scattering interaction with electrons.

(6) $$u_e = \sum_{qj}' \sqrt{\frac{\hbar}{2MN\omega_{qj}}} \left(a_{qj} e^{iq\cdot R_e} + a_{qj}^{+} e^{-iq\cdot R_e}\right) \underbrace{\hat{e}_{qj}}_{\text{assume real}}$$

$N = G^3$

Assume: (1) Neglect basis
(2) $\hat{e}_{qj}$ real

The potential the electron experiences is

(7) $V(r; R_1 + u_1, \ldots, R_e + u_e, \ldots)$

The scattering is conveyed by the lattice displacement changing the potential.

This change can be expressed as:

$$(8)\quad \delta U = V(r; R_1 + u_1, \ldots, R_e + u_e, \ldots) - U(r; \ldots, R_e + u_{e'}, \ldots)$$

$$= \sum_e u_e \cdot \nabla_e U$$

using Taylor's Theorem and keeping only linear terms. This assumes low coupling and interaction with only one phonon at a time. Higher order terms would mean simultaneous creation and annihilation of phonons. We now calculate the matrix element of the perturbing term δU, for the case of the electronic transition $k' \to k$ and the phonon creation by collision $n_{qj} - 1 \to n_{qj}$.

Recall: $\langle n_{qj} \mid a_{qj}^{+} \mid n_{qj} - 1 \rangle = \sqrt{n_{qj}}$

Then:

$$(9)\quad M(k, k') = \langle n_{qj} \mid \int b_n^{*}(k, r)\, \delta U\, b_n(k', r)\, d^3 r \mid n_{qj} - 1 \rangle$$

$$= \langle n_{qj} \mid \sqrt{\frac{\hbar}{2MN\omega_{qj}}}\, a_{qj}^{+} \sum_e e^{-iq \cdot R_e} \int b_n^{*}(k, r)\, \hat{e}_{qj} \cdot \nabla_{R_e} U\, b_n(k', r)\, d^3 r \mid n_{qj} - 1 \rangle$$

since $\langle n_{qj} \mid a_{qj} \mid n_{qj} - 1 \rangle = 0$. We consider only intraband transitions. We may write:

$$b_n(k, r) = e^{ik \cdot R_e}\, b_n(k, r - R_e)$$

which allows a shift of the origin to r', ie, $r' = r - R_e$, $U(r') = U(r)$ by periodicity. Now consider:

$$(10)\quad \sum_e e^{-iq \cdot R_e} \int d^3 r\; b_n^{*}(k, r)\, \nabla_{R_e} U(r)\, b_n(k', r)$$

$$= \sum_e e^{-iq \cdot R_e}\, e^{i(k' - k) \cdot R_e} \int d^3 r'\; b_n^{*}(k, r')\, \nabla_{R_0} U(r')\, b_n(k', r')$$

Hence the integral is now closed and thus independent of R_e since it is in the variable of integration. We can then directly perform the integration or summation.

Recall:

$$(11) \qquad \sum_{\ell} e^{i(k'-k-q)\cdot R_\ell} = \delta_{K,\, k'-k-q}\, N$$

which expresses the conservation of momentum. Now define:

$$(12) \qquad I_{qj}(k,k') \equiv \sqrt{\frac{\hbar}{2MN\omega_{qj}}} \Big/ \sqrt{\frac{\hbar}{2MN\omega_{qj}}} \cdot \int b_n^*(k,r')\, \hat{e}_{qj} \cdot \nabla_{R_0} U\, b_n(k',r')\, d^3r'$$

or:

$$I_{qj}(k,k') \equiv \int b_n^*(k,r')\, \hat{e}_{qj} \cdot \nabla_{R_0} U\, b_n(k',r')\, d^3r'$$

Then:

$$(13) \qquad \boxed{M(k,k') = \sqrt{\frac{\hbar}{2MN\omega_{qj}}}\, I_{qj}(k,k')\, \delta_{k'-k-q,\,K}}$$

Conservation of momentum demands:

$$(14) \qquad \boxed{k' = k + q + K}$$

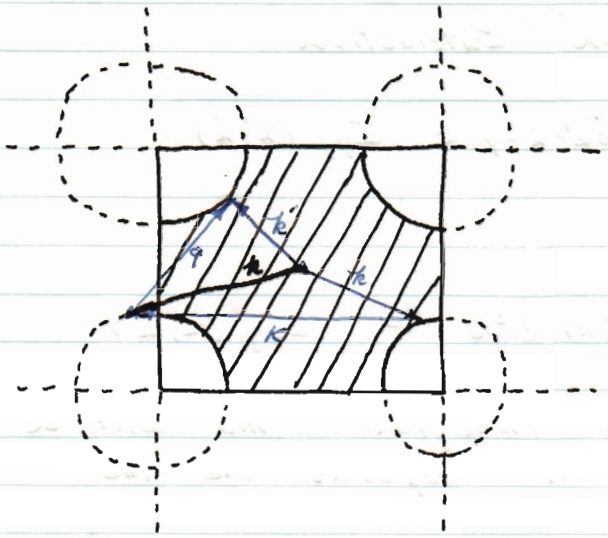
We can divide electron-phonon scattering into two processes:

(1) $K = 0$; Normal (N)

(2) $K \neq 0$; Umklapp (U)

These depend on the zone scheme used to represent the lattice.

To see this, suppose:



Repeated
Reduced

In the repeated zone scheme, we need not consider Umklapp processes. We can now write from time-dependent perturbation theory:

(15) $E_n(k') = E_n(k) + \hbar\omega_{qj}$

which comes from $\psi \sim e^{-iq\cdot Re^{i\omega_{qj}t}}$.
We have completed phonon emission process.
For phonon absorption, $n_{qj} \to n_{qj} - 1$, that is:

emission: $n_{qj} \to n_{qj} + 1$: $\sqrt{n_{qj}+1}$
absorption: $n_{qj} \to n_{qj} - 1$: $\sqrt{n_{qj}}$

LECTURE XVI 1-16-61

Recapitulation: Phonon - Electron Interaction

(1) $$M(k,k') = \sqrt{\frac{\hbar n_{q_1}}{2MN\omega_{q_1}}}\ \delta_{k'-k-q,K}\ I_{q_1}(k';k)$$

(2) $$\int b_n^*(k,r)\,\hat{e}_{q_1}\cdot\nabla_{R_0}U(r)\,b_n(k',r)\,d^3r = I_{q_1}(k,k')$$

We must now estimate this integral. This will be necessarily approximate as it depends on the model for $U(r)$.

Rigid Ion Approximation:

Under lattice displacement, ion moves rigidly. We take for the potential:

(3) $$U(r) = \sum_l U_a(r-R_l)$$

To get feeling, let's look at δU:

(4) $$\delta U = \sum_l \left[U_a(r-R_l-u_l) - U_a(r-R_l)\right]$$

That is, the whole ion moves together.

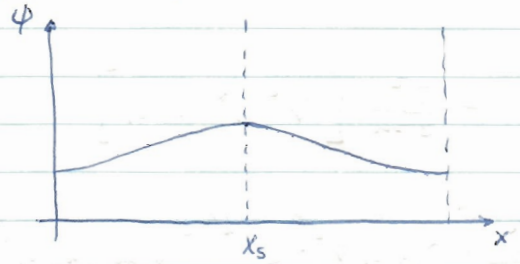
Now:

(5) $$\nabla_{R_0}U(r) = -\nabla_r U(r)$$

Substitute in $I_{q_1}(kk')$. We now introduce the Wigner-Seitz Method:

(1) Divide lattice into polyhedra (analogous to BZ)
(2) Solve in one-electron fashion saying that each polyhedra is electrically neutral.
(3) Assume electron removed, then solve 6 equations for motion of electron in field of ion.
(4) Impose continuity of ψ at boundary of WS cell.
(5) Replace WS cell by sphere of same volume to simplify calculations.

We take solutions at the middle of the BZ, $b(0,r) = b(0,r+R)$ and use the $k\cdot p$ perturbation method. Thus the solution is the same from cell to cell and is continuous. Also, we must have the normal derivative of $b(0,r)$ vanishing at the surface of the WS sphere. That is:



Another assumption implicit in the WS method is:

$$(6)\qquad U(r) = \begin{cases} U_a(r) & r < r_s \\ 0 & r > r_s \end{cases}$$

The potential inside the ion exists only in its cell, outside it is completely screened. Now write the Schroedinger equation in the cell:

$$(7)\qquad \left[-\frac{\hbar^2}{2m}\nabla^2 + U_a(r)\right] b(k',r) = E(k')\, b(k',r)$$

Differentiate and multiply by $b^*(k,r)$. We work in just one band.

$$(8)\qquad b^*(k,r)\,\nabla U_a\, b(k',r) = b^*(k,r)\,\frac{\hbar^2}{2m}\nabla^3 b(k',r)$$

$$+ E(k')\, b^*(k,r)\,\nabla b(k',r) - b^*(k,r)\, U_a\, \nabla b(k',r)$$

From the definition of the Bloch function:

$$(9)\qquad \nabla b(k',r) = i k'\, b(k',r) + e^{i k'\cdot r}\,\nabla u(k',r)$$

Hence:

$$(10)\qquad b^*(k,r)\left\{\nabla U_a\right\} b(k',r) = i k'\, b^*(k,r)\left[\frac{\hbar^2}{2m}\nabla^2 + E(k') - U_a(r)\right] b(k',r)$$

$$+ b^*(k,r)\,\frac{\hbar^2}{2m}\nabla^2\left\{e^{i k'\cdot r}\,\nabla u(k',r)\right\} + b^*(k,r)\left[E(k') - U_a\right] e^{i k'\cdot r}\,\nabla u(k',r)$$

The first term on the RHS vanishes from eq. (7). We now make use of the fact that electron in a metal near the Fermi surface has a much greater energy than the phonon energy $\hbar\omega_q$. Hence we can write:

(11) $E(k') \simeq E(k)$

and:

$$b^*(k,r)\left[E(k') - U_a\right] \simeq -\frac{\hbar^2}{2m}\left[\nabla^2 b^*(k,r)\right]$$

(12) $$b^*(k,r)\left\{\nabla U_a\right\} b(k',r) = \frac{\hbar^2}{2m}\left[b^*(k,r)\,\nabla^2\left\{e^{ik'\cdot r}\,\nabla u(k',r)\right\}\right.$$

$$\left. - \left\{\nabla^2 b^*(k,r)\right\} e^{ik'\cdot r}\,\nabla u(k',r)\right]$$

Now when we integrate over the WS cell we can use Green's Theorem, viz:

(13) $$\int_\Omega \left[\varphi\nabla^2\psi - \psi\nabla^2\varphi\right] d\Omega = \int_S \left[\varphi\nabla\psi - \psi\nabla\varphi\right] dS$$

We now invoke the heart of the WS approximation. Assume $u(k',r) = u(0,r)$ or free-electron like, shows the crudity of the method. Also we must have $\nabla u(0,r)\cdot dS' = 0$. Then all we have left, save 1 term, will vanish when Green's Theorem is used. The result is:

(14) $$\int_0 b^*(k,r)\,\nabla U_a\, b(k',r)\, d^3r$$

$$= \frac{\hbar^2}{2m}\int_0 b^*(k,r)\, e^{ik'\cdot r}\,\underbrace{\nabla^2 b(0,r)}_{\text{Use Schroedinger Equation}}\, dS'$$

$$= \int b^*(k,r_s)\, e^{ik'\cdot r_s}\left[U(r_s) - E(0)\right] b(0,r_s)\, dS'$$

The Schroedinger equation we have used is:

(15) $$-\frac{\hbar^2}{2m}\nabla^2 b(0,r) + U(r)\, b(0,r) = E(0)\, b(0,r)$$

We then say $e^{ik'\cdot r}\, b(0,r) = e^{ik'\cdot r}\, u(0,r) \equiv b(k',r)$

What we finally get, using the volume integral again, is:

$$(16)\qquad \int_0 b^*(k,r)\, \nabla U_a\, b(k',r)\, d^3r = \left[U_a(r_s) - E(0)\right] \int_0 \nabla\left[b^*(k,r)\, b(k',r)\right] d^3r$$

We now make the further approximation, asserting the thought of a free electron in a metal.

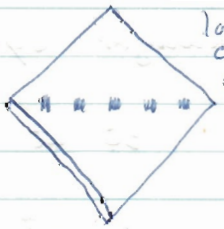
$$(17)\qquad \nabla\, b(k',r) = ik'\, b(k',r)$$

Finally:

$$(18)\qquad \boxed{I_{qj}(k,k') = -iN\left[U(r_s) - E(0)\right] \hat{e}_{qj}\cdot(k'-k) \int_0 b^*(k,r)\, b(k',r)\, d^3r}$$

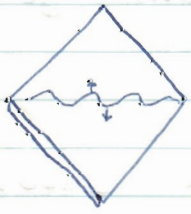
(1) For Normal Processes: $k' \to k+q$

In the transverse modes: $\hat{e}_{qj}\cdot q = 0$. Thus only longitudinal phonons are coupled to electrons by normal processes. To see this, suppose charged rubber sheet, uniform plus background.



longitudinal compressional waves

This would create a sinusoidal field which would be seen by passing electrons.

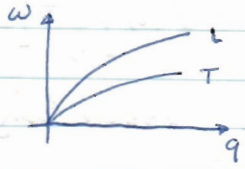


transverse waves

Only dipoles created and in the first order no change in the electric field.

(2) Umklapp Processes:

Transverse modes can be coupled: $\hat{e}_{qj} \cdot (q+k)$ does not vanish because k can have component along $\hat{e}_{qj}$. At low temperatures, transverse modes must be considered.



Now we evaluate $I_{qj}(k'k)$. We first estimate $\mathcal{U}(r_s) - E(0)$. Consider the effect of a longitudinal wave on the WS sphere. The sphere will be dilated or compressed. Assume dilation of the form:

(19) $\Delta = \frac{\delta V}{V}$, then $r_s \to r_s\left(1 + \frac{1}{3}\Delta\right) = r_s'$

$b(0,r) \to b'(0,r)$: although this satisfies the Schroedinger equation, now the boundary conditions are different as they apply at r_s'. This means:

$$E(0) \to E(0) + \delta E = E'(0)$$

Then write the two different Schroedinger equations:

(20) $\left[-\frac{\hbar^2}{2m}\nabla^2 + \mathcal{U}(r)\right] b(0,r) = E(0)\, b(0,r)$ BC at r_s

$\left[-\frac{\hbar^2}{2m}\nabla^2 + \mathcal{U}(r)\right] b'(0,r) = E'(0)\, b'(0,r)$ BC at r_s'

Multiply by $b'(0,r)$, $b(0,r)$ respectively and get:

(21) $-\frac{\hbar^2}{2m}\left[b\nabla^2 b' - b'\nabla^2 b\right] = \delta E\, b'b$

Integrate over undistorted cell and assume $b'b \sim b^2$ or $b' \approx b$, $\int b'b = 1$. Then:

(22) $\delta E = -\frac{\hbar^2}{2m}\int_{S'} (b\nabla b' - \underbrace{b'\nabla b}) \cdot dS'$

0, because $\nabla b \cdot dS' = 0$

We now say that on the surface of the distorted WS sphere, $b' = b'(0, r_s')$. Now expand about r_s:

(23) $$b'(0, r_s') = b'(0, r_s[1+\tfrac{1}{3}\Delta]) \simeq b'(0, r_s) + \tfrac{1}{3}\Delta r_s \nabla b'(0, r_s)$$

Now $$\nabla b'(0, r_s') = 0 = \nabla b'(0, r_s) + \tfrac{1}{3}\Delta r_s \nabla^2 b'(0, r_s)$$

Making $b'(0, r_s) \simeq b(0, r_s)$, we have:

(24) $$\delta E = \tfrac{1}{3} r_s \Delta \int_S b \frac{\hbar^2}{2m} \nabla^2 b \, dS$$

Using the Schroedinger equation:

(25) $$\delta E = \tfrac{1}{3} r_s \Delta \left[\mathcal{U}(r_s) - E(0) \right] \int b^2 \, dS$$

Now, let $b \sim \frac{1}{\sqrt{v_a}}$, then $\int b^2 dS = \frac{1}{v_a} 4\pi r_s^2$.

Now, $\tfrac{1}{3} r_s 4\pi r_s^2 \cdot \frac{1}{v_a} = 1$ since $v_a = \frac{4}{3}\pi r_s^3$

Finally:

(26) $$\delta E = \Delta \left[\mathcal{U}(r_s) - E(0) \right] = E_1 \Delta$$

E_1 is the deformation potential constant or the change of energy at the band edge per unit dilation. We now dilate the metallic crystal. The change in the Fermi level is refected in E_1. We write $\bar{E}(\Delta)$ as the average energy of a free electron gas in a dilated crystal.

(27) $$\bar{E}(\Delta) = E(0) + E_1 \Delta + \frac{1}{N} \int_0^{E_F(\Delta)} E \rho(E) \, dE$$

$$= E(0) + E_1 \Delta + \tfrac{3}{5} E_F(\Delta)$$

Now recall $E_F \sim n^{2/3} \sim \left(\frac{N}{\Omega}\right)^{2/3} \sim \left(\frac{N}{\Omega_s}\right)^{2/3} \frac{1}{(1+\Delta)^{2/3}}$

or: $E_F(\Delta) = \frac{E_F(0)}{(1+\Delta)^{2/3}}$. Now $\frac{\partial \bar{E}(\Delta)}{\partial \Delta} = 0$ at $\Delta = 0$ (equilibrium)

Hence: $E_1 - \frac{3}{5}\frac{2}{3} E_F(0) = 0$. Then:

(28) $E_1 = \frac{2}{5} E_F \sim 1 ev$ for alkali metals.

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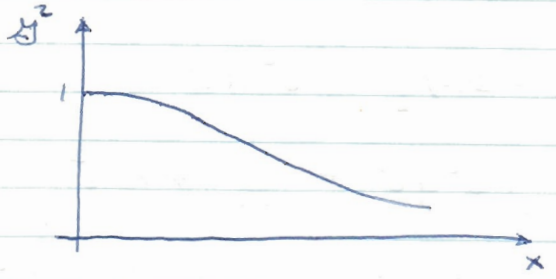
Recapitulation on Rigid Ion Model:

(1) $I_{qq'}(k,k') = -\imath\,(k'-k)\,\hat{e}_{qq'}\,E_1\,N\int_0 b^*(k,r)\,b(k',r)\,d^3r$

If we take free electron type wave functions, the integral reduces to a Green's function $\mathcal{G}(|k-k'|rs)$ where:

(2) $\mathcal{G}(x) = \frac{3}{x^3}(\sin x - x\cos x)$



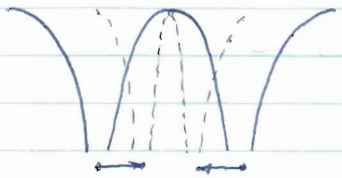
Deformable Ion Model

We take for the potential:

(3) $\delta U = V\{r-u(r)\} - V(r) = -u(r)\,\nabla V$

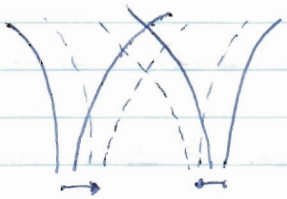
$u(r)$ is different from before because it is a function of a continuous variable.

Deformable Ion



No change in midpoint.

Rigid Ion



Midpoint does change

$u(r)$ is assumed of the form:

(4) $u(r) \sim \sum_{q<q_{Debye}}{}' a_q e^{\imath q\cdot r}$

This model is due to Bardeen (1937).

Consider screening effects of electrons on lattice vibrations. Screened $V(w,q) = \frac{V_k}{\epsilon(0,q)}$ if $\hbar\omega \ll E_F$

$$I \sim \hat{e}_{qj} \cdot \int b^*(k,r)\, \nabla U_k\, b(k',r)\, d^3r$$

$$U = \begin{cases} U_a & r < r_s \\ -\frac{e^2}{r} & r > r_s \end{cases}$$

Assumes for crystal potential:

$$V(r) = \underbrace{U(r)}_{\text{ionic potential}} + \underbrace{\frac{3e^2}{2r_s} - \frac{e^2 r^2}{2r_s^3}}_{\text{uniform negative charge density in ws cell.}}$$

Gets for V_k:

$$V_k \propto \text{unscreened interaction} = -i(k'-k)\cdot\hat{e}_{qj}\left[V(r_s) - E(0) + \frac{4\pi N e^2}{|k'-k|^2}\right] \cdot \mathcal{F}(|k'-k| r_s)$$

Bardeen - Pines Model (PR, 1955)

We use the creation-annihilation operators defined by:

(5) C_{ks} (creation) ; $C_{ks}^\dagger$ (annihilation)

These operators anticommute:

(6) $$[C_{ks}^\dagger, C_{k's'}]_+ = \delta_{kk'}\delta_{ss'}$$

The Hamiltonian is formulated as: (renormalized)

(7) $$H = \sum_{ks} E_k C_{ks}^\dagger C_{ks} + \frac{1}{2}\sum_q \left[P_q^\dagger P_q + \omega_q^2 U_q^\dagger U_q\right] + \sum_q V_q U_q \rho_{-q} + \frac{1}{2}\sum_q v_q \rho_q \rho_{-q} + \cdots$$

(7) $$H = \sum'_{ks} E_k C^+_{ks} C_{ks} + \frac{1}{2}\sum'_q \left[P_q^+ P_q + \omega_q^2 U_q^+ U_q \right]$$
$$+ \sum'_q V_q U_q \rho_{-q} + \frac{1}{2}\sum'_q V_q \rho_q \rho_{-q}$$
$$+ \sum'_q (V_q^2 - V_q) U_q \rho_{-q} + \frac{1}{2}\sum'_q (\Omega_q^2 - \omega_q^2) U_q^+ U_q$$

where $\rho_q = \sum'_{ks} C^+_{k-q,s} C_{ks}$

Make the canonical transformation:

(8) $$H' = e^{-iS/\hbar} H e^{iS/\hbar}$$

and use to eliminate terms linear in U_q, P_q.
Choose:

(9) $$S = i \sum'_{k,q} C_k^+ C_{k-q} \left[f(k,q) U_q - i g(k,q) P_{-q} \right]$$

Choose f and g such that terms in U_q, P_{-q} in first two lines in H disappear. Then choose V_q, ω_q such that terms in U_q, $U_q^+ U_q$ in second term disappear. The results are:

1) $$V(\omega, q) = \frac{V^2(\omega,q)}{\epsilon(\omega,q)}$$

2) $$\omega^2 \propto q^2$$

3) $$H' = \sum'_{kk';ss';q} 2\hbar\omega_q M_q^2 \frac{1}{(E_k - E_{k+q})^2 - \hbar^2\omega_q^2} C^+(k'-q,s')$$
$$\cdot C(k',s') C^+(k+q,s) C(k,s)$$

where $M_q^2 = V_q^2 \frac{\hbar}{2\omega_q}$. This changes electron-phonon into electron-electron.
If $\left(-\frac{2|M_q|^2}{\hbar\omega_q} + \frac{4\pi e^2}{q^2}\right) < 0$, this is the criteria for superconductivity, or beginning of Bardeen, Cooper, Scheffer theory.
Topics not covered: Transport Theory, Band Structure.
END OF COURSE

Notes on AP 295 Lecture Notes

Lattice Vibrations

2 Bravais lattice : 1 atom / unit cell
2 or more = basis lattice, eg, fcc, bcc, etc.

3 For lattice vibration analysis, we assume:
1) equilibrium configuration
2) stability
3) small displacement

$$\frac{\langle u_\ell \rangle^2}{a} \ll 1 \quad ; \quad \vec{r}_\ell = \vec{R}_\ell + \vec{u}_\ell$$

$\vec{R}_\ell \longrightarrow \vec{u}_\ell$ $\vec{u}_\ell$ is displacement from equilibrium vector.

Hamiltonian:

$$H = \frac{1}{2} M \sum_\ell |\dot{\vec{r}}_\ell|^2 + V(\cdots, r_\ell, \cdots)$$

Under above assumptions:

$$H = \frac{1}{2} M \sum_\ell |\dot{\vec{u}}_\ell|^2 + V(\cdots, \vec{R}_\ell + \vec{u}_\ell, \cdots)$$

$$V = V_0 + \sum_{\ell\alpha} \left(\frac{\partial V}{\partial u_{\ell\alpha}}\right)_{u_{\ell\alpha}=0} u_{\ell\alpha} + \frac{1}{2} \sum_{\ell\alpha\,\ell'\alpha'} \left(\frac{\partial^2 V}{\partial u_{\ell\alpha}\, \partial u_{\ell'\alpha'}}\right) u_{\ell\alpha} u_{\ell'\alpha'} + \cdots$$

where α is cartesian component
and $\sum_{\ell\alpha}$ means sum over all ℓ and the cartesian components of each $\vec{R}_\ell$.

5 Higher order terms are neglected but actually give rise to:
1) thermal expansion
2) specific heat
3) thermal conductivity

$\left(\frac{\partial V}{\partial u_{\ell\alpha}}\right)_0 = 0$ since V has extremum at $u_\ell = 0$

5 $\frac{\partial^2 V}{\partial u_{l\alpha} \partial u_{l'\alpha'}} \equiv C_{\alpha\alpha'}(l, l')$

and have the dimensions of a force constant term like in harmonic oscillation

Symmetry of Harmonic Constants:

1) $C_{\alpha\alpha'}(l, l') \equiv C_{\alpha\alpha'}(l - l')$, comes principle all atoms equivalent in surroundings.
2) $C_{\alpha\alpha'}(l - l') = C_{\alpha'\alpha}(l' - l)$ because of exactness of mixed partials.
3) Inversion symmetry: $C_{\alpha\alpha'}(l - l') = C_{\alpha\alpha'}(l' - l)$

Since the lattice is stable, this implies that the sum of the force constants over all atoms vanishes:

4) $\sum_{l'}' C_{\alpha\alpha'}(l - l') = 0$

$\therefore H = \frac{1}{2} M \sum_{l} |\dot{u}_{l\alpha}|^2 + \frac{1}{2} \sum_{l\alpha l'\alpha'}' C_{\alpha\alpha'}(l - l') u_{l\alpha} u_{l'\alpha'}$

6 Use: $\dot{p} = -\frac{\partial H}{\partial q}$

$M \ddot{u}_{l\alpha} = -\sum_{l'\alpha'}' C_{\alpha\alpha'}(l - l') u_{l'\alpha'}$

lumping the '/2 into $C_{\alpha\alpha'}(l - l')$

14 Definition: $\hat{C}_{\alpha\alpha'}(q) \equiv \sum_{l}' C_{\alpha\alpha'}(l) e^{-i\vec{q} \cdot R_l}$

or defining a Fourier transform.

sequence:

$$M u_{l\alpha} = \sum_{l'\alpha'}' C_{\alpha\alpha'}(l - l') u_{l'\alpha'}$$

Postulate $u_{l\alpha} = e_\alpha(q) e^{i(\vec{q} \cdot \vec{R}_l - \omega\{q, t\} t)}$

$$-M\omega^2 e_\alpha(q) = \sum_{l'\alpha'}' C_{\alpha\alpha'}(l') e^{-i\vec{q} \cdot \vec{R}_{l'}} e_{\alpha'}(q)$$

or $-M\omega^2 e_\alpha(q) = \sum_{\alpha'}' \hat{C}_{\alpha\alpha'}(q) e_{\alpha'}(q)$

14 Properties of $\tilde{C}_{\alpha\alpha'}(q)$:

a) $\tilde{C}^*_{\alpha\alpha'}(q) = \tilde{C}_{\alpha\alpha'}(-q)$

b) Hermiticity:

$\tilde{C}_{\alpha\alpha'}(q) = \tilde{C}^*_{\alpha'\alpha}(q)$ because:

$$\tilde{C}_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{-i\vec{q}\cdot\vec{R_\ell}}$$

$$= \sum_{\ell} C_{\alpha'\alpha}(-\ell)\, e^{-i\vec{q}\cdot\vec{R_\ell}} = \sum_{\ell} C_{\alpha'\alpha}(\ell)\, e^{i\vec{q}\cdot\vec{R_\ell}}$$

$$= \tilde{C}^*_{\alpha'\alpha}(q)$$

With inversion symmetry: $\tilde{C}_{\alpha\alpha'}(q) = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{-i\vec{q}\cdot\vec{R_\ell}}$

$$= \sum_{\ell} C_{\alpha\alpha'}(-\ell)\, e^{-i\vec{q}\cdot\vec{R_\ell}} = \sum_{\ell} C_{\alpha\alpha'}(\ell)\, e^{i\vec{q}\cdot\vec{R_\ell}}$$

$$= \tilde{C}_{\alpha\alpha'}(-q)$$

Hence, <u>under inversion symmetry</u>:

$$\tilde{C}_{\alpha\alpha'}(q) = \frac{1}{2}\cdot 2 \sum_{\ell} C_{\alpha\alpha'}(\ell) \cos \vec{q}\cdot\vec{R_\ell}$$

$$= -2 \sum_{\ell} C_{\alpha\alpha'}(\ell) \sin^2 \tfrac{1}{2}\vec{q}\cdot\vec{R_\ell}$$

Get secular equation:

$$\frac{1}{M} \sum_{\alpha'} \tilde{C}_{\alpha\alpha'}(q)\, e_{\alpha'} - \omega^2 e_\alpha = 0$$

$C_{\alpha\alpha'}(q)$ is like quantum mechanical matrix elements.

16 Consequences of symmetry:

a) Since $\tilde{C}_{\alpha\alpha'}(q) = \tilde{C}^*_{\alpha'\alpha}(q)$, ω^2 must be real because diagonal is real.

b) $\omega^2 > 0$

c) Under inversion symmetry:

$\tilde{C}_{\alpha\alpha'}(q) = \tilde{C}_{\alpha'\alpha}(q)$,

$\therefore \omega^2(q) = \omega^2(-q)$

d) $e_\alpha(q) = e^*_\alpha(-q)$

because $\tilde{C}^*_{\alpha\alpha'}(q) = \tilde{C}_{\alpha\alpha'}(-q)$

20 Theorem: $\sum_{\ell} e^{i(\vec{q}-\vec{q}')\cdot\vec{R}_\ell} = G^3 \delta_{q', q+K}$

Shift origin: $\sum_{\ell} e^{i(\vec{q}-\vec{q}')\cdot R_\ell} = \sum_{\ell} e^{i(\vec{q}-\vec{q}')\cdot(\vec{R}_\ell+\vec{R}_{\ell'})}$

$= \left\{ \sum_{\ell} e^{i(q-\vec{q}')\cdot\vec{R}_\ell} \right\} e^{i(\vec{q}'-\vec{q})\cdot\vec{R}_{\ell'}}$

$\sum_{\ell}$ causes each term to cancel only for inversion symmetry. $=$ similar to Dirac delta function.

because of BVK conditions. $= 0$ unless $\vec{q}-\vec{q}' = \vec{K}$. Now $\sum_{\ell} e^{i\vec{K}\cdot\vec{R}_\ell} = G^3$

$\therefore \sum_{\ell} e^{i(\vec{q}-\vec{q}')\cdot\vec{R}_\ell} = G^3 \delta_{q', q+K}$

Orthogonality of Eigenvectors:

We postulate the orthogonality of the eigenfunctions, viz:

$$\sum_{\ell} M_\ell M_\ell^* = \sum_{\ell} e_\alpha(\vec{q}) e^{i\vec{q}\cdot\vec{R}_\ell} e^*(\vec{q}') e^{-i\vec{q}'\cdot\vec{R}_\ell}$$

$$= \eta^2 \delta_{\gamma,\gamma'} \delta_{q,q'} = e(\gamma,\vec{q})\cdot e^*(\gamma',\vec{q}') \sum_{\ell} e^{i(q-q')\cdot\vec{R}_\ell}$$

Choose $\eta^2 = G^3$, $\therefore e(\gamma,\vec{q})\cdot e^*(\gamma',\vec{q}') = \delta_{\gamma,\gamma'}$

This shows that the polarization vectors are mutually orthogonal in monatomic lattice. We have assumed non-degeneracy. Note that this holds true for only the monatomic cell.

30 $$\sum_{q_\alpha=0}^{G-1} e^{i2\pi \frac{l_\alpha q_\alpha}{G}} = \sum_{q_\alpha=0}^{\infty} e^{i2\pi \frac{l_\alpha q_\alpha}{G}} - \sum_{q_\alpha=G}^{\infty} e^{i2\pi \frac{l_\alpha q_\alpha}{G}}$$

$$= \frac{1}{1-e^{i2\pi \frac{l_\alpha}{G}}} \left\{ 1 - \left(1 - e^{i2\pi \frac{l_\alpha}{G}}\right) \sum_{q_\alpha=G}^{\infty} e^{i2\pi \frac{l_\alpha q_\alpha}{G}} \right\}$$

$$= \frac{\sum_{q_\alpha=G}^{\infty} e^{i2\pi \frac{l_\alpha}{G}(q_\alpha+1)}}{1 - e^{i2\pi \frac{l_\alpha}{G}}}$$

$$\sum_{q_\alpha=G}^{\infty} e^{i2\pi \frac{l_\alpha}{G}(q_\alpha+1)} = \sum_{m_\alpha=0}^{\infty} e^{i2\pi \frac{l_\alpha}{G}(m_\alpha+1+G)}$$

30 $$\sum_{q_x=G}^{\infty} \left\{ e^{i2\pi \frac{l_x q_x}{G}} - e^{i2\pi \frac{l_x}{G}(q_x+1)} \right\}$$

$$= \sum_{m_x=0}^{\infty} \left\{ e^{i2\pi \frac{l_x}{G}(m_x+G)} - e^{i2\pi \frac{l_x}{G}(m_x+G+1)} \right\}$$

$$= e^{i2\pi l_x} \sum_{m_x=0}^{\infty} \left\{ e^{i2\pi \frac{l_x m_x}{G}} - e^{i2\pi \frac{l_x}{G}(m_x+1)} \right\} = e^{i2\pi l_x}$$

32 Properties of C or $C_{\alpha\alpha'}(q, bb')$:

$$C_{\alpha\alpha'}(q, bb') \equiv \sum_h C_{\alpha\alpha'}(h, bb') e^{-i\vec{q}\cdot\vec{R}_h}$$

a) Hermitian: $C_{\alpha\alpha'}(q, bb') = C^*_{\alpha'\alpha}(q, bb')$

b) Time Reversal: $C^*_{\alpha'\alpha}(-q, bb') = C_{\alpha'\alpha}(q, bb')$

c) $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q, bb')$

Hermitian because $C_{\alpha\alpha'}(h, bb') = C_{\alpha'\alpha}(h, bb')$
Time reversal obvious. c because
$C_{\alpha\alpha'}(q, bb') = C^*_{\alpha'\alpha}(q, bb') = C_{\alpha'\alpha}(-q, bb')$

33 Commutation:

Given: $u_{q,b} \equiv \frac{1}{G^{3/2}} \sum_q u_{q,b} e^{iq\cdot R_l}$

$$p_{l,b} \equiv \frac{1}{G^{3/2}} \sum_q p_{q,b} e^{-iq\cdot R_l}$$

$$\times \sum_l e^{-iq'\cdot R_l}, \quad \sum_l e^{i(q-q')\cdot R_l} = G^3 \delta_{qq'}$$

$$\therefore u_{qb} = \frac{1}{G^{3/2}} \sum_l u_{lb} e^{-iq\cdot R_l}$$

$$p_{qb} = \frac{1}{G^{3/2}} \sum_l p_{lb} e^{iq\cdot R_l}$$

$$[u_{q'b'}, p_{qb}] = \frac{1}{G^3} \sum_{ll'} e^{iq\cdot R_l - iq'\cdot R_{l'}} [u_{l'b'}, p_{lb}]$$

$$= \frac{1}{G^3} i\hbar \sum_{ll'} e^{iq\cdot R_l - iq'\cdot R_{l'}} \delta_{ll'} \delta_{bb'}$$

$$= i\hbar \cdot \delta_{qq'} \delta_{bb'}$$

33 Heisenberg Equations of motion:

$$i\hbar \frac{dF}{dt} = [F, H]$$

$$i\hbar \dot{u}_{qb} = \left[u_{qb}, \frac{1}{2} \sum_{q'b'} \frac{1}{M_{b'}} p_{-q'b'} p_{q'b'} \right]$$

$$= \frac{1}{2} \sum_{q'b'}' \frac{1}{M_{b'}} \left\{ \underbrace{[u_{qb}, p_{-q'b'}]}_{i\hbar \delta_{q,-q'} \delta_{bb'}} p_{q'b'} + p_{-q'b'} [u_{qb}, p_{q'b'}] \right\}$$

$$= \frac{i\hbar}{M_b} p_{-q,b} \quad , \text{ or } \quad \dot{u}_{qb} = \frac{p_{-qb}}{M_b}$$

as expected classically, because:

$$\dot{u}_{qb} = \frac{p_{qb}}{M_b} \quad \text{and from definition of transforms.}$$

35 Equation (11) holds because $C_{\alpha\alpha'}(q, bb') = C_{\alpha'\alpha}(-q\, bb')$

43
$$a_q \equiv \frac{i}{\sqrt{2\hbar\omega_q}} p_q^+ + \sqrt{\frac{\omega_q}{2\hbar}} u_q \; ; \quad a_q^+ = \frac{-i}{\sqrt{2\hbar\omega_q}} p_q + \sqrt{\frac{\omega_q}{2\hbar}} u_q^+$$

$$a_{-q}^+ \equiv \frac{-i}{\sqrt{2\hbar\omega_q}} p_q^+ + \sqrt{\frac{\omega_q}{2\hbar}} u_q \; ; \quad a_{-q} = \frac{i}{\sqrt{2\hbar\omega_q}} p_q + \sqrt{\frac{\omega_q}{2\hbar}} u_q^+$$

$$a_q a_q^+ = \frac{1}{2\hbar\omega_q} p_q^+ p_q + \frac{\omega_q}{2\hbar} u_q u_q^+ + \frac{i}{2\hbar} p_q^+ u_q^+ - \frac{i}{2\hbar} u_q p_q$$

$$a_{-q}^+ a_{-q} = \frac{1}{2\hbar\omega_q} p_q^+ p_q + \frac{\omega_q}{2\hbar} u_q u_q^+ - \frac{i}{2\hbar} p_q^+ u_q^+ + \frac{i}{2\hbar} u_q p_q$$

$$a_q^+ a_q = \frac{1}{2\hbar\omega_q} p_q p_q^+ + \frac{\omega_q}{2\hbar} u_q^+ u_q + \frac{i}{2\hbar} u_q^+ p_q^+ - \frac{i}{2\hbar} p_q u_q$$

$$p_q = \sum_{\alpha b}' \frac{1}{\sqrt{M_b}} e_\alpha(q\, b) \cdot p_{\alpha q b}$$

$$p_q^+ p_q = \sum_{\alpha'\alpha bb'}' \frac{1}{\sqrt{M_b M_{b'}}} e_{\alpha'}^*(q\, b') \, p_{\alpha' q b'}^\dagger \, e_\alpha(q\, b) \, p_{\alpha q b}$$

$$= p_q p_q^+$$

43 $$[u^\dagger_{q,b}, p^\dagger_{q',b'}] = \frac{1}{G^3}\sum_{\ell\ell'} e^{iq\cdot R_\ell - iq'\cdot R_{\ell'}} \underbrace{[u^T_{\ell b}, p^T_{\ell' b'}]}_{i\hbar\,\delta_{\ell\ell'}\delta_{bb'}}$$

$$= i\hbar\,\delta_{qq'}\delta_{bb'}$$

$$\therefore \quad u_q^\dagger p_q^\dagger = i\hbar\,\delta_{qq} - p_q^\dagger u_q^\dagger = 1 - p_q^\dagger u_q^\dagger$$

$$p_q u_q = i\hbar\,\delta_{qq} - u_q p_q = 1 - u_q p_q$$

$$\therefore \quad a^\dagger_{-q} a_{-q} = a_q^\dagger a_q$$

$$[N_q, u_{q'}] = [a_q^\dagger a_q, q_{q'}^\dagger a_{q'}]$$

$$= [a_q^\dagger a_q, a_{q'}^\dagger]a_{q'} + a_{q'}^\dagger [a_q^\dagger a_q, a_{q'}]$$

$$= a_q^\dagger \underbrace{[a_q, a_{q'}^\dagger]}_{\delta_{qq'}} a_{q'} + \underbrace{[a_q^\dagger, a_{q'}^\dagger]}_{0} a_q a_{q'} + a_{q'}^\dagger a_q^\dagger \underbrace{[a_q, a_{q'}]}_{0} + a_{q'}^\dagger \underbrace{[a_q^\dagger, a_{q'}^\dagger]}_{-\delta_{q'q}} a_q$$

$$[a_q, a_{q'}] = \frac{-i}{2\hbar\sqrt{\omega_q\omega_{q'}}}[p_q^\dagger, p_{q'}^\dagger] + \frac{\sqrt{\omega_q\omega_{q'}}}{2\hbar}[u_q, u_{q'}]$$

$$+ \frac{i}{\sqrt{2\hbar\omega_q}}\cdot\sqrt{\frac{\omega_{q'}}{2\hbar}}[p_q^\dagger, u_{q'}] + \sqrt{\frac{\omega_q}{2\hbar}}\cdot\frac{i}{\sqrt{2\hbar\omega_{q'}}}[u_q, p_{q'}^\dagger] = 0$$

$$[a_q^\dagger, a_{q'}^\dagger] = 0 \quad ; \quad \therefore \quad [N_q, N_{q'}] = 0$$

50 Note that $\sum_{q}'$ is understood and is not the same as $\sum_{n}'$.

Single Electron in Periodic Potential

61 $E_F = \frac{\hbar^2 k_F^2}{2m}$, $k_F = [3\pi^2 n]^{1/3}$

$\therefore E_F = \frac{\hbar^2}{2m}[3\pi^2 n]^{2/3}$

63 $[V(r), T_\ell]\psi = V(r) T_\ell \psi - T_\ell \{V(r)\psi\}$

T_ℓ operating on a function in the group theory sense means to replace r everywhere by $r + R_\ell$.

$\therefore [V(r), T_\ell]\psi(r) = V(r) T_\ell \psi(r) - T_\ell \{V(r)\psi(r)\}$

$= V(r) T_\ell \psi(r) - V(r+R_\ell)\psi(r+R_\ell) = V(r) T_\ell \psi(r) - V(r)\psi(r+R_\ell)$

$= V(r) T_\ell \psi(r) - V(r) T_\ell \psi(r) = 0$

$\therefore [H, T_\ell] = 0$ and the eigenvalues (any eigenfunctions) of T_ℓ are also eigenfunctions of H. (If no degeneracy is present)

79 Periodic Potential Perturbation

Given:

$$\frac{\hbar^2}{2m}(k+K)^2 \chi_n(k+K) + \sum_{K'}' V(K')\chi_n(k+K+K') = E_n(k)\chi_n(k+K)$$

Because $V(r) = \sum_K V(K) e^{-i K\cdot r}$ and $V(r)$ has the periodicity of the lattice, we would expect the strongest contribution to come from $V(0)$ because this is the coefficient of the "fundamental" term in the Fourier expansion. Thus:

$V(0) \Rightarrow V^{(0)}(0)$; $V(K) \Rightarrow V^{(1)}(K)$

and we take:

$\chi_n(k) = \chi_n^{(0)}(k) + \lambda \chi_n^{(1)}(k) + \cdots$

$\chi_n(k+K) = \lambda\chi_n^{(1)}(k+K) + \lambda^2 \chi_n^{(2)}(k+K) + \cdots$ (same reason as above)

$E_n(k) = E_n^{(0)}(k) + \lambda E_n^{(1)}(k) + \cdots$

79 For $K = 0$:

$$\frac{\hbar^2}{2m} k^2 \left\{ \chi_n^{(0)}(k) + \lambda \chi_n^{(1)}(k) + \cdots \right\} + V^{(0)}(0) \left\{ \lambda \chi_n^{(1)}(k) + \lambda^2 \chi_n^{(2)}(k) + \cdots \right\}$$

$$+ \sum_{K'}{}' \lambda V^{(1)}(K') \left\{ \lambda \chi_n^{(0)}(k+K') + \lambda^2 \chi_n^{(1)}(k+K') + \cdots \right\} + V^{(0)}(0)\, \chi_n^{(0)}(k)$$

$$= \left\{ E_n^{(0)}(k) + \lambda E_n^{(1)}(k) + \cdots \right\} \left\{ \chi_n^{(0)}(k) + \lambda \chi_n^{(1)}(k) + \cdots \right\}$$

In the zeroth order:

$$\left\{ \frac{\hbar^2}{2m} k^2 + V^{(0)}(0) \right\} \chi_n^{(0)}(k) = E_n^{(0)}(k)\, \chi_n^{(0)}(k)$$

In the first order:

$$\left\{ \frac{\hbar^2}{2m} k^2 + V^{(0)}(0) \right\} \chi_n^{(1)}(k) = E_n^{(0)}(k)\, \chi_n^{(1)}(k) + E_n^{(1)}(k)\, \chi_n^{(0)}(k)$$

Second Order:

$$\left\{ \frac{\hbar^2}{2m} k^2 + V^{(0)}(0) \right\} \chi_n^{(2)}(k) + \sum_{K'}{}' V^{(1)}(K')\, \chi_n^{(1)}(k+K')$$

$$= E_n^{(0)}(k)\, \chi_n^{(2)}(k) + E_n^{(1)}(k)\, \chi_n^{(1)}(k) + E_n^{(2)}(k)\, \chi_n^{(0)}(k)$$

Thus we have: $E_n^{(0)}(k) = V^{(0)}(0) + \frac{\hbar^2 k^2}{2m}$; $E_n^{(1)}(k) = 0$

and:

$$E_n^{(2)}(k)\, \chi_n^{(0)}(k) = \sum_{K'}{}' V^{(1)}(K')\, \chi_n^{(1)}(k+K')$$

For $K \neq 0$: Because we need an expression for $\chi_n^{(1)}(k+K')$:

$$\frac{\hbar^2}{2m} (k+K)^2 \left\{ \lambda \chi_n^{(1)}(k+K) + \lambda^2 \chi_n^{(2)}(k+K') + \cdots \right\}$$

$$+ V^{(0)}(0) \left\{ \lambda \chi_n^{(1)}(k+K) + \lambda^2 \chi_n^{(2)}(k+K) + \cdots \right\} + \lambda V^{(1)}(-K) \left\{ \chi_n^{(0)}(k) + \lambda \chi_n^{(1)}(k) + \cdots \right\} \quad \text{NB}$$

$$+ \sum_{K' \neq 0, -K}{}'' \lambda V^{(1)}(K') \left\{ \lambda \chi_n^{(1)}(k+K+K') + \lambda^2 \chi_n^{(2)}(k+K+K') + \cdots \right\}$$

$$= \left\{ E_n^{(0)}(k) + \lambda E_n^{(1)}(k) + \cdots \right\} \left\{ \lambda \chi_n^{(1)}(k+K) + \lambda^2 \chi_n^{(2)}(k+K) + \cdots \right\}$$

First Order:

$$\left\{ \frac{\hbar^2}{2m} (k+K)^2 + V^{(0)}(0) \right\} \chi_n^{(1)}(k+K) + V^{(1)}(-K)\, \chi_n^{(0)}(k) = E_n^{(0)}(k)\, \chi_n^{(1)}(k+K)$$

79 $\therefore \quad \chi_n^{(1)}(k+K) = \dfrac{V^{(1)*}(K)\ \chi_n^{(0)}(k)}{\frac{\hbar^2}{2m}\left\{k^2 - (k+K)^2\right\}}$

since $\quad V(r) = \sum_K{}' V(K)\, e^{-iK\cdot r} \quad ; \quad V(K) = \frac{1}{\Omega}\int V(r)\, e^{iK\cdot r}\, d^3r$

$\therefore \quad E_n(k) = V^{(0)}(0) + \frac{\hbar^2 k^2}{2m} + \sum_{K'}{}' \dfrac{|V^{(1)}(K')|^2}{\frac{\hbar^2}{2m}\left\{k^2 - (k+K')^2\right\}}$

What about $K' = 0$? Must consider degenerate case. Work in the zeroth order before applying any higher perturbations. Write the zeroth order Schroedinger equations for two states, k, and $k+K$, assuming the same energy for each:

$$+\frac{\hbar^2}{2m}(k+K)^2\,\chi(k+K) + \sum_{K'}{}' V(K')\,\chi(k+K+K') = E\,\chi(k+K)$$

$$+\frac{\hbar^2}{2m}k^2\,\chi(k) + \sum_{K}{}' V(K')\,\chi(k+K') = E\,\chi(k)$$

We need only pick out in the sums those terms that couple k to $k+K$, assuming all values of K don't contribute. Hence:

$$\left\{+\frac{\hbar^2}{2m}(k+K)^2 + V(0)\right\}\chi(k+K) + V(-K)\,\chi(k) = E\,\chi(k+K)$$

$$\left\{+\frac{\hbar^2}{2m}k^2 + V(0)\right\}\chi(k) + V(K)\,\chi(k+K) = E\,\chi(k)$$

and so forth. The assumption of close coupling between only the two levels is the usual in degenerate perturbation theory.

89 Summary of Brillouin Zone Properties

A. All zones have the same volume in reciprocal space.

B. We can neglect all zones but the first if we take E as a multiple-valued function of k.

C. Each zone contains $2G^3$ states.

D. Correspondence to X-ray diffractions.

89 E. Translational symmetry applies to BZ.

F. Two nearest neighboring zones may have overlapping energy bands.

The total number of states in the BZ is $2G^3$ because:

$$b_n(k, r + RG) = b_n(k, r)$$

where R_G is the length of a side of the crystal of G atoms along a side.

$$\therefore e^{-ik \cdot R_G} = 1 \qquad k R_G = 2n\pi \quad , \quad \bar{R}_G = G\bar{a}$$

$$\vec{k} = \frac{2\pi}{G}(s_1 \bar{b}_1 + s_2 \bar{b}_2 + s_3 \bar{b}_3)$$

$$\therefore \vec{k} \cdot \vec{R_G} = 2\pi(s_1 + s_2 + s_3)$$

The density of states per unit volume of k space is $\frac{\Omega}{8\pi^3} d^3k$ where $\Omega = G^3 a^3$

The volume of k space $\sim \frac{1}{a^3}$ and we need 2 for spin, hence we get C above.

90 Wannier Functions:

Definition:

$$a_n(R_e, r) = \frac{1}{\sqrt{G^3}} \sum_{k \text{ 1st BZ}} e^{-ik \cdot R_e} b_n(k, r)$$

Properties:

A. $a_n(R_e, r) = a_n(r - R_e)$: Translate by lattice vector, write $R_e \to R_e + R$, $r \to r + R$

$$\therefore a_n(R_e + R, r + R) = \frac{1}{\sqrt{G^3}} \sum_k e^{-ik \cdot (R_e + R)} b_n(k, r + R)$$

$$= \frac{1}{\sqrt{G^3}} \sum_k e^{-ik \cdot (R_e + R)} e^{ik \cdot R} b_n(k, r)$$

Let $R = -R_e$: $a_n(r - R_e) = \frac{1}{\sqrt{G^3}} \sum_k e^{-ik \cdot R_e} b_n(k, r)$

QED.

B. Localization Property: Take $u_n(k, r)$ independent of k like in tight binding. This is like taking the Kronig-Penney model and letting $V \to \infty$.

90 $\therefore \quad b_n(k,r) = \frac{1}{\sqrt{\Omega}} e^{ik\cdot r} u_n(r)$

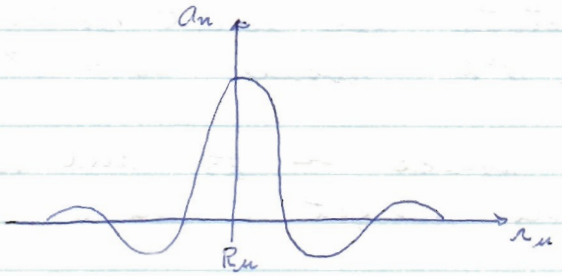
and $a_n(r-R_\ell) = \frac{1}{\sqrt{G^3\Omega}} u_n(r) \sum_k' e^{-ik\cdot(r-R_\ell)}$

We proceed in only one dimension:

$$\sum_{k_n}' e^{ik_n(r_n-R_n)} \to \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk_n\, e^{ik_n(r_n-R_n)}$$

$$= \frac{L}{2\pi} \frac{2i}{i(r_n-R_n)} \sin k_n(r_n-R_n)$$

$$= \frac{L}{\pi} \frac{\sin k_n(r_n-R_n)}{k_n(r_n-R_n)}$$



Transform of $a_n(r-R_\ell) = \frac{1}{\sqrt{G^3}} \sum_k e^{-ik\cdot R_\ell} b_n(k,r)$

$$\sum_\ell e^{ik'\cdot R_\ell} a_n(r-R_\ell) = \frac{1}{\sqrt{G^3}} \sum_{\ell k} e^{i(k'-k)\cdot R_\ell} b_n(k,r)$$

$$= \sqrt{G^3}\, b_n(k',r)$$

$$\therefore \quad b_n(k,r) = \frac{1}{\sqrt{G^3}} \sum_\ell e^{ik\cdot R_\ell} a_n(r-R_\ell)$$

Orthogonality of Wannier Functions:

$$\int a_{n'}^*(r-R_{\ell'})\, a_n(r-R_\ell)\, d^3r$$

$$= \frac{1}{G^3} \sum_{kk'} e^{ik'\cdot R_{\ell'} - ik\cdot R_\ell} \underbrace{\int b_{n'}^*(k',r)\, b_n(k,r)\, d^3r}_{\delta_{k'k}\,\delta_{n'n}}$$

$$= \frac{\delta_{nn'}}{G^3} \sum_k' e^{ik\cdot(R_{\ell'}-R_\ell)} = \delta_{nn'}\,\delta_{\ell\ell'} \quad \text{QED}$$

93 Crystal Coordinate and Momentum Operators:

We define a set of operators that are diagonal in the representation of the Bloch and Wannier functions:

$$\hat{k}\, b_n(k,r) \equiv k\, b_n(k,r)$$

$$\hat{R}\, a_n(r-R_\ell) \equiv R_\ell\, a_n(r-R_\ell)$$

Applying them to their opposite transform of the pair:

$$\hat{R}_\alpha\, b_n(k,r) = \frac{1}{\sqrt{\Omega}} \sum_\ell e^{ik\cdot R_\ell} \underbrace{\hat{R}_{\ell\alpha}\, a_n(r-R_\ell)}_{R_{\ell\alpha}\, a_n(r-R_\ell)}$$

$$= -i \frac{\partial}{\partial k_\alpha}\, b_n(k,r)$$

similarly, $\hat{k}_\alpha\, a_n(r-R_\ell) = i \frac{\partial}{\partial R_{\ell\alpha}}\, a_n(r-R_\ell)$

Note that $\hat{R}_\alpha$ and $\hat{k}_\alpha$ will operate only on functions of r which is why we are able to pass them thru the integral sign (sum sign) and past the exponential. This is in keeping with the usual practice.

Also note that the eigenvalues of $\hat{R}$ are indexed by ℓ while those $\hat{k}$ have their indexing implicit.

We define a new system function as our representation as expanded in terms of Bloch functions:

$$\bar{\Psi}^n(r) = \sum_{n'k'} \varphi_{n'}(k')\, b_{n'}(k',r)$$

since $H\bar{\Psi}(r) = E\bar{\Psi}(r)$, we readily form

$$\sum_{n'k'} \langle nk|H|n'k'\rangle\, \varphi_{n'}(k') = E\, \varphi_n(k)$$

which is the Schroedinger equation in the Crystal Momentum Representation (CMR)

94 Consider $\hat{R}_\alpha \mathcal{F}(r) = \sum_{nk}' q_n(k) \hat{R}_\alpha b_n(k,r)$

$= \sum_{nk}' q_n(k) - r \frac{\partial}{\partial k_\alpha} b_n(k,r)$

$\rightarrow \sum_n \int d^3k \left\{ -r \frac{\partial}{\partial k_\alpha} \right\} \left\{ q_n(k)\, b_n(k,r) \right\}$ (A)

$- \sum_n' \int d^3k \; b_n(k,r) \left\{ -r \frac{\partial}{\partial k_\alpha} \right\} q_n(k)$ (B)

(A) vanishes because in the limit of the BVK boundary conditions, we have an integral over the first BZ. This integral is taken over the volume or *period* of the derivative of a periodic function in k space and hence it vanishes.

$\therefore \sum_{nk}' q_n(k) \left\{ -r \frac{\partial}{\partial k_\alpha} \right\} b_n(k,r) = \sum_{nk}' b_n(k,r) \left\{ r \frac{\partial}{\partial k_\alpha} \right\} q_n(k)$

The (B) term does not vanish necessarily because integrals over periodic functions can have finite areas.

Many Electron Methods

168: The generalized density matrix:

$$\Gamma(x_1' \cdots x_N' | x_1 \cdots x_N) = \Psi^*(x_1' \cdots x_N)\,\Psi(x_1 \cdots x_N)$$

and

$$\Gamma(x_1' \cdots x_p' | x_1 \cdots x_p) = \binom{N}{p} \int \Psi^*(x_1' \cdots x_p' \cdots x_N)\,\Psi(\cdots)\, dx_{p+1} \cdots dx_N$$

is akin to the usual multi-variate probability distribution (AP215) and has the same interpretation.

169: When we write $\rho(x_1', x_2)$, we mean an element of the usual density matrix. The definition given here holds only at $T = 0$. Also, the matrices are taken to be "continuous" in the Dirac sense.

172:

$$\sum_{\xi\xi'} \rho_{\xi\xi'}(xx')\,\rho_{\xi'\xi}(x'x)$$

$$= \sum_{\xi\xi'} \sum_{kk'} \psi_k^*(x)\,\psi_k(x')\,\eta_k^*(\xi)\,\eta_{k'}(\xi') \cdot \psi_{k'}^*(x')\,\psi_{k'}(x)\,\eta_{k'}^*(\xi')\,\eta_k(\xi)$$

$$= \sum_{\xi'} \sum_{kk'} \psi_k^*(x)\,\psi_k(x')\,\eta_k(\xi')\,\psi_{k'}^*(x')\,\psi_{k'}(x)\,\eta_{k'}^*(\xi')\,\delta_{kk'}$$

$$= \sum_{\xi'} \sum_{k} \psi_k^*(x)\,\psi_k(x')\,\eta_k(\xi')\,\psi_k^*(x')\,\psi_k(x)\,\eta_k^*(\xi')$$

$$= \sum_{k} \psi_k^*(x)\,\psi_k(x')\,\psi_k^*(x')\,\psi_k(x)$$

Take $\int dx \int dx'$ and get N

PROBLEM SET 1

Problems I

Applied Physics 295

1. a) Find the number of nearest and next nearest neighbors for the simple cubic, body-centered cubic, face-centered cubic, and diamond lattices.

   b) Suppose hard sticky spheres are packed into crystalline arrangements having the preceding structures and also the hexagonal close packed structure. Calculate the fraction of the crystal volume occupied by the spheres for this case. Comment on the numbers obtained.

2. By comparing the results obtained for a linear monatomic lattice with (a) periodic boundary conditions, (b) fixed ends, and (c) free ends, show that the density of normal modes is independent of the boundary conditions when the number of atoms in the chain is large.

3. Consider a linear monoatomic lattice with nearest and next nearest neighbor interactions.

   a) Obtain an expression for ω vs. q and plot ω vs. q for various values of the ratio of the interaction constants.

   b) Show in general (for this lattice) that $\frac{d\omega}{dq} = 0$ for $q = \pm \frac{\pi}{a}$.

4. If the dispersion relation for a linear monatomic lattice is

$$\omega^2 = c^2\left(q^2 - \frac{a^2}{2\pi^2} q^4\right),$$

where a is the lattice constant, determine the values of the interaction constants $C(0)$ and $C(\ell)$ required to produce this dispersion relation.

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Problems II

Applied Physics 295

5.

a) Find the number of independent parameters $C_{\alpha\alpha'}(\ell)$ when only nearest neighbor forces are acting in the fcc and bcc lattices displaying the symmetry operations leading to your results. Write out the matrices $C(\ell)$ which you obtain.

b) How are the results in a) modified when central forces are acting between nearest neighbors?

6.

a) For the fcc lattice, set up the secular equations determining the frequency dispersion curve (ω vs. q) and the polarization vectors e(q, j) for nearest neighbor non-central forces.

b) Sketch solutions of ω vs. q determined from part a) when nearest neighbor central forces are acting, and waves are propagating in the [100] direction. Do the same for waves propagating in [110] directions. Sketch constant frequency surfaces for x-y plane (as in Ziman, p. 34, Fig. 9).

c) Discuss the motion of atoms in the face centered cube for $q \approx 0$ and at the Brillouin zone face in the [100] direction.

7. Give reasons why the sc and bcc lattices are unstable when only central nearest neighbor forces are acting. Is the fcc stable under these conditions?

Problem III

Applied Physics 295

8. a) Show that the wave functions $\Psi_n(q) = A(a_q^+)^n \Psi_o(q)$ are orthogonal.

b) Find the normalization constant A.

c) Show that $\partial N_q / \partial t = 0$, so that $N_q = a_q^+ a_q$ is a constant of the motion.

d) Write out the matrices U_q and P_q in occupation number representation. Are they Hermitian?

e) Show that the operators a_q have a harmonic time dependence.

Assignment #1
Problem Set #1

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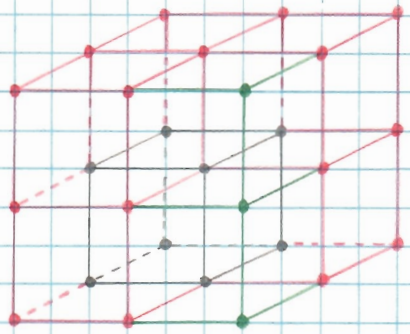
1. a.

SIMPLE CUBIC

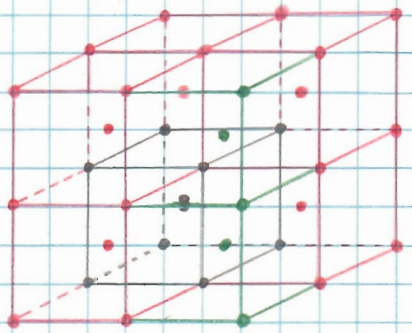


✓ 6 NEAREST NEIGHBORS "a" units

✓ 8 NEXT NEAREST "$\sqrt{2}$ a" units

12 Black atoms form unit cell

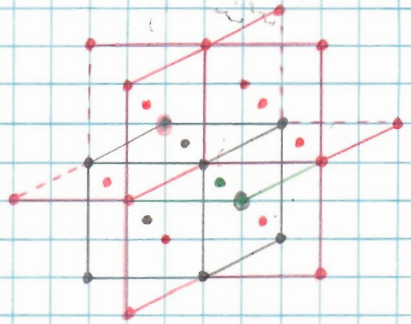
BODY CENTERED CUBIC



✓ 8 NEAREST NEIGHBORS "$\frac{\sqrt{3}}{2}$ a" units

✓ 6 NEXT NEAREST "a" units

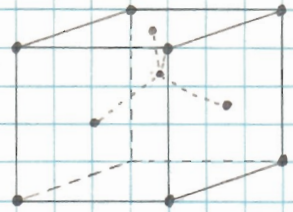
FACE CENTERED CUBIC



✓ 12 NEAREST NEIGHBORS "$\frac{\sqrt{2}}{2}$ a" units

✓ 6 NEXT NEAREST "a" units

DIAMOND



✓ 4 NEAREST NEIGHBORS : "$\frac{\sqrt{3}a}{4}$" units

✓ 12 NEXT NEAREST : "$\frac{\sqrt{2}}{2}a$" units

---

1. b. SIMPLE CUBIC
(View ⊥ to [100] plane)

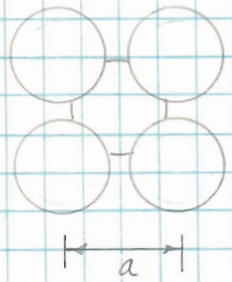
(1) Vol. unit cell = $a^3 = V_{uc}$

(2) radius atom : $r = a/2$

(3) 1 atom / unit cell : $V_a = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{1}{6}\pi a^3$

(4) $V_a / V_{uc} = 1/6\,\pi = .525$ ✓

BODY CENTERED CUBIC
(View ⊥ to [100] plane)



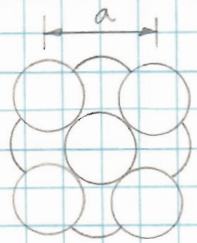
(1) $V_{uc} = a^3$

(2) $4r = \sqrt{3}\,a$, $r = \frac{\sqrt{3}}{4}a$

(3) 2 atm/uc : $V_a = (2)\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}\right)^3 a^3$

(4) $V_a/V_{uc} = \frac{\sqrt{3}}{8}\pi = .68$ ✓

FACE CENTERED CUBIC
(View ⊥ to [100] plane)



(1) $V_{uc} = a^3$

(2) $4r = \sqrt{2}\,a$, $r = \frac{\sqrt{2}}{4}a$

(3) 4 atm/uc : $V_a = (4)\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}\right)^3 a^3$

(4) $V_a/V_{uc} = \frac{\sqrt{2}}{6}\pi = .74$ ✓

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1. b. DIAMOND TYPE
(see diagram, prob. 1 a)

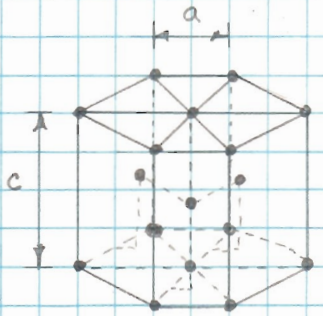
(1) $V_{uc} = a^3$

(2) $2r = \frac{\sqrt{3}}{4} a$, $r = \frac{\sqrt{3}}{8} a$

(3) 8 atoms / uc : $V_a = (8) \frac{4}{3} \pi \left(\frac{\sqrt{3}}{8}\right)^3 a^3$

(4) $V_a / V_{uc} = \frac{\sqrt{3}}{16} \pi = .340$

HEXAGONAL CLOSE PACKED



(1) Area Hexagon = $\frac{3}{2} a^2 \sqrt{3}$

(2) height "h" of tetrahedron of side "a" $= \sqrt{\frac{2}{3}} a$

(3) $c = 2h = 2\sqrt{\frac{2}{3}} a$

(4) $V_{uc} = 3\sqrt{2}\, a^3$

(5) 6 atoms / uc : $V_a = (6)\ 4/3\ \pi \left(\frac{1}{8}\right) a^3$

atom radius = $a/2$

(6) $\frac{V_a}{V_{uc}} = \frac{\sqrt{2}}{6} \pi = .74$

As expected, the h.c.p. and the f.c.c. have the highest $\frac{V_a}{V_{uc}}$ ratio as these two are the close-packed structures. They are the same because either one is equally close-packed. The diamond structure, valence four crystal structure, has the poorest packing density because of the need to satisfy the valence requirements leaving two voids in the unit cell. A similar structure is that of CaF_2 except that there is complete symmetry within the unit cell.

Good ↑

(9)

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2. a. (1) The dispersion equation for a linear, monatomic lattice is:

$$M\omega^2 = \sum_{l} c(l) \cos qla$$

indicating $-\pi/a < q \leq \pi/a$ as the region of the principle values of q.

(2) Our equation of motion is:

$$M \ddot{u}_l + \sum_{l'} c(l-l')\, u_{l'} = 0$$

To which we propose the solution:

$$u_l(t) = u^\circ e^{i(\omega t \pm iqla)}$$

(3) The Born - von Karman boundary conditions are:

$$u_l = u_{l+N}$$

(4) Substituting into (3):

$$e^{\pm iqla} = e^{\pm iq(l+N)a} \quad ; \quad e^{\pm iqNa} = 1$$

(5) Thus $qNa = 2n\pi$, $q = \dfrac{2n\pi}{Na}$ ✓

However, the principle values of q must still be satisfied, viz,

$$-\pi/a < \frac{2n\pi}{Na} \leq \pi/a \quad , \quad -N/2 < n \leq N/2$$

$$\therefore \quad q = \frac{2n\pi}{Na} \quad , \quad n = \pm 1, \pm 2, \pm 3, \ldots \pm N/2$$

or $q = \dfrac{n\pi}{Na}$, $n = 1, 2, 3, \ldots N$ No! Not true that $e^{\frac{i\pi}{Na}(l+N)a} = e^{\frac{i\pi}{Na}la}$

considering n to proceed in steps of one instead of two.

NB: Since atom 0 and atom N are the same atom, there are N atoms in the chain.

2. b. (1) Consider the following boundary conditions for a chain of N atoms:

$u_0 = u_{N-1} = 0$

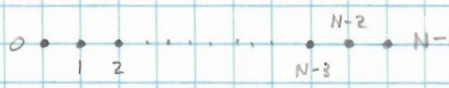
(2) Such boundary conditions lead to standing wave solutions of equation (2) such as the following:

$$u_e(t) = u^\circ e^{i\omega t} \sin qla$$

(3) $\sin q(N-1)a = 0$; $q(N-1)a = n\pi$; $q = \dfrac{n\pi}{(N-1)a}$ ✓

Since we are dealing with standing waves; q must be positive and n is counted over the number of movable atoms, viz.; $n = 1, 2, 3, \ldots, N-2$

c. (1) Consider the following boundary conditions for a chain of N atoms:



Free Ends.

(2) These boundary conditions suggest the solution:

$$u_e(t) = u^\circ e^{i\omega t} \cos qla$$

for which $\dfrac{d^2u_0}{dl^2} = \dfrac{d^2u_{N-1}}{dl^2} = 0$, taking a cue from the boundary conditions in a longitudinally vibrating bar with free ends. Therefore:

(3) $\cos q(N-1)a = 0$, $q(N-1)a = n\dfrac{\pi}{2}$; n odd

or $q = \dfrac{(n+\frac{1}{2})\pi}{(N-1)a}$, $n = 0, 1, 2, \ldots, N-1$

(4) For the case of nearest neighbor interaction, we have for each of the three boundary conditions:

Cyclic: $n = \dfrac{2N}{\pi}\sin^{-1}\dfrac{\omega}{\omega_{max}}$; $\rho(\omega) = \dfrac{dn}{d\omega} = \dfrac{2N}{\pi}\left[\omega_{max}^2 - \omega^2\right]^{-1/2}$

Fixed Ends: $n = \dfrac{2(N-1)}{\pi}\sin^{-1}\dfrac{\omega}{\omega_{max}}$; $\rho(\omega) = \dfrac{dn}{d\omega} = \dfrac{2(N-1)}{\pi}\left[\omega_{max}^2 - \omega^2\right]^{-1/2}$

Free Ends: $n = \dfrac{2\cdot(N-1)}{\pi}\sin^{-1}\dfrac{\omega}{\omega_{max}} - 1/2$; $\rho(\omega) = \dfrac{dn}{d\omega} = \dfrac{2(N-1)}{\pi}\left[\omega_{max}^2 - \omega^2\right]^{-1/2}$

Since $\lim\limits_{N\to\infty}\dfrac{N}{N-1} = 1$; it is easy to see that for large N, the density of oscillators is independent of the boundary conditions.

(8)

Assignment #1
Problem Set #1
Continued

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3. a. (1) We take the expression for $\omega = \omega(q)$ for a linear, monatomic lattice as:

$$M\omega^2 = \sum_{\ell} C(\ell) \cos q\ell a$$

(2) We shall consider interaction between near and next nearest atoms in the chain; that is, between the atom at $\ell = 0$ and the atoms at $\ell = 1$, $\ell = 2$, $\ell = -1$, and $\ell = -2$. Using the rigid displacement condition, viz.,

$$\sum_{\ell} C(\ell) = 0, \text{ we write } \sum_{\ell=-2}^{2} C(\ell) = 0 = 2C(2) + 2C(1) + C(0)$$

also using lattice inversion symmetry.

(3) Using equation (1),

$$M\omega^2 = \sum_{-2}^{2} C(\ell) \cos q\ell a = C(0) + 2C(1)\cos qa + 2C(2)\cos 2qa$$

we may eliminate either $C(0)$, $C(1)$, or $C(2)$ and obtain three equations:

(4) $$M\omega^2 = C(0)\left[1 - \cos 2qa\right] + 2C(1)\left[\cos qa - \cos 2qa\right]$$

$$M\omega^2 = C(0)\left[1 - \cos qa\right] - 2C(2)\left[\cos qa - \cos 2qa\right]$$

$$M\omega^2 = -2C(1)\left[1 - \cos qa\right] - 2C(2)\left[1 - \cos 2qa\right]$$

Simplifying:

(5) $$M\omega^2 = 2C(0)\sin^2 qa + 4C(1)\sin\tfrac{3}{2}qa \sin\tfrac{1}{2}qa$$

$$M\omega^2 = 2C(0)\sin^2\tfrac{1}{2}qa - 4C(2)\sin\tfrac{3}{2}qa \sin\tfrac{1}{2}qa$$

$$M\omega^2 = -4C(1)\sin^2 1/2\, qa - 4C(2)\sin^2 qa$$

(6) $$M\omega^2 = 2C(0)\left[\sin^2 qa + 2\frac{C(1)}{C(0)}\sin 3/2\, qa \cdot \sin\tfrac{1}{2}qa\right]$$

$$M\omega^2 = 2C(0)\left[\sin^2\tfrac{1}{2}qa - 2\frac{C(2)}{C(0)}\sin\tfrac{3}{2}qa \cdot \sin\tfrac{1}{2}qa\right]$$

$$M\omega^2 = -4C(1)\left[\sin^2\tfrac{1}{2}qa + \frac{C(2)}{C(1)}\sin^2 qa\right]$$

We are not free to randomly choose values of the ratio of the force constants as this ratio must satisfy equation (2). That is:

(7) $\frac{c(1)}{c(0)} = -\frac{1}{2} - \frac{c(2)}{c(0)}$; $\frac{c(2)}{c(0)} = -\frac{1}{2} - \frac{c(1)}{c(0)}$

One equation, two unknowns.

It is seen that the ratios $\frac{c(1)}{c(0)}$, $\frac{c(2)}{c(0)}$, are not independent of each other. No!

Taking a cue from the nearest neighbor case, we will fix $c(0)$, take it as positive and make the ratios of the other force constants relative to it. In the limiting case of $c(2) = 0$; $c(1)$ is negative.

Since our interest lies in determining the effect of the next-nearest neighbor, let us choose the second equation in (6) as the one which will best display this effect. We further define the pseudo-normalized frequency

(8) $\omega_n = \omega \Big/ \sqrt{\frac{2c(0)}{M}}$; $\omega_n = \omega/\omega_{max}$ when $c(2) = 0$

Thus:

(9) $\omega_n = \left| \left[\sin^2 \tfrac{1}{2} qa - 2 \frac{c(2)}{c(0)} \sin \tfrac{3}{2} qa \cdot \sin \tfrac{1}{2} qa \right]^{1/2} \right|$

We also stipulate that ω_n must be real, therefore:

(10) $\frac{c(2)}{c(0)} \leq \frac{1}{2} \frac{\sin \frac{1}{2} qa}{\sin \frac{3}{2} qa} = \frac{1}{2} \frac{1}{4 - 3\sin^2 \frac{1}{2} qa}$

Thus the maximum value of $\frac{c(2)}{c(0)}$ depends upon qa, and the inequality (10) must hold on each point on q for ω vs. q with $c(2)/c(0)$ held constant. Therefore, the maximum value of $c(2)/c(0)$ is the minimum of the right hand side of the inequality.

(11) $\frac{d}{d\theta} \left[\frac{1}{4 - 3\sin^2 \theta} \right] = \left[4 - 3\sin^2 \theta \right]^{-2} \left[-6 \sin\theta \cos\theta \right] = 0$

The extrema are at $\theta = 0, \pi/2, \pi, 3\pi/2, \ldots$, with the minima at $0, \pi, 2\pi, \ldots$. The maximum value of the ratio is then:

(12) $c(2)/c(0) \leq \frac{1}{8}$

It is also seen that $c(2)$ is positive from the right hand side of the inequality. Therefore, we may state:

(13) $0 \leq \frac{c(2)}{c(0)} \leq \frac{1}{8}$

Where did you get $c_2 \geq 0$?

Assignment #1
Problem Set #1
Continued

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3a Continued:

For values larger than 1/8, there would certain regions in q where ω_n would be a pure imaginary. Physically, what we are doing is this: We are considering the interaction with the nearest neighbor to be constant while measuring the effect of the next nearest neighbor interaction in varying degrees. We will assume that the magnitude of the next nearest neighbor interaction does not change the magnitude of C(0). If this is not assumed, then a relation must be given between C(2) and C(0) asserting the degree of dependence. If we look upon the interaction in the usual manner, viz., as springs linking the various atoms each with independent spring constants, we see that the assumption has validity. This in no way violates equation (7) as C(1) is redundant and its dependence on C(2) was taken care of in eliminating it from our dispersion equation, thus we need not consider its dependence on C(2). We could have equally well have chosen to eliminate C(0) and consider C(1) as expressing the interaction between nearest neighbors. As a matter of fact, it will always be possible to eliminate C(0) with any degree of interaction among the atoms in the lattice. Considering the third relation in equation (6); upon simplification:

No reason for this assumption.

$$(14)\quad \omega^2 = \frac{-4C(1)}{M}\sin^2 \tfrac{1}{2}qa\left[1 + 4\frac{C(2)}{C(1)}\cos^2 \tfrac{1}{2}qa\right]$$

If we take C(2) = 0 and C(1) negative to keep ω real, we merely have the usual dispersion relation for nearest neighbor interaction, with C(1) the Hooke's Law force constant. Thus:

$$(15)\quad \omega_n = \frac{\omega}{\sqrt{\frac{4C(1)}{M}}} = \left|\sin \tfrac{1}{2}qa\right|\left[1 - \frac{4C(2)}{C(1)}\cos^2 \tfrac{1}{2}qa\right]^{1/2}$$

How did you get from

with the restriction:

$$(16)\quad \frac{C(2)}{C(1)} \leq 1/4$$

$$= \sqrt{i}\,\sin\frac{qa}{2}\left[1 + \frac{4C(2)}{C(1)}\cos^2 qa/2\right]^{1/2}$$

I get to

If $\frac{C(2)}{C(1)}$ increases past 1/4, the lattice becomes unstable because ω is imaginary.

$\omega^2 > 0 \Rightarrow$

$$\frac{1}{2}\sum_l l^2 C(l) < 0 \Rightarrow C(1) + 4C(2) < 0$$

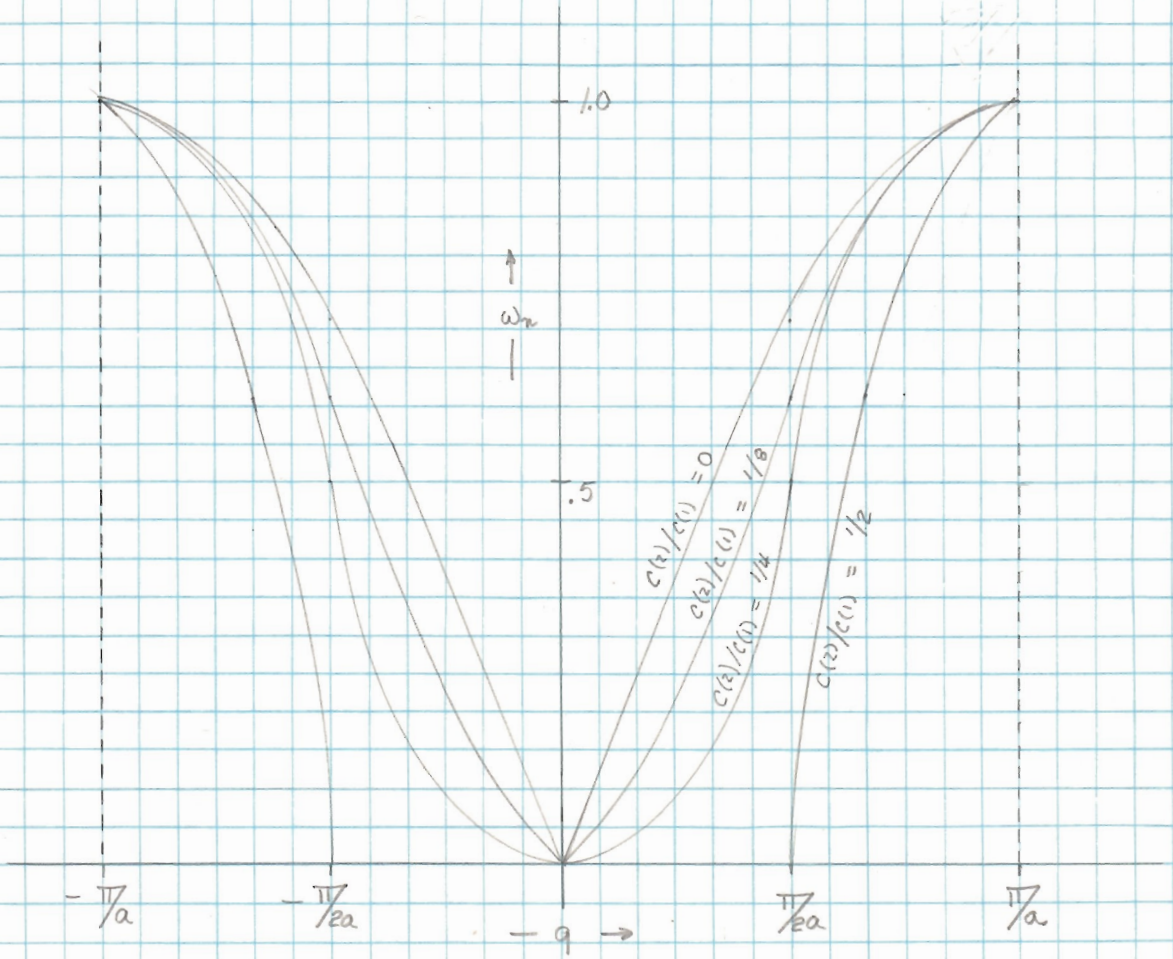
For $C(1) < 0$, $C(2)/C(1) > -1/4$

or $C(1)/C(2) < -1/4$

We may choose to plot either equation (9) or equation (15). Equation (15) expresses slightly more clear the effect of the strength of next-nearest neighbor interactions while considering nearest neighbor interaction the same as before: Let us examine the group velocity at $q = 0$.

(17) $$\left(\frac{d\omega_n}{dq}\right)_{q=0} = \frac{a}{2}\left[1 - 4\frac{c(2)}{c(1)}\right]^{1/2}$$

$$\frac{c(2)}{c(1)} = 0, \quad \left(\frac{d\omega}{dq}\right)_0 = \frac{a}{2}; \quad \frac{c(2)}{c(1)} = \frac{1}{4}, \quad \left(\frac{d\omega_n}{dq}\right)_0 = 0$$



Dispersion Curve For Next Nearest, Nearest Nieghbor Interactions in a Linear Monatomic Lattice with $c(2)/c(1)$ as a Parameter.

It is seen that for $c(2)/c(1) > 1/4$, a sort of "forbidden" region appears for values of long wavelength. If $c(2)/c(1) \to \infty$, the dispersion curve degenerates to δ function on π/a covering all values of ω_n.

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3. b. (1) The general dispersion relation for a linear monatomic lattice is:

$$\omega = \left[\frac{1}{M} \sum_{\ell} C(\ell) \cos q\ell a \right]^{1/2}$$

(2) Now:

$$\frac{d\omega}{dq} = \frac{1}{2} \left[\frac{1}{M} \sum_{\ell} C(\ell) \cos q\ell a \right]^{-1/2} \cdot -\frac{a}{M} \sum_{\ell} \ell C(\ell) \sin q\ell a$$

(3) At $q = \pm \pi/a$; $\sin q\ell a = \sin(\pm \ell \pi) = 0$

We regard the possibility of the denominator of (2) vanishing:

(4) $$\sum_{\ell} C(\ell) \cos q\ell a \Big|_{q=\pm\pi/a} = \sum_{\ell} C(\ell) (-1)^{\ell} \neq 0$$

(5) $$\therefore \left(\frac{d\omega}{dq}\right)_{q=\pm\pi/a} = \frac{1}{2} \left[\frac{1}{M} \sum_{\ell} C(\ell)(-1)^{\ell} \right]^{-1/2} [0] = 0 \text{ , QED.}$$

Assignment #1
Problem Set #1
Continued

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4. (1) $\omega^2(q) = c^2\left(q^2 - \frac{a^2}{2\pi^2} q^4\right)$

In the absence of boundary conditions, we will take our linear, monatomic lattice to be infinite in extent and consider interaction between all atoms in the chain. Therefore,

(2) $$\omega^2(q) = \frac{1}{M} \sum_{l=-\infty}^{\infty} C(l) \cos qla$$

$$= \frac{C(0)}{M} + \frac{2}{M} \sum_{l=1}^{\infty} C(l) \cos qla$$

$C(0)$ and $C(l)$ are now seen to be the coefficients of a Fourier cosine series and are represented by the following integrals:

(3) $$C(0) = \frac{a}{\pi} \int_0^{\pi/a} M\omega^2(q)\, dq \quad ; \quad C(l) = \frac{a}{\pi} \int_0^{\pi/a} M\omega^2(q) \cos qla\, dq$$

considering $\omega^2(q)$ to be defined over the interval $-\pi/a \leq q \leq \pi/a$

(4) $$C(0) = \frac{aMc^2}{\pi} \int_0^{\pi/a} q^2\, dq - \frac{a^3 Mc^2}{2\pi^3} \int_0^{\pi/a} q^4\, dq$$

$$= \frac{aMc^2}{3\pi} \left(\frac{\pi}{a}\right)^3 - \frac{a^3 Mc^2}{10\pi^3} \left(\frac{\pi}{a}\right)^5$$

$$= \frac{Mc^2\pi^2}{3a^2} - \frac{M\pi^2c^2}{10a^2} = \frac{7}{30} \frac{M\pi^2c^2}{a^2}$$

(5) $$C(l) = \frac{aMc^2}{\pi} \int_0^{\pi/a} q^2 \cos qla\, dq - \frac{a^3 Mc^2}{2\pi^3} \int_0^{\pi/a} q^4 \cos qla\, dq$$

Let $x = qa$, $dq = \frac{dx}{a}$, $q = \frac{x}{a}$,

$(x)_{q=\pi/a} = \pi$

(6) $$C(l) = \frac{Mc^2}{\pi a^2}\int_0^\pi x^2 \cos lx\,dx - \frac{Mc^2}{2a^2\pi^3}\int_0^\pi x^4 \cos lx\,dx$$

(7) $$\int_0^\pi x^2 \cos lx\,dx = \frac{x^2}{l}\sin lx - \frac{2}{l}\int x \sin lx\,dx$$

$$= \frac{x^2}{l}\sin lx - \frac{2}{l}\left[-\frac{x}{l}\cos lx + \frac{1}{l}\int \cos lx\,dx\right]$$

$$= \frac{x^2}{l}\sin lx + \frac{2x}{l^2}\cos lx - \frac{2}{l^3}\sin lx$$

$$= \frac{(l^2x^2-2)\sin lx + 2lx\cos lx}{l^3}\Bigg]_0^\pi = \frac{2\pi(-1)^l}{l^2}$$

(8) $$\int_0^\pi x^4 \cos lx\,dx = \frac{(l^4x^4 - 12l^2x^2 + 24)\sin lx + 4(l^3x^3 - 6lx)\cos lx}{l^5}\Bigg]_0^\pi$$

$$= \frac{4\pi}{l^4}(l^2\pi^2 - 6)(-1)^l$$

(9) $$C(l) = \frac{Mc^2}{\pi a^2}\cdot\frac{2\pi(-1)^l}{l^2} - \frac{Mc^2}{2a^2\pi^3}\cdot\frac{4\pi}{l^4}(l^2\pi^2-6)(-1)^l$$

$$= \frac{12\,Mc^2}{a^2\pi^2}\frac{(-1)^l}{l^4}\,; \quad l = \pm 1, \pm 2, \pm 3, \ldots$$

Let us now check our results to see that they satisfy the known symmetry conditions of the elastic constants. Given:

$$C(0) = \frac{7}{30}\frac{M\pi^2c^2}{a^2}\,; \quad C(l) = \frac{12\,Mc^2}{a^2\pi^2}\frac{(-1)^l}{l^4}, \; l = \pm 1, \pm 2, \ldots$$

we require $C(l) = C(-l)$ which is obviously true. Also, we require that under rigid displacement:

(10) $$\sum_{l=-\infty}^{\infty} C(l) = 0\,, \quad \text{thus}$$

(11) $$\frac{7}{30}\frac{M\pi^2c^2}{a^2} + \frac{24\,Mc^2}{a^2\pi^2}\sum_{l=1}^{\infty}\frac{(-1)^l}{l^4} = 0$$

if the calculations are correct.

Assignment #1
Problem Set #1
Continued

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4. Continued

To perform the check, we must evaluate the series. By the Markoff transformation:

$$(12)\quad \sum_{l=1}^{\infty} \frac{(-1)^{l+1}}{l^{2v}} = (-1)^{v-1} \frac{(2^{2v-1}-1)\pi^{2v}}{(2v)!} B_{2v} = -\sum_{l=1}^{\infty} \frac{(-1)^{l}}{l^{2v}}$$

where B_{2v} are the Bernoulli numbers and $v = 2$, we have,

$$(13)\quad \sum_{l=1}^{\infty} \frac{(-1)^{l}}{l^{4}} = \frac{7\pi^4}{24} B_4 = \frac{7\pi^4}{24} \cdot \frac{-1}{30} = -\frac{7\pi^4}{24\cdot 30}$$

Substituting in (11),

$$(14)\quad \frac{1}{30} \frac{M\pi^2 c^2}{a} + \left[-\frac{7\pi^4}{24\cdot 30} \cdot \frac{24 M c^2}{a^2 \pi^2} \right] \equiv 0$$

REMARKS: The Fourier coefficients (or $c(e)$) were calculated on the assumption of an infinite lattice and interaction between each atom. Although this may be inconsistent with boundary conditions, it permits the easy application of Fourier techniques as a method of calculating the elastic constants and for a large crystal represents a good approximation. Also, the function $\omega^2(q)$ which was given was taken to apply over the principal values of the argument of the cosine term in the series and to be periodic with this interval although that is not explicitly stated.

Nice! (10)

Assignment #1
Problem Set #1
Continued

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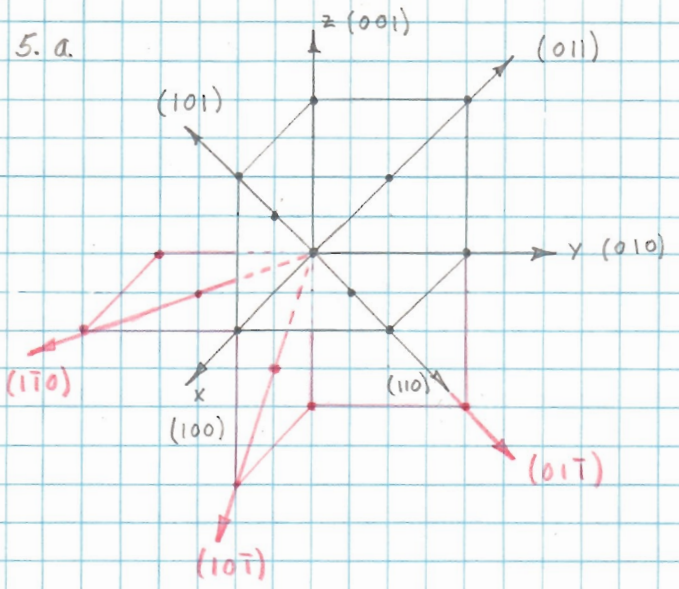
5. a.



Face Centered Cubic: nearest neighbors along face diagonals.

For the (110) direction, the appropriate symmetry operation to keep this direction invariant is:

(1) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} y \\ x \\ z \end{pmatrix}$

which is a rotation of 180° around this direction, with a reflection thru the xy plane.

(2) $S = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

(3) $\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} c_{12} & c_{11} & c_{13} \\ c_{22} & c_{21} & c_{23} \\ c_{32} & c_{31} & c_{33} \end{pmatrix}$

$= \begin{pmatrix} c_{22} & c_{21} & c_{23} \\ c_{12} & c_{11} & c_{13} \\ c_{32} & c_{31} & c_{33} \end{pmatrix}$ From which we deduce: $c_{22} = c_{11}$, $c_{21} = c_{12}$

(4) A second symmetry operation leaving (110) invariant is a simple reflection thru the xy plane:

$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$; $S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

(5) $\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & -c_{13} \\ c_{21} & c_{22} & -c_{23} \\ -c_{31} & -c_{32} & c_{33} \end{pmatrix}$

From which we deduce: $c_{13} = -c_{13} = 0$, $c_{32} = -c_{32} = 0$
$c_{23} = -c_{23} = 0$, $c_{31} = -c_{31} = 0$

Therefore there are only 3 independent parameters:

(6) $C(110) = \begin{pmatrix} \alpha & \gamma & 0 \\ \gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$ ✓

For the other directions we have:

(011): $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$; $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$; $C(011) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & \gamma \\ 0 & \gamma & \alpha \end{pmatrix}$

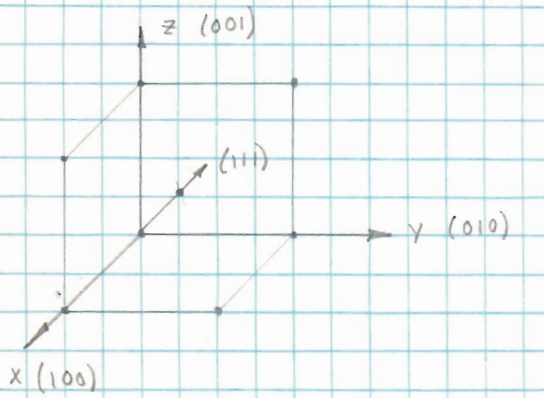
$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$ $\quad S = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

(101): $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} z \\ y \\ x \end{pmatrix}$; $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$; $C(101) = \begin{pmatrix} \alpha & 0 & \gamma \\ 0 & \beta & 0 \\ \gamma & 0 & \alpha \end{pmatrix}$

$S = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ $\quad S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

C(0)? what about C(1,-1)?

The negatives of these three directions have identical matrices from inversion symmetry



Body Centered Cubic: nearest neighbors in direction of cubic diagonal.

An appropriate symmetry operation leaving the (111) direction invariant is:

(1) $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} y \\ x \\ z \end{pmatrix}$; $S = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

From which:

$C_{11} = C_{22}$, $C_{23} = C_{13}$

$C_{21} = C_{12}$, $C_{31} = C_{32}$

(2) A second proper symmetry operation is:

$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ z \\ y \end{pmatrix}$; $S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$; From which: $C_{22} = C_{33}$, $C_{12} = C_{13}$

$C_{32} = C_{23}$, $C_{31} = C_{21}$

Therefore, there are only 2 independent parameters:

(3) $C(111) = \begin{pmatrix} \alpha & \gamma & \gamma \\ \gamma & \alpha & \gamma \\ \gamma & \gamma & \alpha \end{pmatrix}$; these α's and γ's are not necessarily the same as above.

Since $\vec{F}_i = C \vec{u}_e$, we could have for the force on the nearest neighbor, in the, say, (110) direction:

(4) $F_x = \alpha u_x + \gamma u_y$

$F_y = \gamma u_x + \alpha u_y$

$F_z = \beta u_z$

C(0)? C(1,-1,1)?

which checks with me's intuitive feeling about the forces on this atom.

Assignment #1
Problem Set #1
Continued

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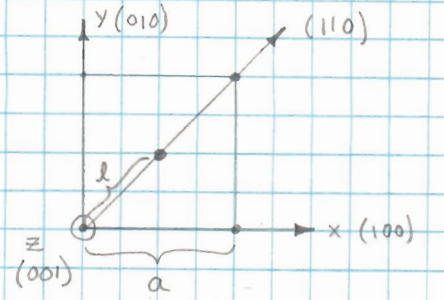
5. b. (1) For nearest neighbor central forces, we have, in general:

$$\mathbb{C}(l) = \frac{1}{2}\frac{k}{l^2}\begin{pmatrix} l_x l_x & l_x l_y & l_x l_z \\ l_y l_x & l_y l_y & l_y l_z \\ l_z l_x & l_z l_y & l_z l_z \end{pmatrix}$$

For the face centered cubic in the (110) direction:



It is seen that there is no z component of l, so that $l_z = 0$ and all matrix elements containing it vanish. Also, from the squareness of the xy (001) plane, $l_x = l_y$.

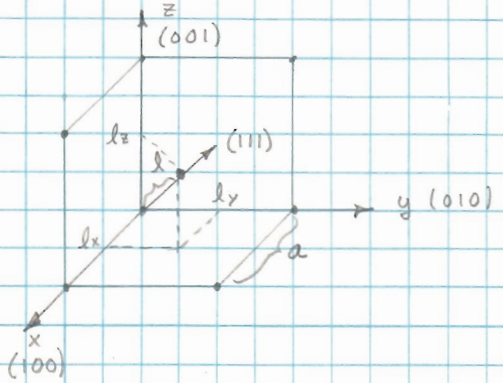
Now: $l = \frac{\sqrt{2}}{2}a$, $l^2 = \frac{a^2}{2}$

$$l_x = l_y = a/2$$

(2) Thus: $\mathbb{C}(110) = \frac{k}{2}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$; $\mathbb{C}(011) = \frac{k}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}$; ✓

$$\mathbb{C}(101) = \frac{k}{2}\begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$

For the body centered cubic in the (111) direction:



From the cubic symmetry:

$$l = \frac{\sqrt{3}}{2}a, \quad l^2 = \frac{3}{4}a^2$$

$$l_x = l_y = l_z = \frac{a}{2}$$

$$\mathbb{C}(111) = \frac{1}{3}k\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$$ ✓

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Since they will be needed later, we will now compute the matrices for the $(1\bar{1}0)$, $(01\bar{1})$, and $(10\bar{1})$ directions of nearest neighbor interaction in the f.c.c. It is evident that these matrices will be of the same form as (110), (011) and (101). The question now arises as to the sign of the independent parameters. The central force model can be of help here when we note the sign changes of the off-diagonal elements for each of the three above directions. Therefore:

$$\mathbb{C}(1\bar{1}0) = \begin{pmatrix} \alpha & -\gamma & 0 \\ -\gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix} \quad ; \quad \mathbb{C}(01\bar{1}) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & -\gamma \\ 0 & -\gamma & \alpha \end{pmatrix} \quad ; \quad \mathbb{C}(10\bar{1}) = \begin{pmatrix} \alpha & 0 & -\gamma \\ 0 & \beta & 0 \\ -\gamma & 0 & \alpha \end{pmatrix}$$

$$= \mathbb{C}(\bar{1}10) \qquad = \mathbb{C}(0\bar{1}1) \qquad = \mathbb{C}(\bar{1}01)$$

by inversion symmetry:

For the body centered cubic, using the same reasoning as above based on the central force model:

$$\mathbb{C}(111) = \mathbb{C}(\bar{1}\bar{1}\bar{1}) \quad \text{by lattice inversion symmetry.}$$

$$\mathbb{C}(\bar{1}11) = \begin{pmatrix} \alpha & -\gamma & -\gamma \\ -\gamma & \alpha & \gamma \\ -\gamma & \gamma & \alpha \end{pmatrix} \quad ; \quad \mathbb{C}(11\bar{1}) = \begin{pmatrix} \alpha & -\gamma & \gamma \\ -\gamma & \alpha & -\gamma \\ \gamma & -\gamma & \alpha \end{pmatrix} \quad ; \quad \mathbb{C}(1\bar{1}1) = \begin{pmatrix} \alpha & \gamma & -\gamma \\ \gamma & \alpha & -\gamma \\ -\gamma & -\gamma & \alpha \end{pmatrix}$$

$$= \mathbb{C}(1\bar{1}\bar{1}) \qquad = \mathbb{C}(\bar{1}1\bar{1}) \qquad = \mathbb{C}(\bar{1}\bar{1}1)$$

Since nothing has been said concerning the location of the atoms along each direction (except in the central force model) the above matrices with different values for their elements but of the same arrangement are general for any location of the atom along the direction. For example, a matrix of the form $\mathbb{C}(110)$ could be used for next nearest neighbor interaction in the simple cubic.

Assignment #1
Problem Set #1
Continued

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6.a.(1) We have the general relation:

$$\mathcal{C}(\bar{q}) = \sum_{l} \mathcal{C}(l) \exp\left[\lambda \bar{q} \cdot \bar{R}_l\right]$$

We take l to be a set of direction numbers to the atoms of interest from the $l=0$ atom. In this case these are the nearest neighbors of the f.c.c. That is,

$l = (l_x\, l_y\, l_z)$ and the atom in the (110) direction would have $l = (110)$.

$\bar{R}_l$ is the vector position of an atom of interest in the crystal from the position $l=0$, with the direction numbers $l_x\, l_y\, l_z$. For the nearest neighbor in the (110) direction in a f.c.c.,

$$\bar{R}_{(110)} = \frac{a}{2}(\bar{\imath} + \bar{\jmath}) \quad \text{where } \bar{\imath}, \bar{\jmath}, \bar{k} \text{ are the usual cartesian unit vectors.}$$

In general, for nearest neighbor in the f.c.c.,

$$\bar{R}_l = \frac{a}{2}\left(l_x\bar{\imath} + l_y\bar{\jmath} + l_z\bar{k}\right)$$

$\bar{q}$ is the direction of propagation of the lattice and is taken to be a magnitude times a direction vector, viz

$$\bar{q} = q\,\frac{\left(l_x\bar{\imath} + l_y\bar{\jmath} + l_z\bar{k}\right)}{\left[l_x^2 + l_y^2 + l_z^2\right]^{1/2}} = q\left(\bar{\imath}\cos\theta_x + \bar{\jmath}\cos\theta_y + \bar{k}\cos\theta_z\right)$$

(2) We have from considerations in Problem 5:

$\mathcal{C}(110) = \mathcal{C}(\bar{1}\bar{1}0)$ $\quad$ $\mathcal{C}(1\bar{1}0) = \mathcal{C}(\bar{1}10)$

$\mathcal{C}(011) = \mathcal{C}(0\bar{1}\bar{1})$ $\quad$ $\mathcal{C}(01\bar{1}) = \mathcal{C}(0\bar{1}1)$

$\mathcal{C}(101) = \mathcal{C}(10\bar{1})$ $\quad$ $\mathcal{C}(10\bar{1}) = \mathcal{C}(\bar{1}01)$

The distances to the nearest neighbors are:

$$\bar{R}_{(110)} = \frac{a}{2}(\bar{\imath}+\bar{\jmath}) = -\bar{R}_{(\bar{1}\bar{1}0)} \qquad \bar{R}_{(1\bar{1}0)} = \frac{a}{2}(\bar{\imath}-\bar{\jmath}) = -\bar{R}_{(\bar{1}10)}$$

$$\bar{R}_{(011)} = \frac{a}{2}(\bar{\jmath}+\bar{k}) = -\bar{R}_{(0\bar{1}\bar{1})} \qquad \bar{R}_{(01\bar{1})} = \frac{a}{2}(\bar{\jmath}-\bar{k}) = -\bar{R}_{(0\bar{1}1)}$$

$$\bar{R}_{(101)} = \frac{a}{2}(\bar{\imath}+\bar{k}) = -\bar{R}_{(\bar{1}0\bar{1})} \qquad \bar{R}_{(10\bar{1})} = \frac{a}{2}(\bar{\imath}-\bar{k}) = -\bar{R}_{(\bar{1}01)}$$

(3) Evaluating (1) over the 12 nearest neighbors:

$$\mathcal{C}(\bar{q}) = \mathcal{C}(0) + \mathcal{C}(110)\left\{\exp\left(\bar{q}\cdot\bar{R}_{(110)}\right) + \exp\left(-\bar{q}\cdot\bar{R}_{(110)}\right)\right\}$$
$$+ \mathcal{C}(011)\left\{\exp\left(\bar{q}\cdot\bar{R}_{(011)}\right) + \exp\left(-\bar{q}\cdot\bar{R}_{(011)}\right)\right\} + \cdots$$

$$= \mathcal{C}(0) + 2\mathcal{C}(110)\cos\bar{q}\cdot\bar{R}_{(110)} + 2\mathcal{C}(011)\cos\bar{q}\cdot\bar{R}_{(011)} + \cdots$$

(4) $$\sum_{l}\mathcal{C}(l) = \mathcal{C}(0) + 2\mathcal{C}(110) + 2\mathcal{C}(011) + \cdots = 0$$

(5) $$\mathcal{C}(\bar{q}) = -4\left[\mathcal{C}(110)\,\mathrm{sm}^2\tfrac{1}{2}\bar{q}\cdot\bar{R}_{(110)} + \mathcal{C}(011)\,\mathrm{sm}^2\tfrac{1}{2}\bar{q}\cdot\bar{R}_{(011)} + \cdots\right]$$

(6) From $\sum_{\alpha'}\left[\frac{1}{M}C_{\alpha\alpha'}(q) - \delta_{\alpha\alpha'}\omega^2\right]e_{\alpha'} = 0$, and simplifications of (5), we have the following for the eigenvalue determinant for the nearest neighbor interaction in the f.c.c. with arbitrary direction of $\bar{q}$:

$$\begin{vmatrix}
-\frac{4\alpha}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{j}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{j})\right. & -\frac{4\gamma}{M}\sin\frac{a}{2}\bar{q}\cdot\bar{i}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{j} & -\frac{4\gamma}{M}\sin\frac{a}{2}\bar{q}\cdot\bar{i}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{k} & e_1 \\
\left. + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{k})\right\} & & & \\
-\frac{4\beta}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}-\bar{k})\right\} - \omega^2 & & & \\
 & -\frac{4\alpha}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{j}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{j})\right. & & \\
-\frac{4\gamma}{M}\sin\frac{a}{2}\bar{q}\cdot\bar{i}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{j} & \left. + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}-\bar{k})\right\} & -\frac{4\gamma}{M}\sin\frac{a}{2}\bar{q}\cdot\bar{j}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{k} & e_2 = 0 \\
 & -\frac{4\beta}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{k})\right\} - \omega^2 & & \\
 & & -\frac{4\alpha}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{k})\right. & \\
-\frac{4\gamma}{M}\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{i}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{k} & -\frac{4\gamma}{M}\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{j}\,\mathrm{sm}\frac{a}{2}\bar{q}\cdot\bar{k} & \left. + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}+\bar{k}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{j}-\bar{k})\right\} & e_3 \\
 & & -\frac{4\beta}{M}\left\{\mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}+\bar{j}) + \mathrm{sm}^2\frac{a}{4}\bar{q}\cdot(\bar{i}-\bar{j})\right\} - \omega^2 &
\end{vmatrix}$$

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6. b. (1) For central forces, we have from problem 5:

$\beta = 0$, $\alpha = \gamma = \frac{K}{2}$

For wave propagation in the (100) direction: $\bar{q} = q\bar{\imath}$

Under these conditions, we have for the secular equation in the "a" part:

(2)

$$\begin{bmatrix} -\frac{8K}{M}\sin^2\frac{aq}{4} - \omega^2 & 0 & 0 \\ 0 & -\frac{4K}{M}\sin^2\frac{aq}{4} - \omega^2 & 0 \\ 0 & 0 & -\frac{4K}{M}\sin^2\frac{aq}{4} - \omega^2 \end{bmatrix} \begin{bmatrix} \bar{e}_1 \\ \bar{e}_2 \\ \bar{e}_3 \end{bmatrix} = 0$$

Thus: $\omega^2 = -\frac{8K}{M}\sin^2\frac{aq}{4}$ ✓

$\omega^2 = -\frac{4K}{M}\sin^2\frac{aq}{4}$

(3) Following Ziman, we take the highest frequency at a given q for the frequency of the longitudinal mode. The other two are considered the frequencies of the transverse modes. In this case, $\bar{e}_1$ is the eigenvector corresponding to the longitudinal mode. The two transverse modes are seen to be completely degenerate for $\bar{q}$ in this direction.

Longitudinal and transverse have physical meanings.

(4) Now consider $\bar{q}$ in the (110) direction: $\bar{q} = \frac{q}{\sqrt{2}}(\bar{\imath} + \bar{\jmath})$

We then have for the secular equation, substituting the proper values in equation (6) of part a:

$$\begin{bmatrix} -\frac{2K}{M}\left(\sin^2\frac{\sqrt{2}}{4}aq + 2\sin^2\frac{\sqrt{2}}{8}aq\right)-\omega^2 & -\frac{2K}{M}\sin^2\frac{\sqrt{2}}{4}aq & 0 \\ -\frac{2K}{M}\sin^2\frac{\sqrt{2}}{4}aq & -\frac{2K}{M}\left(\sin^2\frac{\sqrt{2}}{4}aq+2\sin^2\frac{\sqrt{2}}{8}aq\right)-\omega^2 & 0 \\ 0 & 0 & -\frac{8K}{M}\sin^2\frac{\sqrt{2}}{8}aq-\omega^2 \end{bmatrix}\begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$$

(5) $\omega^2 = -\frac{8K}{M}\sin^2\frac{\sqrt{2}}{8}aq$. Let φ be $\frac{\sqrt{2}}{8}qa$, then

(6) $\omega^4 - \frac{4K}{M}\left(\sin^2 2\varphi + 2\sin^2\varphi\right)\omega^2 + \frac{16K^2}{M^2}\sin^2\varphi\left(\sin^2 2\varphi + \sin^2\varphi\right) = 0$

(7) $\omega^2 = -\frac{4K}{M}\sin^2\varphi = -\frac{4K}{M}\sin^2\frac{\sqrt{2}}{8}aq$

$\omega^2 = -\frac{4K}{M}\sin^2\varphi\left(4\cos^2\varphi+1\right) = -\frac{4K}{M}\sin^2\frac{\sqrt{2}}{8}aq\left(4\cos^2\frac{\sqrt{2}}{8}aq+1\right)$

No! $\epsilon_3 \perp [110]$

In this case, $\bar{e}_3$ corresponds to the longitudinal mode. The two transverse modes are now degenerate only at $\frac{\sqrt{2}}{8}aq = \pi/2$.

We now make the argument that K is a negative number in order to satisfy a Hooke's Law type force, that is, a restoring force which acts opposite to the direction of displacement of the atom from its equilibrium position. Thus we have:

$\bar{q}(100)$: $\omega_n = \sqrt{2}\left|\sin\frac{aq}{4}\right|$; Longitudinal

$\omega_n = \left|\sin\frac{aq}{4}\right|$; Transverse

$\bar{q}(110)$: $\omega_n = \sqrt{2}\left|\sin\frac{\sqrt{2}}{8}aq\right|$; Longitudinal

$\left.\begin{aligned}\omega_n &= \left|\sin\frac{\sqrt{2}}{8}aq\right| \\ \omega_n &= \left|\sin\frac{\sqrt{2}}{8}aq\right|\left[4\cos^2\frac{\sqrt{2}}{8}aq+1\right]^{1/2}\end{aligned}\right\}$ Transverse

where $\omega_n \equiv \frac{\omega}{\sqrt{\frac{4K}{M}}}$

Assignment #I
Problem Set #I
Continued

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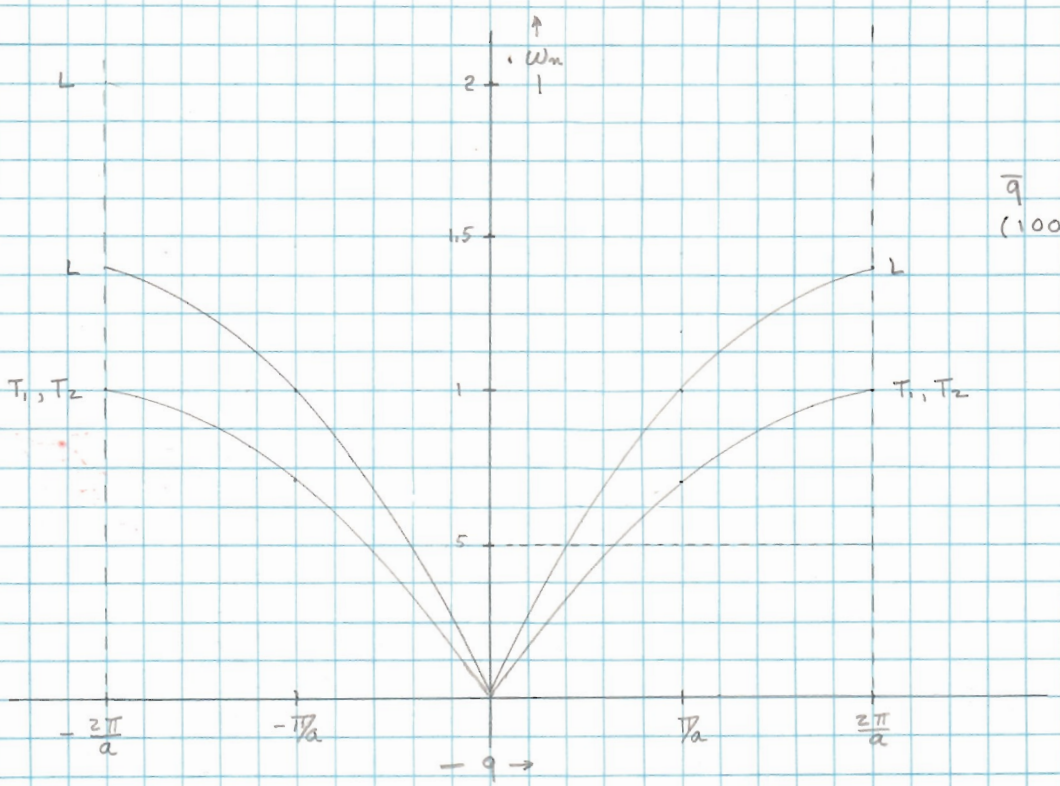
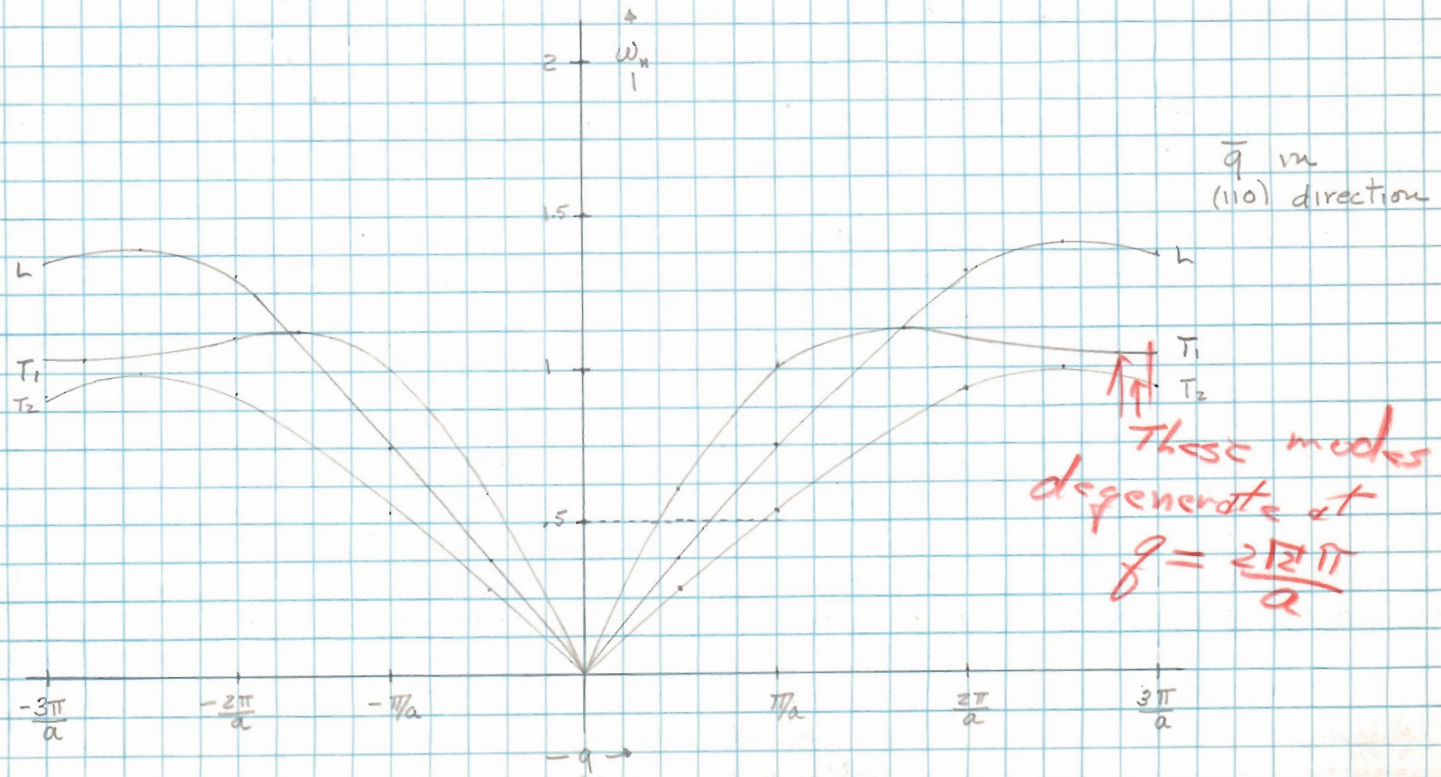
Problem 6
Continued

Dispersion Relationships in The Face-Centered Cubic



$\bar{q}$ in (100) direction



$\bar{q}$ in (110) direction

These modes degenerate at $q = \frac{2\sqrt{2}\pi}{a}$

For the purpose of analyzing waves in an arbitrary direction in the x-y plane, we could do the following:

(8) $\bar{q} = q(\bar{i}\cos\theta_x + \bar{j}\cos\theta_y + \bar{k}\cos\theta_z)$

where $\theta_x, \theta_y, \theta_z$ are the direction angles to $\bar{q}$ from the principal axes of the cube. In the x-y plane, $\cos\theta_z = 0$ and $\cos\theta_y = \sin\theta_x$

(9) $\therefore \quad \bar{q} = q(\bar{i}\cos\theta_x + \bar{j}\sin\theta_x) = q(\bar{i}A + \bar{j}B)$

Substituting in the general secular equation:

$$\begin{bmatrix} -\frac{2K}{M}\left\{\sin^2\frac{a}{4}q(A+B) + \sin^2\frac{a}{4}q(A-B) + 2\sin^2\frac{a}{4}qA\right\} - \omega^2 & -\frac{2K}{M}\sin\frac{a}{2}qA\sin\frac{a}{2}qB & 0 \\ -\frac{2K}{M}\sin\frac{a}{2}qA\sin\frac{a}{2}qB & -\frac{2K}{M}\left\{\sin^2\frac{a}{4}q(A+B) + \sin^2\frac{a}{4}q(A-B) + 2\sin^2\frac{a}{4}qB\right\} - \omega^2 & 0 \\ 0 & 0 & -\frac{2K}{M}\left\{2\sin^2\frac{a}{4}qA + 2\sin^2\frac{a}{4}qB\right\} - \omega^2 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix} = 0$$

Hypothetically, the secular equation could be solved for a set of three equations in polar co-ordinates implicit in the variables (q, θ_x) considering ω a constant parameter. From these equations, with the aid of computing machinery, one could calculate a family of constant frequency surfaces for propagation in the x-y plane.

We will merely use the results from the (100) and (110) directions along with the crystal symmetry to effect a crude sketch.

Taking $\omega_n = .5$:

	L	T_1	T_2
(100)	$.4\,\pi/a$	$.65\,\pi/a$	$.65\,\pi/a$
(110)	$.7\,\pi/a$	$.4\,\pi/a$	$.95\,\pi/a$

The (010) $(1\bar{1}0)$, $(\bar{1}00)$, $(\bar{1}\bar{1}0)$, $(0\bar{1}0)$, $(\bar{1}10)$ directions follow from the obvious symmetry of the f.c.c.

It is to be noted that in this range of ω_n, following the convention of Ziman and Walker, T_1 becomes the longitudinal branch and L the T_1 (upper transverse) branch.

Assignment #1
Problem Set #1
Continued

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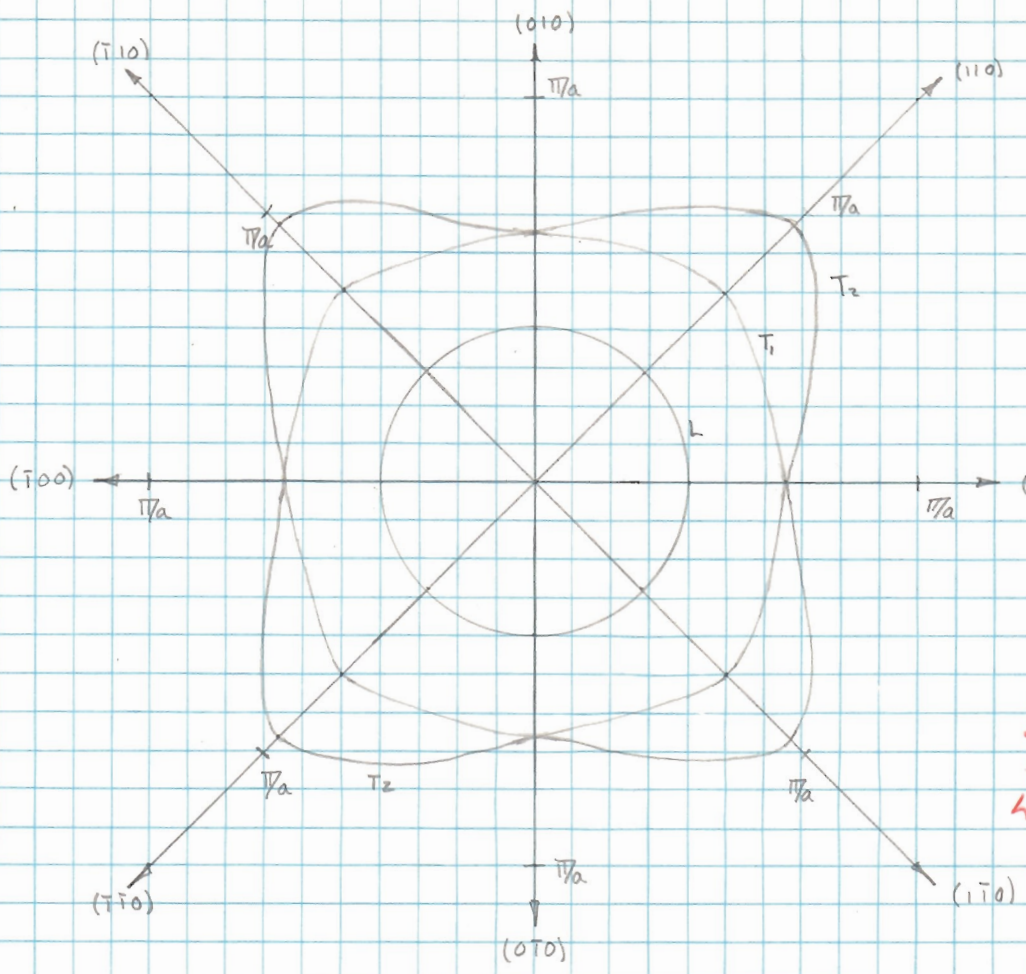

See previous comments. These curves not connected correctly.

Constant Frequency ($\omega_n = .5$) Surfaces in the x-y Plane in the Face-Centered Cubic

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6.c.(1) For wave motion in the (100) direction of the f.c.c. we have from before:

$$\omega_n = \sqrt{2}\left|\sin\frac{aq}{4}\right| \quad ; \text{ Longitudinal}$$

$$\omega_n = \left|\sin\frac{aq}{4}\right| \quad ; \text{ Transverse}$$

(2) For $q \doteq 0$, $\sin\frac{aq}{4} \doteq \frac{aq}{4}$

$$\omega_n = \frac{\sqrt{2}\,a}{4}\,q \quad ; \text{ Longitudinal}$$

$$\omega_n = \frac{a}{4}\,q \quad ; \text{ Transverse}$$

Comparing these equations with $\omega_n = C_n q$ where C_n is the "normalized" velocity of propagation, we see that at long wavelengths, the longitudinal wave is propagated with a velocity 1.414 times that of the transverse waves.

At the Brillouin zone face in the (100) direction:

(3) $q = 2\pi/a$

$(\omega_n)_L = \sqrt{2}\,(\omega_n)_T$ which is always true in this direction regardless of q, however:

(4) $(\omega_n)_L = \sqrt{2}$, $(\omega_n)_T = 1$ } in the neighborhood of the Brillouin zone face, standing waves develop and the lattice vibrations will not propagate.

7

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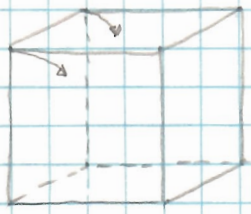
7. The central forces between nearest neighbors in a crystal must be more attractive than repulsive for obvious reasons. In this case, it is possible to collapse a simple cubic without changing the distance between the atoms:



Therefore, the simple cubic is unstable under these conditions.

For the body centered cubic, it is possible to collapse into the (110) plane:

Thus, the body centered cubic is unstable.

10

For the face-centered cubic, one can easily see no collapse can take place without changing the distance between nearest neighbors, and thus it is the only one that is stable under nearest neighbor central forces. One would intuitively expect this from the fact that the f.c.c. is one of the most dense structures.

A review of this question is given in Leibfried, Handbook of Physics, Vol VII/1 pp. 154-155.

Assignment #1
Problem Set #1
Continued

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8.a.(1) Given $\psi_{nq} = A\,(a_q^+)^n \psi_{oq}$ describing the states in the occupation space.

Define: $|n_q\rangle = (a_q^+)^n \psi_{oq}$, neglecting for the moment the normalization constant

$|n_q'\rangle = (a_q^+)^{n'} \psi_{oq}$

We wish to show $\langle n_q' | n_q\rangle \sim \delta_{qq'} = \delta_{nn'}$ to prove orthogonality of the ψ_{nq}'s

(2) Now: $\langle n_q' | n_q\rangle = \langle n_q' | a_q^+ | n_q - 1\rangle$

(3) Consider the following relation which was proven in the lecture:

$$\langle n_q' | [a_q^+, N_q] | n_q\rangle = \langle n_q' | a_q^+ | n_q\rangle (n_q - n_q') = -\langle n_q' | a_q^+ | n_q\rangle$$

or $(n_q - n_q' + 1)\langle n_q' | a_q^+ | n_q\rangle = 0$

Since this relation holds between any two states, we may let n_q become $n_q - 1$ and get:

(4) $(n_q - n_q')\langle n_q' | a_q^+ | n_q - 1\rangle$

$= (n_q - n_q')\langle n_q' | n_q\rangle = 0$ ✓

(5) Thus, if $n_q \neq n_q'$ or $n \neq n'$; $\langle n_q' | n_q\rangle = 0$, thereby giving the orthogonality condition in part. We now investigate the condition for $n = n$.

(6) We now write $\langle n_q | n_q\rangle = \langle n_q | a_q^+ | n_q - 1\rangle$

Consider $\langle n_q | N_q | n_q\rangle = n_q = \langle n_q | a_q^+ a_q | n_q\rangle$ ← This is true only if $\langle n_q | n_q\rangle = 1$

$= \langle n_q | a_q^+ | n_q - 1\rangle \langle n_q - 1 | a_q | n_q\rangle$ $|n_q\rangle = a_q^+ |n_q - 1\rangle$ only if we ignore normalizations

(7) Now: $\langle n_q - 1 | a_q | n_q\rangle = (\psi_{nq-1}, a_q \psi_{nq}) = (a_q^+ \psi_{nq-1}, \psi_{nq})$

$= (\psi_{nq}, a_q^+ \psi_{nq-1})^* = \langle n_q | a_q^+ | n_q - 1\rangle^*$

(8) $\therefore |\langle n_q | a_q^+ | n_q - 1\rangle|^2 = |\langle n_q | n_q\rangle|^2 = n_q = n$

$\langle n_q | n_q\rangle = \sqrt{n}$, considering the phase factor to be unity.

(9) Finally: $\langle n_q' | n_q \rangle = \sqrt{n}\, \delta_{nn'}$

which is the complete orthogonality condition.

b. (1) We can now identify: $(\psi_{nq'}, \psi_{nq}) = |A|^2 \langle n_q' | n_q \rangle = |A|^2 \sqrt{n}\, \delta_{nn'}$

(2) We demand that $(\psi_{nq'}, \psi_{nq}) = \delta_{nn'}$

Therefore $A = n^{-1/4}$ X

c. (1) The general rule for time differentiation of an operator is:

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \frac{1}{i\hbar}[H, A]$$

(2) We hold that N_q is not an explicit function of time, so that:

$$\frac{dN_q}{dt} = \frac{1}{i\hbar}[H, N_q]$$

(3) $[H, N_q] = \left[\sum_{q'} \hbar\omega_{q'}\left(N_{q'} + \tfrac{1}{2}\right), N_q\right] = 0$, since $[N_{q'}, N_q] = 0$ ~~because it is diagonal~~

(4) $\therefore \frac{dN_q}{dt} = 0$, and $N_q = a_q^\dagger a_q$ is a constant of the motion. ✓

should show this.

d. (1) $u_{eb} = G^{-3/2} \sum_q u_{qb}\, e^{i\bar{q}\cdot\bar{R}_e}$

$$u_{qb} = \frac{1}{\sqrt{M_b}} \sum_j \bar{e}(qb_j)\, U_{qj}$$

$$U_{qj} = \sqrt{\frac{\hbar}{2\omega_{qj}}}\left(a_{qj} + a_{-qj}^\dagger\right)$$

(2) $\therefore u_{eb} = \sum_{qj}\left[\frac{\hbar}{2M_b G^3 \omega_{qj}}\right]^{1/2} \bar{e}(qb_j)\left(a_{qj} + a_{-qj}^\dagger\right) e^{i\bar{q}\cdot\bar{R}_e}$

$$= \sum_{qj}\left[\frac{\hbar}{2M_b G^3 \omega_{qj}}\right]^{1/2}\left[\bar{e}(qb_j)\, a_{qj}\, e^{i\bar{q}\cdot\bar{R}_e} + \bar{e}^*(qb_j)\, a_{qj}^\dagger\, e^{-i\bar{q}\cdot\bar{R}_e}\right]$$

$$= \sum_{qj}\left[\frac{1}{M_b G^3}\right]^{1/2} \bar{e}(qb_j)\, e^{i\bar{q}\cdot\bar{R}_e} \cdot \sqrt{\frac{\hbar}{2\omega_{qj}}}\left[a_{qj} + \frac{\bar{e}^*(qb_j)}{\bar{e}(qb_j)}\, a_{qj}^\dagger\, e^{-2i\bar{q}\cdot\bar{R}_e}\right]$$

Assignment #1
Problem Set #1
Continued

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8. d. (3) $$a^{\dagger}_{-q_\beta} = \frac{\bar{e}^*(qb_\beta)}{\bar{e}(qb_\beta)}\, a^{\dagger}_{q_\beta}\, e^{-2\pi \bar{q}\cdot\bar{R}_\ell} = \left\{\bar{e}^*(qb_\beta)\right\}^2 a^{\dagger}_{q_\beta}\, e^{-2\pi \bar{q}\cdot\bar{R}_\ell}$$

(4) $$\therefore\ u_{q_\beta} = \sqrt{\frac{\hbar}{2\omega_{q_\beta}}}\,\left(a_{q_\beta} + a^{\dagger}_{q_\beta}\right)$$

$$= \sqrt{\frac{\hbar}{2\omega_{q_\beta}}} \begin{vmatrix} 0 & \sqrt{1} & 0 & \cdots \\ \left\{\bar{e}^*\right\}^2 e^{-2\pi\bar{q}\cdot\bar{R}_\ell}\sqrt{1} & 0 & \sqrt{2} & \cdots \\ 0 & \left\{\bar{e}^*\right\}^2 e^{-2\pi\bar{q}\cdot\bar{R}_\ell}\sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}$$

(5) $$P_{q_\beta} = \imath\sqrt{\frac{\hbar\omega_{q_\beta}}{2}}\left(a^{\dagger}_{q} - a_{-q}\right) = \imath\sqrt{\frac{\hbar\omega_{q_\beta}}{2}}\left[a^{\dagger}_{q} - \left\{\bar{e}(qb_\beta)\right\}^2 a_{q_\beta}\, e^{2\pi\bar{q}\cdot\bar{R}_\ell}\right]$$

$$= \imath\sqrt{\frac{\hbar\omega_{q_\beta}}{2}} \begin{vmatrix} 0 & -\left\{\bar{e}\right\}^2 e^{2\pi\bar{q}\bar{R}_\ell}\sqrt{1} & 0 & 0 & \cdots \\ \sqrt{1} & 0 & -\left\{\bar{e}\right\}^2 e^{2\pi\bar{q}\cdot\bar{R}_\ell}\sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & & \\ \vdots & \vdots & \vdots & & \end{vmatrix}$$

Are they Hermitian?

8.e. (1) Beginning with:

$$a_q = \frac{\imath}{\sqrt{2\hbar\omega_q}}\, p_q^\dagger + \sqrt{\frac{\omega_q}{2\hbar}}\, u_q$$

$$u_{qj} = \sum_b \sqrt{M_b}\; \bar{e}^*(qb_j)\; u_{qb}$$

$$p_{qj}^\dagger = \sum_b \frac{1}{\sqrt{M_b}}\; \bar{e}^*(qb_j)\; p_{qb}^\dagger$$

$$u_{qb} = \frac{1}{G^{3/2}} \sum_l u_{lb}\, e^{-\imath \bar{q}\cdot\bar{R}_l}$$

$$p_{qb}^\dagger = \frac{1}{G^{3/2}} \sum_l p_{lb}^\dagger\, e^{-\imath \bar{q}\cdot\bar{R}_l}$$

$$u_{lb} = \sum_{qj} \bar{e}(qb_j)\, e^{\imath(\bar{q}\cdot\bar{R}_l - \omega_{qj} t)}$$

$$p_{lb}^\dagger = M_b \dot{u}_{lb}^\dagger = \sum_{qj} M_b\, \bar{e}^*(qb_j)\, (\imath\omega_q)\, e^{-\imath(\bar{q}\cdot\bar{R}_l - \omega_{qj} t)}$$

(2) Combining, we have:

$$a_q = \frac{1}{G^{3/2}} \sum_{blq_j} \sqrt{\frac{M_b\,\omega_{qj}}{2\hbar}} \left[e^{-\imath\omega_{qj} t} - \left\{ \bar{e}^*(qb_j) \right\}^2 e^{2\imath\bar{q}\cdot\bar{R}_l}\, e^{\imath\omega_{qj} t} \right]$$

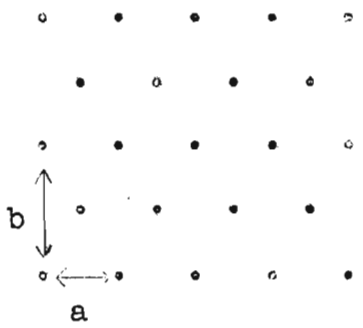
thus demonstrating that the operators a_q, $a_q^\dagger$, $a_{-q}^\dagger$ will have a harmonic time dependence.

This equation cannot be correct. The label q stands for q and j on the left hand side. On the R.H.S. you sum over $q \neq j$ and leave no labels remaining.

Problems IV

Applied Physics 295

9. Construct the first five Brillouin zones for the two dimensional face centered lattice shown below, assuming b = 2a.



Plot E vs. k, for k in [10] and [11] directions, assuming an empty lattice. Show the first five energy bands. Indicate briefly, and without calculations, how the band structure is modified when a weak periodic potential is applied.

10. Consider the one-dimensional Kronig-Penney problem with

$$V(x) = a\,V_o \sum_n \delta(x-na)$$

Assume the cells to be labelled by the n corresponding to the δ-function bounding it to the left. If x_n is the coordinate in the cell with respect to this δ-function as origin, show that the two allowed solutions of the Schrödinger equation are:

$$\psi_1 = \cos nka \sin\alpha a \cos\alpha x_n + \left[\cos(n+1)ka - \cos nka \cos\alpha a\right] \sin\alpha x_n$$

$$\psi_2 = \sin nka \sin\alpha a \cos\alpha x_n + \left[\sin(n+1)ka - \sin nka \cos\alpha a\right] \sin\alpha x_n$$

Show that the two unallowed solutions may be written in the form:

$$\psi_{1,2} = r_{1,2}^{n} \left[\sin\alpha a \cos\alpha x_n + (r_{1,2} - \cos\alpha a) \sin\alpha x_n \right]$$

Why are these solutions physically allowed and unallowed, respectively?

11. For the Kronig-Penney problem described in Problem 10, show that the energy in the various bands as a function of the reduced wave vector k satisfies the relation

$$1 + V_o \sum_{\mu} \left[\frac{1}{\frac{h^2}{2m}(k_o + \frac{2\pi\mu}{a})^2 - E} \right] = 0$$

12. Compute the density of states and Fermi energy at absolute zero temperature for a band containing n electrons per unit volume for which E vs. k is given by

$$E = \frac{h^2}{2m} \left[a_{11}k_x^2 + a_{22}k_y^2 + a_{33}k_z^2 + a_{12}k_x k_y + a_{13}k_x k_y + a_{23}k_y k_z \right]$$

Problems V

Applied Physics 295

13. Prove that an arbitrary, but reasonably behaved function $f(E_n(k))$ satisfies the relationship

$$\frac{\partial}{\partial k_\alpha} f(E_n(k)) = i \langle nk | \left[f(H), x_\alpha \right] | nk \rangle$$

where $H|nk\rangle = E_n(k)|nk\rangle$ and $|nk\rangle \rightarrow b_n(k,r)$.

14. Consider a band in a cubic crystal with extremum at $k = 0$. Let the wave functions have p symmetry, so that at $k = 0$, the degenerate set

$|x\rangle = u^{(1)}(0,r) = xf(r)$, $|y\rangle = u^{(2)}(0,r) = yf(r)$, $|z\rangle = u^{(3)}(0,r) = zf(r)$ must be considered. Use the $\underline{k}\cdot\underline{p}$ perturbation method to show that the coefficients a_{ij} determining the correct linear combinations

$$u_i(k,r) = \sum_j a_{ij} u^{(j)}(0,r)$$

and the second order correction to the energy $E_i^{(2)}$ are determined by the equation

$$\begin{bmatrix} L k_x^2 + M(k_y^2 + k_z^2) & Nk_yk_x & Nk_xk_z \\ Nk_xk_y & Lk_y^2 + M(k_x^2 + k_z^2) & Nk_yk_z \\ Nk_xk_z & Nk_yk_z & Lk_z^2 + M(k_x^2 + k_y^2) \end{bmatrix} \begin{bmatrix} a_{i1} \\ a_{i2} \\ a_{i3} \end{bmatrix} = E_i^{(2)} \begin{bmatrix} a_{i1} \\ a_{i2} \\ a_{i3} \end{bmatrix}$$

15. Prove that an arbitrary, but reasonably behaved function $f(\vec{p}^{\,2}(x))$ satisfies the relationship

$$\int_{-\infty}^{\infty} f(\vec{p}^{\,2}(x))\,dx = \int_{-\infty}^{\infty} f(\vec{p}^{\,2}(x))\,dp_x$$

16. Consider a band in a cubic crystal with extrema at the wave functions have p dependence

$$|x\rangle = u^{(1)}(0,r) = xf(r)\,|\lambda\rangle = u^{(2)}(0,r) = yf(r)\,|\lambda\rangle = u^{(3)}(0,r) =$$

a $f(r)$ must be considered. Use the $\vec{k}\cdot\vec{p}$ perturbation method to show that the coefficients c_{ij} satisfy the correct linear combinat

$$u^{(1)}(0,r)$$

and the second order correction to the energy $E^1_{(s)}$ are determined by the equation

$$\begin{bmatrix} K_x^S + M(K_S \quad K_\lambda^S) & MK_\lambda K_x & MK_x K_s & c_{11} \\ MK_\lambda K_x & LM_S^\lambda + M(K_S^x + K_s^S) & MK_\lambda K_s & c_{12} \\ MK_x K_s & K_\lambda^s & LM_S^s + M(K_S^x + K_\lambda^S) & c_{13} \end{bmatrix}$$

where

$$L = \frac{\hbar^2}{m^2} \sum_i \frac{\langle x|p_x|i\rangle\langle i|p_x|x\rangle}{E_o - E_i}$$

$$M = \frac{\hbar^2}{m^2} \sum_i \frac{\langle x|p_y|i\rangle\langle i|p_y|x\rangle}{E_o - E_i}$$

$$N = \frac{\hbar^2}{m^2} \sum_i \frac{\langle x|p_x|i\rangle\langle i|p_y|y\rangle + \langle x|p_y|i\rangle\langle i|p_x|y}{E_o - E_i}$$

Here E is defined by $H_o|x\rangle = E_o|x\rangle$; $H_o = \frac{p^2}{2m} + V(r)$,

and similarly for $|y\rangle$ and $|z\rangle$. E_i are energies of other bands at k = 0. For purposes of this problem possible degeneracies in the bands $i \neq 0$ may be neglected.

Describe <u>qualitatively</u> the E vs. k curves and the shape of the constant energy surfaces obtained if the secular equation for $E_\lambda^{(2)}(k)$ were to be solved.

<u>Hints</u>: (1) The treatment of second-order degenerate perturbation theory, as given in Schiff's <u>Quantum Mechanics</u> (Sec. 25), will be useful.

(2) Be sure to use symmetry arguments to eliminate as many vanishing matrix elements as possible at each appropriate step of the calculation.

15. Show that in the crystal momentum representation, the Schrödinger eq. in the presence of a perturbation U(r), depending only on r takes the form

$$\left[E + U(\underline{R} + \mathbb{X}) - i\hbar\frac{\partial}{\partial t}\right]\underline{\Phi}(k) = 0$$

where $\underline{R} = i\nabla_k$,

$$E = \begin{bmatrix} E_1(k) & 0 & 0 & \cdot \\ 0 & E_2(k) & 0 & \cdot \\ 0 & 0 & E_3(k) & \cdot \\ & \cdot & \cdot & \cdot \end{bmatrix} \qquad \underline{\Phi} = \begin{bmatrix} \Phi_1(k) \\ \Phi_2(k) \\ \Phi_3(k) \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}$$

$$\mathbb{X} = \begin{bmatrix} X_{11}(k) & X_{12}(k) & \cdot \\ X_{21}(k) & X_{21}(k) & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}$$

The subscripts are band indices.

Problems VI

Applied Physics 295

16. Show that the Fermi level E_F of a free electron gas in a uniform magnetic field H is related to E_F^o, the Fermi level in the absence of a magnetic field, by the relationship

$$\frac{2}{3}\left(\frac{E_F^o}{\hbar\omega_o}\right)^{3/2} = \sum_{n=o}^{n_{max}} \left[\frac{E_F}{\hbar\omega_o} - (n + \tfrac{1}{2})\right]^{1/2}$$

where $\omega_o = eH/mc$. Sketch the behavior of $E_F/\hbar\omega_o$ as a function of $E_F^o/\hbar\omega_o$ and interpret the results.

17. Show that in the limit that $T \longrightarrow 0$, the electronic specific heat of a free electron gas has the temperature dependence $C \sim T/|\log T|$ when exchange is included. You may follow the treatment of the problem given by E.P. Wohlfarth [Phil. Mag. 41, 534 (1950)], but include only enough of the calculation to obtain the above asymptotic form. Give a physical discussion of your results.

ASSIGNMENT #2
Problems
9-15

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11-21-60

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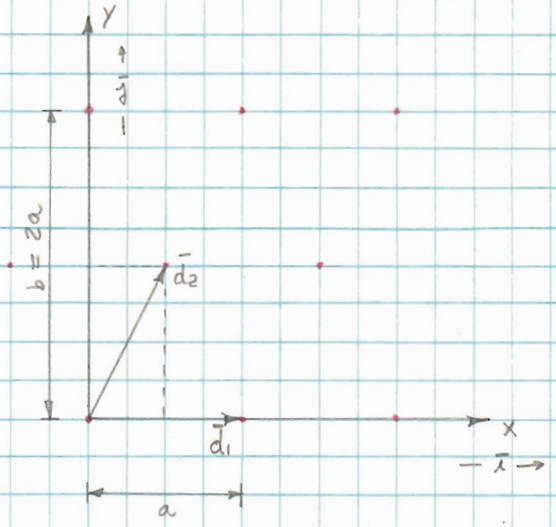
9. Consider the following two dimensional lattice:



Although the lattice is a face-centered rectangle, we will consider it as a monatomic lattice generated by the basis vectors $\bar{d}_1$ and $\bar{d}_2$ for the purpose of constructing the reciprocal lattice.

We will follow the method of Brillouin (Ch. 6, Wave Propagation in Periodic Structures) for finding the reciprocal lattice vectors $\bar{b}_1$ and $\bar{b}_2$ in a two dimensional lattice.

(1) $\bar{b}_\ell \cdot \bar{d}_k = \delta_{\ell k}$; $\ell, k = 1,2$ must be satisfied, we write the matrices of the vectors and multiply to obtain (1):

(2) $$(\bar{b}_1 \quad \bar{b}_2)\cdot\begin{pmatrix}\bar{d}_1\\ \bar{d}_2\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = \mathbb{1} \quad , \text{ or } B'D = \mathbb{1} \; , \; \therefore B = (D^{-1})'$$

where $$B = \begin{pmatrix}\bar{b}_1\\ \bar{b}_2\end{pmatrix} = \begin{pmatrix}b_{1x} & b_{1y}\\ b_{2x} & b_{2y}\end{pmatrix} \; ; \quad D = \begin{pmatrix}\bar{d}_1\\ \bar{d}_2\end{pmatrix} = \begin{pmatrix}d_{1x} & d_{1y}\\ d_{2x} & d_{2y}\end{pmatrix}$$

(3) $$(D^{-1})' = \begin{pmatrix}\frac{d_{2y}}{|D|} & -\frac{d_{2x}}{|D|}\\ -\frac{d_{1y}}{|D|} & \frac{d_{1x}}{|D|}\end{pmatrix} \; ; \quad b_{1x} = \frac{d_{2y}}{|D|} \; , \quad b_{1y} = -\frac{d_{2x}}{|D|}$$

$$b_{2x} = -\frac{d_{1y}}{|D|} \; , \quad b_{2y} = \frac{d_{1x}}{|D|}$$

(4) $$\bar{b}_1 = \frac{1}{|D|}\left(\bar{i}\, d_{2y} - \bar{j}\, d_{2x}\right)$$

$$\bar{b}_2 = \frac{1}{|D|}\left(-\bar{i}\, d_{1y} + \bar{j}\, d_{1x}\right)$$

$$|D| = d_{1x}d_{2y} - d_{1y}d_{2x}$$

It is clear that we can define the following pseuso-vector operations in a plane in order to write the expressions more compactly:

$$|D| = |\bar{d}_1 \times \bar{d}_2| = \left\| \begin{matrix} \bar{i} & \bar{j} & \bar{k} \\ d_{1x} & d_{1y} & 0 \\ d_{2x} & d_{2y} & 0 \end{matrix} \right\| \; ; \quad \bar{u} \times \bar{d}_1 = \left| \begin{matrix} \bar{i} & \bar{j} & \bar{k} \\ 0 & 0 & 1 \\ d_{1x} & d_{1y} & 0 \end{matrix} \right|$$

$$\bar{d}_2 \times \bar{u} = \left| \begin{matrix} \bar{i} & \bar{j} & \bar{k} \\ d_{2x} & d_{2y} & 0 \\ 0 & 0 & 1 \end{matrix} \right|$$

(5) $\therefore \quad \bar{b}_1 = \dfrac{\bar{d}_2 \times \bar{u}}{|\bar{d}_1 \times \bar{d}_2|} \; ; \quad \bar{b}_2 = \dfrac{\bar{u} \times \bar{d}_1}{|\bar{d}_1 \times \bar{d}_2|}$, with $|\bar{d}_1 \times \bar{d}_2|$ the area of the unit cell.

In this case: $d_{1x} = a$, $d_{1y} = 0$

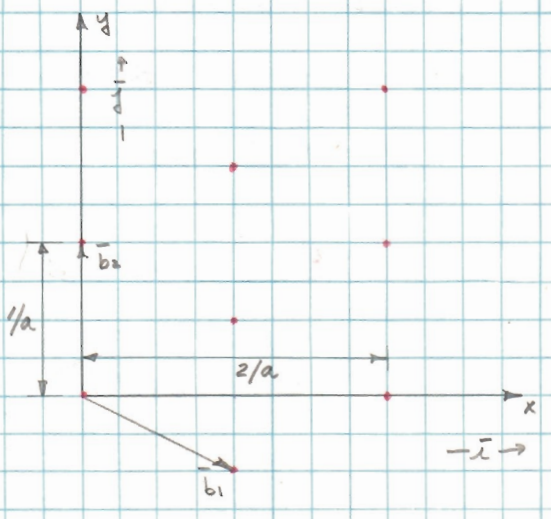
$d_{2x} = a/2$, $d_{2y} = a$

$\Big\}$ $|A| = a^2$

and we have:

(6) $\bar{b}_1 = \bar{i}\,\frac{1}{a} - \bar{j}\,\frac{1}{2a} \; ; \quad \bar{b}_2 = \bar{j}\,\frac{1}{a}$

The reciprocal lattice is then:



This is merely the direct lattice rotated thru 90°.

(7) Consider the following equation for an empty lattice. This is a paraboloid of revolution.

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2)$$

Thus, a cross-section along any direction will yield a simple parabola.

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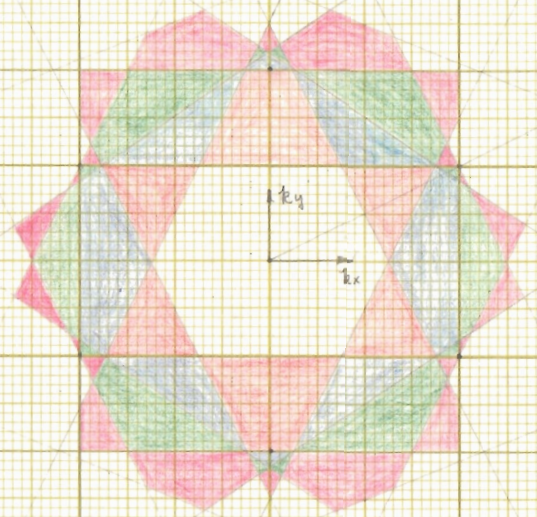
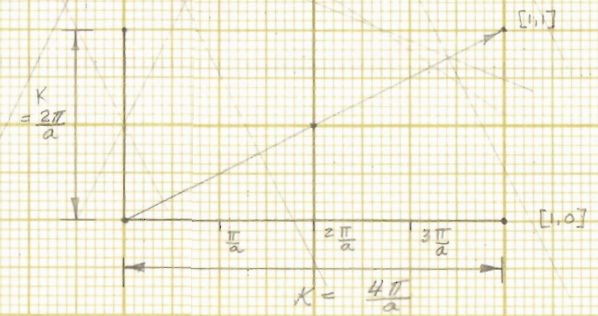
Problem 9



Colour : 87

White : 1
Red : 2
Blue : 3
Green : 4
Pink : 5



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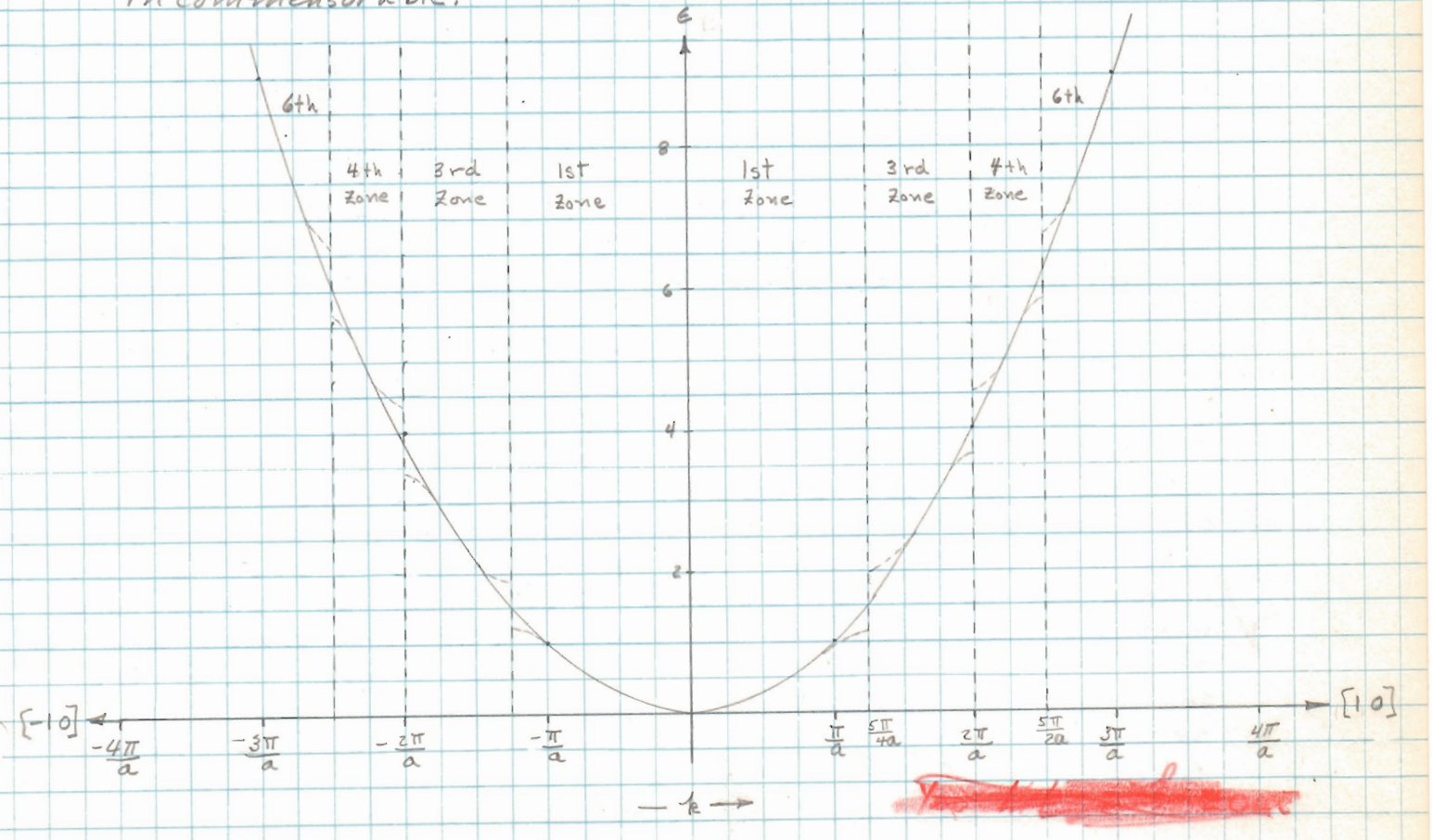
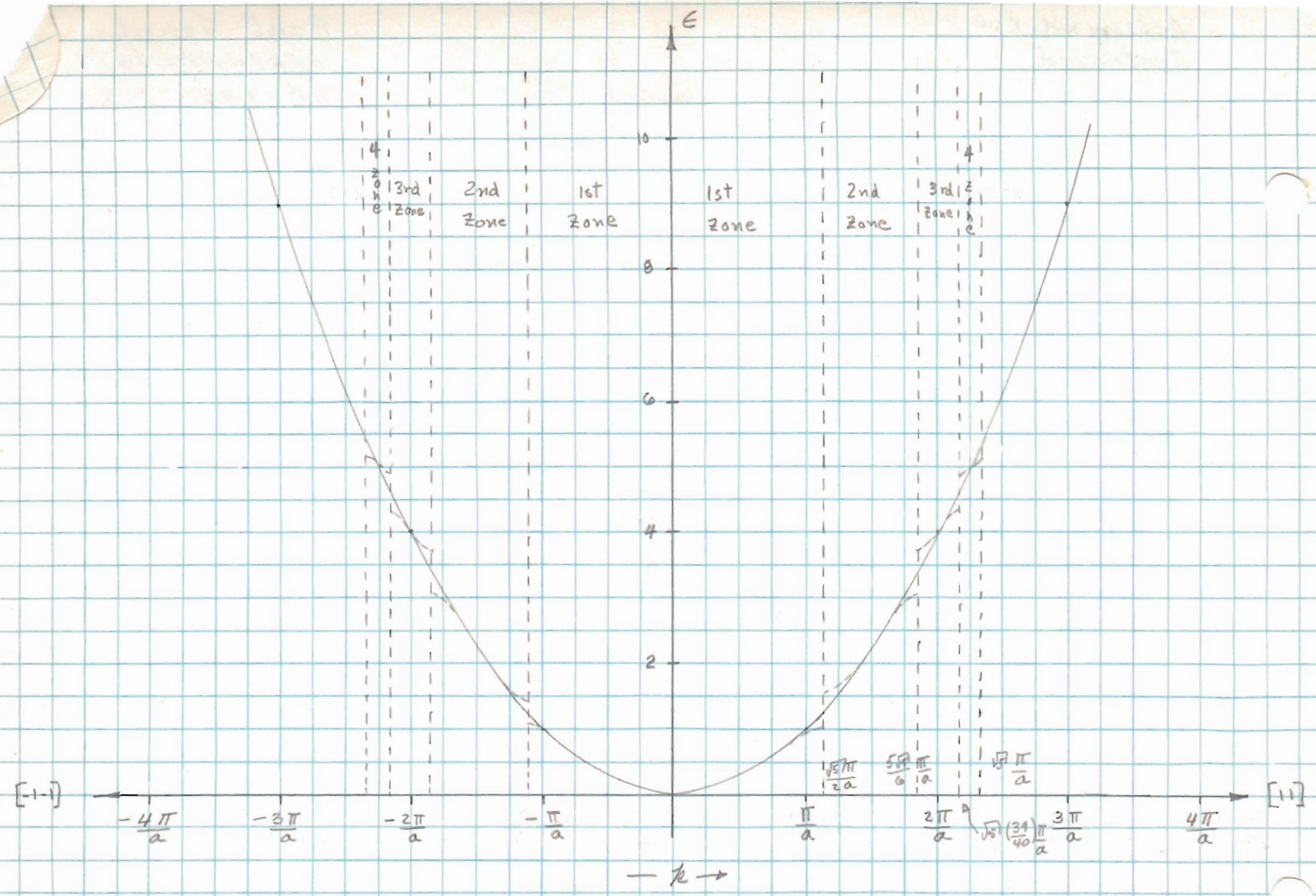
9. Continued

(B) Against this background, we will superpose the effect of the lattice. At this point, the procedure becomes somewhat obscure to me. It seems as if the proper way to proceed would be to extend lines in the desired direction on the two-dimensional diagram of the Brillouin zones and indicate a zone interval on the one dimensional plot whenever we intersect a zone face on the two dimensional plot. However, in some directions, the [1,0] for example, this would cause not only aperiodicity in the one dimensional plot, but even the absence of some zones altogether. On the other hand, since all zones can be mapped into the first on the two-dimensional plot, one feels that there should be some periodicity in the one dimensional diagram. If one considers the reduced zone scheme in both plots, all the bands in the one dimensional plot must extend over the first zone, since all the zones on the two dimensional diagram will have be mapped into the first zone. The paradox seems incommensurable.



Define the normalized energy: $\epsilon = \frac{2mEa}{\hbar^2\pi}$



NB: The scale is the acual distance along the [11] direction, found by the square root of the sum of the squares of the (k_x, k_y) coordinates of the intersection with a BZ face.

When the lattice is introduced as a perturbation, the degeneracies that appear at BZ faces will be removed, as shown in the diagram, by the application of degenerate perturbation theory. Hence, there will be a gap appearing in the energy function as it intersects the faces of the BZ.

It seems a little clearer now that one must not confuse the one dimensional BZ with the two dimensional BZ. When one plots a cross-section of a two dimensional E vs k relation, there is no reason to expect a one dimensional E vs k result. Only when all zones are mapped into the first in the 2-D representation can we show a 1-D cross-section that would have 5 bands spanning the first zone. We cannot reduce the extended zones in the 1-D crosseotion because we would only be mapping back that portion of those zones intersected by the line of cross-section.

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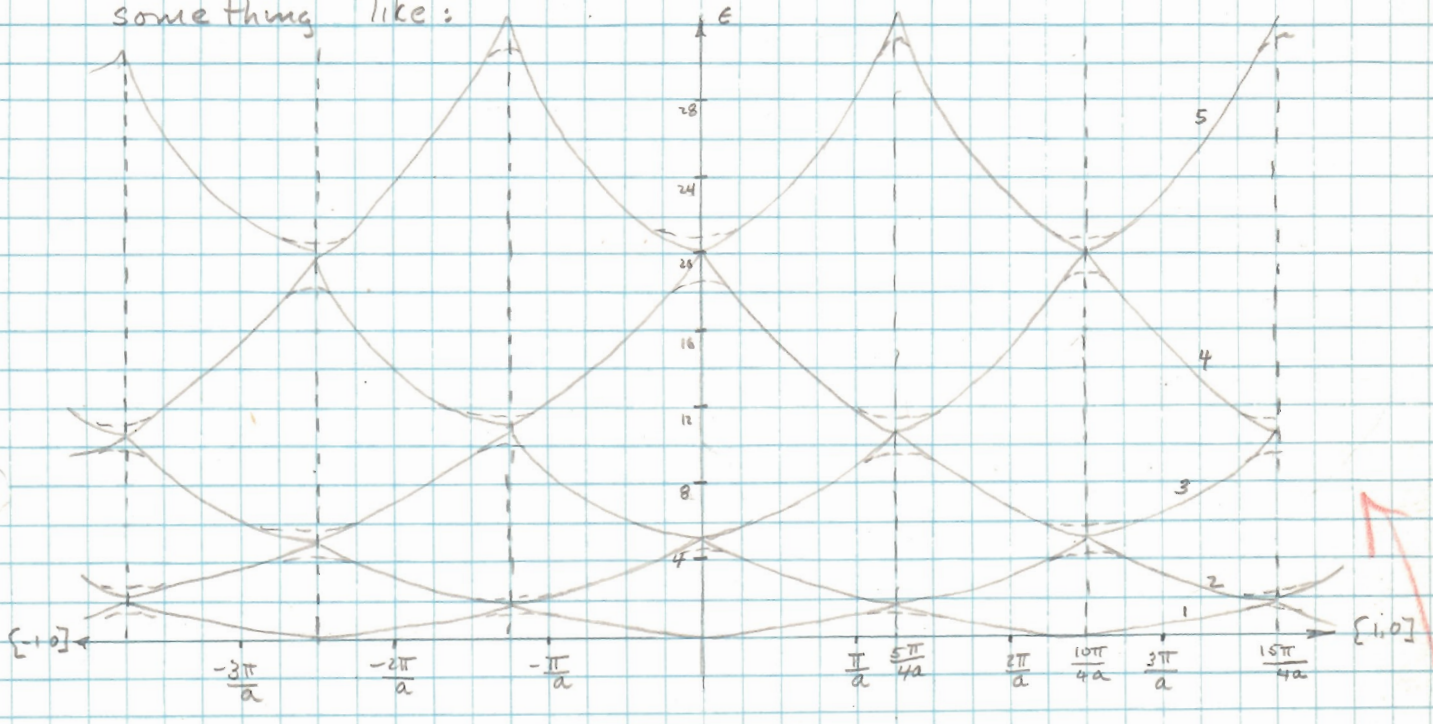
9 Continued:

In this problem, we could have used the repeated zone scheme, repeating the first BZ over the plane of the lattice. This would have given periodic BZ's in the cross-sections along the various directions. The higher zones could be mapped back into the first zone also and then repeated over the plane of the lattice. Thus the resulting picture would be something like:



A similar diagram for the [11] direction can be found from the diagram on the preceeding page using the 1st BZ as the period. It will have the same shape as above except the period will be $\frac{\sqrt{2}\pi}{2a}$.

No, there is degeneracy.
Must get this by mapping

(10)

Assignment # 2
Continued

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10. (1) Before embarking on this problem, we give a fast proof of the Bloch Theorem so as to indicate that quantum mechanically there will exist allowed and non-allowed solutions of the Schroedinger equation for motion in a periodic field, viz:

$$V(x+a) = V(x) \quad , \text{with}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V\{x\})\psi = 0$$

with two linearly independent solutions $u(x)$ and $v(x)$. Two other possible obvious solutions are $u(x+a)$, $v(x+a)$. However, the equation must only have two linearly independent solutions and thus we must be able to form $u(x+a)$ and $v(x+a)$ from linear combinations of $u(x)$, $v(x)$:

$$u(x+a) = \alpha u(x) + \beta v(x)$$

$$v(x+a) = \gamma u(x) + \delta v(x)$$

(2) It is well-known that the Wronskian of a linear second order differential equation with the first derivative term absent is equal to a constant. Whether or not this constant is non-zero depends upon whether or not the solutions are quadratically integrable. If they are not, then the Wronskian is non-vanishing. In our case, we shall take the wave functions to be non-quadratically integrable and show later that this is indeed the case. Therefore:

$$\begin{vmatrix} u(x) & v(x) \\ u'(x) & v'(x) \end{vmatrix} = \begin{vmatrix} u(x+a) & v(x+a) \\ u'(x+a) & v'(x+a) \end{vmatrix}$$

$$= \begin{vmatrix} \alpha u(x) + \beta v(x) & \gamma u(x) + \delta v(x) \\ \alpha u'(x) + \beta v'(x) & \gamma u'(x) + \delta v'(x) \end{vmatrix} = \begin{vmatrix} u(x) & v(x) \\ u'(x) & v'(x) \end{vmatrix} \begin{vmatrix} \alpha & \gamma \\ \beta & \delta \end{vmatrix}$$

$$= \text{constant}$$

(3) Obviously: $\begin{vmatrix} \alpha & \gamma \\ \beta & \delta \end{vmatrix} = 1$, $\alpha\delta - \beta\gamma = 1$

(4) It would now be convenient to express $\psi(x+a)$ as a multiplication of a constant times the $\psi(x)$, say $\lambda\,\psi(x)$, instead of a linear combination of $u(x)$ and $v(x)$. What this amounts to is a diagonalization of the matrix of coefficients of the $u(x), v(x)$:

$$\begin{pmatrix} u(x+a) \\ v(x+a) \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} \begin{pmatrix} u(x) \\ v(x) \end{pmatrix}$$

$$\begin{vmatrix} \alpha-\lambda & \beta \\ \gamma & \delta-\lambda \end{vmatrix} = (\alpha-\lambda)(\delta-\lambda) - \beta\gamma = 0$$

$$\lambda^2 - \delta\lambda - \alpha\lambda + \delta\alpha - \beta\gamma = \lambda^2 - (\delta+\alpha)\lambda + 1 = 0$$

$$\lambda = \tfrac{1}{2}(\delta+\alpha) \pm \tfrac{1}{2}\left[(\delta+\alpha)^2 - 4\right]^{1/2}$$

$$\lambda_1 \lambda_2 = 1$$

(5) There are several possibilities for λ_1, λ_2:

a) They are real and reciprocals for energies corresponding to $(\delta+\alpha)^2 > 4$. In this case, we write:

$$\lambda_1, \lambda_2 = e^{\mu a}, e^{-\mu a} = \Omega_1, \Omega_2$$ ✓

b) They are complex conjugates for $(\delta+\alpha)^2 < 4$. We write:

$$\lambda_1, \lambda_2 = e^{ika}, e^{-ika}$$ ✓

c) $\lambda_1, \lambda_2 = \pm 1$ which is a special case of (a).

a) $\psi_1(x+a) = e^{\mu a}\psi_1(x)$; $\psi_2(x+a) = e^{-\mu a}\psi_2(x)$

b) $\psi_1(x+a) = e^{ika}\psi_1(x)$; $\psi_2(x+a) = e^{-ika}\psi_2(x)$

(6) The following solution to the Schroedinger equation has the above properties:

$$\psi(x) = e^{\alpha x}u(x), \text{ where } \alpha = \pm\mu, \pm ik, \quad u(x) = u(x+a)$$

because: $\psi(x+a) = e^{\alpha(x+a)}u(x+a) = e^{\alpha a}e^{\alpha x}u(x) = e^{\alpha a}\psi(x)$.

This completes the quick proof of Bloch's Theorem. ✓

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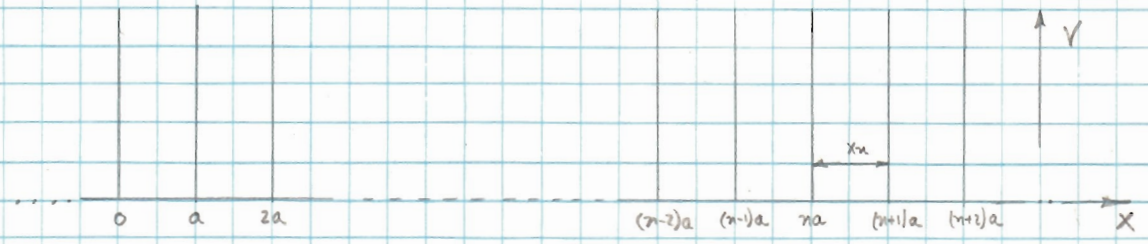
(7) Consider the potential $V(x) = a V_0 \sum_n \delta(x - na)$



(8) For $na < x_n < (n+1)a$; $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0$, $n = 0, 1, 2, 3, \ldots$

(9) $\psi = A \sin \alpha x + B \cos \alpha x$; $\alpha = \sqrt{\frac{2mE}{\hbar^2}}$

(10) Use solutions of the form (6) ; $\psi(x+a) = e^{ika} \psi(x)$

Then $\psi(a) = e^{ika} \psi(0)$; $\psi(2a) = e^{ika} \psi(a) = e^{ik2a} \psi(0)$, etc.

so that $\psi(\{n+1\}a) = e^{ikna} \psi(a) = e^{ik(n+1)a} \psi(0)$

which we now impose on (9):

(11) $A e^{ikna} \sin \alpha a + B e^{ikna} \cos \alpha a = B e^{ik(n+1)a}$

$$A = \frac{B e^{-ikna}}{\sin \alpha a} \left[e^{ik(n+1)a} - e^{ikna} \cos \alpha a \right]$$

(12) $$\psi_1 = \frac{B e^{-ikna}}{\sin \alpha a} \left\{ \left[e^{ik(n+1)a} - e^{ikna} \cos \alpha a \right] \sin \alpha x + e^{ikna} \sin \alpha a \cos \alpha x \right\}$$

Now, in $x \to x_n$, $\frac{B e^{-ikna}}{\sin \alpha a}$ is a constant which we call $B\eta$

(13) $\therefore$ $$\psi_1 = B\eta \left\{ e^{ik(n+1)a} \sin \alpha x_n - e^{ikna} \cos \alpha a \sin \alpha x_n + e^{ikna} \sin \alpha a \cos \alpha x_n \right\}$$

$$\psi_2 = B\eta^* \left\{ e^{-ik(n+1)a} \sin \alpha x_n - e^{-ikna} \cos \alpha a \sin \alpha x_n + e^{-ikna} \sin \alpha a \cos \alpha x_n \right\}$$

(14) It is well-known that combinations of products of these solutions with arbitrary constants are also solutions. We choose to form the following two new solutions:

$$\Psi_1 = \frac{1}{2Bn}\Psi_1 + \frac{1}{2Bn^*}\Psi_2 \quad ; \quad \Psi_2 = \frac{1}{2iBn}\Psi_1 - \frac{1}{2iBn^*}\Psi_2$$

which are independent. Thus:

(15) $$\Psi_1 = \cos nka \sin\alpha a \cos\alpha x_n + \left[\cos(n+1)ka - \cos nka \cos\alpha a\right] \sin\alpha x_n$$

$$\Psi_2 = \sin nka \sin\alpha a \cos\alpha x_n + \left[\sin(n+1)ka - \sin nka \cos\alpha a\right] \sin\alpha x_n$$

(16) For solutions of the type (a); $e^{\pm ika} \rightarrow \Lambda_1, \Lambda_2$

and we have, from (13):

$$\Psi_1 = C\left\{\Lambda_1^{n+1} \sin\alpha x_n - \Lambda_1^n \cos\alpha a \sin\alpha x_n + \Lambda_1^n \sin\alpha a \cos\alpha x_n\right\}$$

$$\Psi_2 = C'\left\{\Lambda_2^{n+1} \sin\alpha x_n - \Lambda_1^n \cos\alpha a \sin\alpha x_n + \Lambda_1^n \sin\alpha a \cos\alpha x_n\right\}$$

(17) We choose: $\Psi_1 = \frac{1}{C}\Psi_1$, $\Psi_2 = \frac{1}{C'}\Psi_2$

Then $$\Psi_{1,2} = \left\{\Lambda_{1,2}^{n+1} \sin\alpha x_n + \Lambda_{1,2}^n \cos\alpha a \sin\alpha x_n + \Lambda_{1,2}^n \sin\alpha a \cos\alpha x_n\right\}$$

$$= \Lambda_{1,2}^n \left\{\sin\alpha a \cos\alpha x_n + \left(\Lambda_{1,2} - \cos\alpha a\right) \sin\alpha x_n\right\}$$

(18) The solutions must be well behaved regardless of which cell they are in. Since the lattice is taken infinite in extent, it is clear that in a cell far from the origin, (15) will remain bounded while (17), because of Λ^n, will eventually become unbounded as one moves to higher and higher cells. This could have been perceived before hand from the derivation of the Bloch Theorem. Recall:

$\psi(x) = e^{\alpha x} u(x)$. If α is imaginary, $\psi(x)$ will remain bounded as one approaches large x (or large n as in (15)). If α is real $\psi(x)$ becomes unbounded for large x (or large n as in (17)) and thus violates the finiteness postulate for quantum mechanical wave functions. The same holds for $-\alpha$ as one goes to $-\infty$.

Note that (c) $(\lambda_1, \lambda_2, = \pm 1)$ is an allowed solution and corresponds to the case when $k = \pi/a$ in (15). That is, (c) represents the solution at the BZ faces or when one passes from (b) to (a) or from a band into a forbidden gap.

(10) Nice - A pleasure to read.

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11. (1) Consider the Schroedinger equation with Bloch functions for eigen functions:

$$\left[\frac{p^2}{2m} + V(r)\right] b_n(k,r) = E_n(k)\, b_n(k,r)$$

(2) Define the following transformations:

$$b_n(k,r) = \sum_K \chi_n(k,K)\, e^{i(k+K)\cdot r}$$

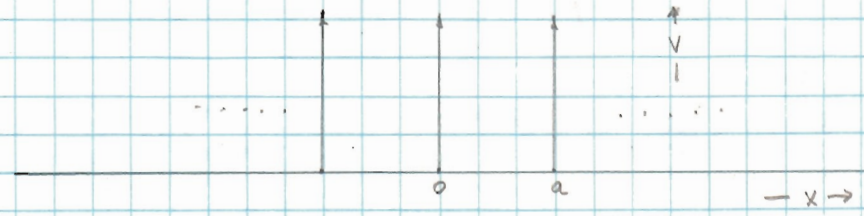
$$V(r) = \sum_K V(K)\, e^{-iK\cdot r}$$

(3) with the aid of the identity $\int e^{i(K-K'')\cdot r}\, d^3r = \Omega\, \delta_{KK''}$

we substitute the transformations in the Schroedinger equation and arrive at:

$$\frac{\hbar^2}{2m}(k+K)^2\, \chi_n(k,K) + \sum_{K'} V(K')\, \chi_n(k,K+K') = E_n(k)\, \chi_n(k,K)$$

(4) The model is the Kronig-Penney δ function potential:



The cell index will be considered on the left of the δ function.

$$V(x) = aV_0 \sum_n \delta(x-na)$$

or: $V(x) = aV_0\, \delta(0)$; $x = 0$

$= 0$; $0 < x < a$

etc.

(5) To find $V(K)$, we operate on $V(r) = \sum_K V(K)\, e^{-iK\cdot r}$ with $\int e^{ik'\cdot r}\, d^3r$ and get:

$$\int V(r)\, e^{ik'r}\, d^3r = \sum_K V(K) \int e^{i(k'-K)\cdot r}\, d^3r$$

$$= \sum_K V(K)\, \Omega\, \delta_{k'K} = \Omega\, V(k')$$

(6) Letting $K' \to K$: $V(K) = \frac{1}{\Omega} \int V(r)\, e^{i K \cdot r}\, d^3 r$

(7) In one dimension and when $V(r)$ is periodic, we reduce to the usual expression for Fourier coefficients:

$$V(K) = \frac{1}{a} \int_0^a V(x)\, e^{i K x}\, dx$$

(8) For this model, clearly, $V(K) = V_0 \int_0^a \delta(0)\, e^{i K x}\, dx$

$$= V_0\, e^{i K \cdot a}$$

Now $K = \frac{2\pi n}{a}$, $n = 0, 1, 2, 3, \ldots$ ✓

$$\therefore \quad V(K) = V_0$$

(9) Substituting in (3): $\frac{\hbar^2}{2m} (k+K)^2 \chi_n(k, K) + V_0 \sum_{K'} \chi_n(k, K+K')$

$$= E_n(k)\, \chi_n(k, K)$$ ✓

(10) We change the variable of summation in $\sum_{K'} \chi_n(k, K+K')$ from $K+K'$ to K''. This is analogous to a similar operation in integration. Divide by $\frac{\hbar^2}{2m}(k+K)^2 - E_n(k)$:

$$\chi_n(k, K) + V_0 \sum_{K''} \frac{\chi_n(k, K'')}{\frac{\hbar^2}{2m}(k+K)^2 - E_n(k)} = 0$$

(11) Now sum over K: $\sum_K \chi_n(k, K) + V_0 \sum_{K K''} \frac{\chi_n(k, K'')}{\frac{\hbar^2}{2m}(k+K)^2 - E_n(k)} = 0$

or $\sum_K \chi_n(k, K) + V_0 \sum_{K''} \chi_n(k, K'') \sum_K \frac{1}{\frac{\hbar^2}{2m}(k+K)^2 - E_n(k)} = 0$ ✓

(12) Now $\sum_K \chi_n(k, K) \equiv \sum_{K''} \chi_n(k, K'')$, since the variable of summation does not affect the final result in the same manner that the result of a definite integral does not depend on the variable of integration.

$$\therefore \quad 1 + V_0 \sum_K \frac{1}{\frac{\hbar^2}{2m}(k+K)^2 - E_n(k)} = 0$$ ✓ (10)

(13) In the extended zone scheme, K is the reciprocal lattice vector which takes us into different zones & bands as it is indexed. In the reduced zone scheme, K merely can be thought of as going from band to band. From (8), $K = \frac{2\pi n}{a}$, we can then just sum on the band number n in the reduced zone scheme.

$$\therefore \quad 1 + V_0 \sum_n \frac{1}{\frac{\hbar^2}{2m}\left(k + \frac{2n\pi}{a}\right) - E} = 0$$

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12. (1) Consider the following E vs. k relation.

$$E = \frac{\hbar^2}{2m}\left[\alpha_{11}k_x^2 + \alpha_{22}k_y^2 + \alpha_{33}k_z^2 + \alpha_{12}k_xk_y + \alpha_{13}k_xk_z + \alpha_{23}k_yk_z\right]$$

This is the equation of a general quadric surface centered about $k_x, k_y, k_z = 0$. We make the following assumption: None of the coefficients is negative so that the surface is a general ellipsoid or that it is completely closed and does not intersect the faces of the Brillouin zone as we know nothing about the zone surfaces.

(2) We now transform to a co-ordinate system coincident with the principle axes of the ellipsoid by the well known method for reducing quadric forms. That is, we transform to a new set of axes such that:

$$\epsilon = \lambda_1\xi^2 + \lambda_2\eta^2 + \lambda_3\zeta^2$$

where $\epsilon \equiv E \cdot \frac{2m}{\hbar^2}$

We now diagonalize the matrix of the coefficients of the quadratic:

$$\begin{vmatrix} \alpha_{11}-\lambda & \alpha_{12}/2 & \alpha_{13}/2 \\ \alpha_{12}/2 & \alpha_{22}-\lambda & \alpha_{23}/2 \\ \alpha_{13}/2 & \alpha_{23}/2 & \alpha_{33}-\lambda \end{vmatrix} = 0$$

The result is the following cubic:

$$\lambda^3 - (\alpha_{33}+\alpha_{22}+\alpha_{11})\lambda^2 + \left\{\alpha_{22}\alpha_{33} + \alpha_{11}\alpha_{33} + \alpha_{11}\alpha_{22} - \frac{1}{4}(\alpha_{23}^2 + \alpha_{12}^2 + \alpha_{13}^2)\right\}\lambda - \left\{\alpha_{11}\alpha_{22}\alpha_{33} + \frac{1}{4}\alpha_{12}\alpha_{13}\alpha_{23} - \frac{1}{4}(\alpha_{13}^2\alpha_{22} + \alpha_{23}^2\alpha_{11} + \alpha_{12}^2\alpha_{33})\right\} = 0$$

(3) This cubic can be solved by the use of the following equation taken from the CRC tables:

$$\lambda^3 + p\lambda^2 + q\lambda + r = 0$$

Let $\lambda = x - \frac{p}{3}$; $a = \frac{1}{3}(3q - p^2)$; $b = \frac{1}{27}(2p^3 - 9pq + 27r)$

Then the equation reduces to:

$$x^3 + ax + b = 0$$

In the solution, let:

$$A = \left\{ -\frac{b}{2} + \left[\frac{b^2}{4} + \frac{a^3}{27} \right]^{1/2} \right\}^{1/3} ; \quad B = \left\{ -\frac{b}{2} - \left[\frac{b^2}{4} + \frac{a^3}{27} \right]^{1/2} \right\}^{1/3}$$

Then $x = A + B$; $-\frac{1}{2}(A+B) + i\frac{\sqrt{3}}{2}(A-B)$; $-\frac{1}{2}(A+B) - i\frac{\sqrt{3}}{2}(A-B)$

(4) The actual substitution of p, q, r in terms of the α's is a matter of extremely laborious algebra and is not important in the physical aspect of the problem. What is important is that the three roots of the secular equation can be found and that they are the coefficients of co-ordinates in the equation of the ellipsoid with respect to its major axes, providing we assume that the original equation is physically valid in that:

$$\frac{b^2}{4} + \frac{a^3}{27} \leq 0$$ for which three real roots exist.

NB: This appears to be the case at this point. Please the end of the problem.

(5) Proceeding, then, we have:

$$\epsilon = \lambda_1 \xi^2 + \lambda_2 \eta^2 + \lambda_3 \zeta^2 = E \cdot \frac{2m}{\hbar^2}$$

(6) We wish to calculate the density of states:

$$\rho(E)\,dE = \frac{\Omega}{8\pi^3} d^3k \rightarrow \frac{\Omega}{4\pi^3} dk_x\, dk_y\, dk_z \quad \text{(spin)}$$

where Ω is the volume of the crystal.

Now: $dk_x\, dk_y\, dk_z = |J(\xi, \eta, \zeta)|\, d\xi\, d\eta\, d\zeta$

where $|J(\xi, \eta, \zeta)| = \begin{vmatrix} \frac{\partial k_x}{\partial \xi} & \frac{\partial k_y}{\partial \xi} & \frac{\partial k_z}{\partial \xi} \\ \frac{\partial k_x}{\partial \eta} & \frac{\partial k_y}{\partial \eta} & \frac{\partial k_z}{\partial \eta} \\ \frac{\partial k_x}{\partial \zeta} & \frac{\partial k_y}{\partial \zeta} & \frac{\partial k_z}{\partial \zeta} \end{vmatrix}$

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12. continued

(7) The coefficients of the quadric underwent the orthogonal transformation:

$$C^{-1} \alpha C = \Lambda$$

such that $C^{-1} = C'$. Also we demand that our transformation be a simple rotation so that there is no distortion in any direction of space. Thus we have:

$$|C| = 1$$

Now $$\begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} \xi \\ \eta \\ \zeta \end{pmatrix}$$

Thus $$|J(\xi, \eta, \zeta)| = |C| = 1 \quad ; \quad dk_x\, dk_y\, dk_z = d\xi\, d\eta\, d\zeta$$

(8) $$\epsilon = E \cdot \frac{2m}{\hbar^2} = \lambda_1 \xi^2 + \lambda_2 \eta^2 + \lambda_3 \zeta^2$$

with $$\rho(E)\, dE = \frac{\Omega}{4\pi^3}\, d\xi\, d\eta\, d\zeta$$

(9) The distance between E and $E + dE$ is $\dfrac{dE}{|\nabla E|}$

Thus an element of volume can be written:

$$d\xi\, d\eta\, d\zeta = dE \int \frac{dS}{|\nabla E|}$$

and $$\rho(E)\, dE = \frac{\Omega}{4\pi^3}\, dE \int \frac{dS}{|\nabla E|}$$

or $$\rho(E) = \frac{m\Omega}{2\hbar^2 \pi^3} \int \frac{dS}{|\nabla \epsilon|}$$

(10) We throw this into the standard form for a surface integral.

$$\int_S \varphi(x, y, z)\, dS = \iint \varphi\{x, y, z = f(x, y)\} \left[\left(\frac{\partial z}{\partial x}\right)^2 + \left(\frac{\partial z}{\partial y}\right)^2 + 1 \right]^{1/2} dx\, dy$$

This holds only if the surface is smooth and single valued which is the reason we first had to transform to the major axes co-ordinates before we could evaluate using this form.

(11) $\varphi\left[\xi, \eta, \zeta = f(\xi,\eta)\right] = |\nabla \epsilon|^{-1}$; $\zeta = \left[\frac{\epsilon - \lambda_1 \xi^2 - \lambda_2 \eta^2}{\lambda_3}\right]^{1/2}$

$$|\nabla \epsilon| = 2\left[\lambda_1^2 \xi^2 + \lambda_2^2 \eta^2 + \lambda_3^2 \zeta^2\right]^{1/2}$$

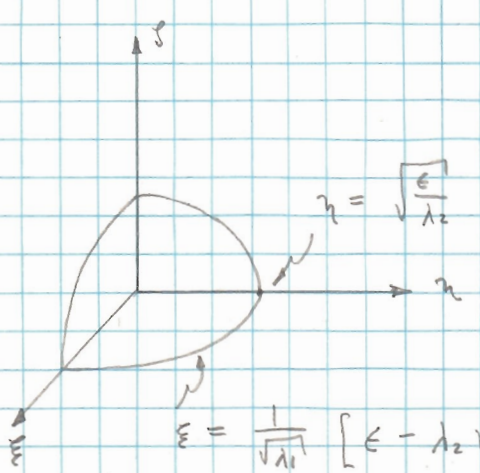
$$= 2\left[\lambda_1^2 \xi^2 + \lambda_2^2 \eta^2 + \lambda_3 \epsilon - \lambda_3 \lambda_1 \xi^2 - \lambda_3 \lambda_2 \eta^2\right]^{1/2}$$

(12) $$\left[\left(\frac{\partial \zeta}{\partial \xi}\right)^2 + \left(\frac{\partial \zeta}{\partial \eta}\right)^2 + 1\right]^{1/2} = \left[\frac{\frac{\lambda_1^2}{\lambda_3}\xi^2 + \frac{\lambda_2^2}{\lambda_3}\eta^2}{\epsilon - \lambda_1 \xi^2 - \lambda_2 \eta^2} + 1\right]^{1/2}$$

$$= \left[\frac{\lambda_1^2 \xi^2 + \lambda_2^2 \eta^2 + \lambda_3 \epsilon - \lambda_3 \lambda_1 \xi^2 - \lambda_3 \lambda_2 \eta^2}{\lambda_3 (\epsilon - \lambda_1 \xi^2 - \lambda_2 \eta^2)}\right]^{1/2}$$

(13) $$\varphi\left[\xi, \eta, \zeta = f(\xi,\eta)\right]\left[\left(\frac{\partial \zeta}{\partial \xi}\right)^2 + \left(\frac{\partial \zeta}{\partial \eta}\right)^2 + 1\right]^{1/2}$$

$$= \frac{1}{2\sqrt{\lambda_3}} \frac{1}{(\epsilon - \lambda_1 \xi^2 - \lambda_2 \eta^2)^{1/2}}$$



From the symmetry, that is:

$$I(-\xi, -\eta, -\zeta) = I(\xi, \eta, \zeta),$$

changing any one sign does not change the integrand, so that the integral calculated over the first quadrant is 1/8 the total value.

(14) $$\rho(E) = \frac{4 m_n \Omega}{2 \hbar^2 \pi^3 \sqrt{\lambda_3}} \int_0^{\sqrt{\frac{\epsilon}{\lambda_2}}} \int_0^{\frac{1}{\sqrt{\lambda_1}}\left[\epsilon - \lambda_2 \eta^2\right]^{1/2}} \frac{d\xi\, d\eta}{(\epsilon - \lambda_1 \xi^2 - \lambda_2 \eta^2)^{1/2}}$$

(15) $$\int_\xi \frac{d\xi}{\left[(\epsilon - \lambda_2 \eta^2) - \lambda_1 \xi^2\right]^{1/2}} = \frac{1}{\sqrt{\lambda_1}} \int_\xi \frac{d\xi}{\left[\frac{\epsilon}{\lambda_1} - \frac{\lambda_2}{\lambda_1}\eta^2 - \xi^2\right]^{1/2}}$$

$$= \frac{1}{\sqrt{\lambda_1}} \text{ arc sin } \frac{\frac{1}{\sqrt{\lambda_1}}\left[\epsilon - \lambda_2 \eta^2\right]^{1/2}}{\left[\frac{\epsilon}{\lambda_1} - \frac{\lambda_2}{\lambda_1}\eta^2\right]^{1/2}} = \frac{1}{\sqrt{\lambda_1}} \pi/2$$

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12. Continued

(16) $$\rho(E) = \frac{2m\Omega}{2\hbar^2\pi^2\sqrt{\lambda_1\lambda_2\lambda_3}} \int_0^{\sqrt{\frac{E}{\lambda_2}}} d\eta = \frac{2m\Omega}{2\hbar^2\pi^2\sqrt{\lambda_1\lambda_2\lambda_3}} \sqrt{E}$$

$$= \frac{\Omega}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\sqrt{E}}{\sqrt{\lambda_1\lambda_2\lambda_3}}, \quad \text{Q.E.D.}$$

See posted solution for easier method.

(17) The number of electrons in the energy range E to $E+dE$ is given by the density of available states in the region times the probability that the electrons will have an energy lying in the range of available states, that is:

$$n\,dE = \rho(E)\,F(E)\,dE$$

where $F(E) = \frac{1}{e^{(E-E_F)/kT}+1}$ is the Fermi-Dirac probability distribution function.

(18) Thus, writing $n \to n/\Omega$, the number of electrons per unit volume, we have for the volumetric density of electrons over some energy range:

$$n = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\sqrt{\lambda_1\lambda_2\lambda_3}} \int \frac{\sqrt{E}\,dE}{e^{E-E_F/kT}+1}$$

(19) At absolute zero: $F(E) = 1$, $E < E_F$; $= 0$, $E > E_F$ } E_F is the Fermi energy at absolute zero

We can thus find this energy by a simple calculation if we take as zero reference energy, say, the bottom of the band above which lies the Fermi level. We also know that under these conditions the electrons in the band will all be between the fermi level and the bottom of the band, so the electron density can be taken as a given constant of the problem, as we know with probability one they (electrons) will all be within the range of integration.

(20) $$n = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\sqrt{\lambda_1 \lambda_2 \lambda_3}} \int_0^{E_F} \sqrt{E}\, dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\sqrt{\lambda_1 \lambda_2 \lambda_3}} (E_F)^{3/2} \cdot \frac{2}{3}$$

(21) $$\therefore \quad E_F = \left(3n\pi^2\right)^{2/3} \cdot \frac{\hbar^2}{2m} \cdot \left(\lambda_1 \lambda_2 \lambda_3\right)^{1/3}$$ ✓

where $\lambda_1, \lambda_2, \lambda_3$ can be expressed in terms of the α's as shown.

Explicit expression of the product $\lambda_1 \lambda_2 \lambda_3$:

Consider the cubic: $\lambda^3 + p\lambda^2 + q\lambda + r = 0$

which can be factored into the form:

$(\lambda - \lambda_1)(\lambda - \lambda_2)(\lambda - \lambda_3) = 0$, where $\lambda_1, \lambda_2, \lambda_3$ are the roots.

Upon multiplying this out:

$$\lambda^3 - (\lambda_1 + \lambda_2 + \lambda_3)\lambda^2 + (\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)\lambda - \lambda_1\lambda_2\lambda_3 = 0$$

We now see that $\lambda_1 \lambda_2 \lambda_3 = -r$. This procedure can in fact be generalized for a polynomial of any degree. Therefore, for this problem:

$$\lambda_1 \lambda_2 \lambda_3 = \left\{ \alpha_{11}\alpha_{22}\alpha_{33} + \frac{1}{4}\alpha_{12}\alpha_{13}\alpha_{23} - \frac{1}{4}\left(\alpha_{13}^2\alpha_{22} + \alpha_{23}^2\alpha_{11} + \alpha_{12}^2\alpha_{33}\right)\right\}$$

from equation (2). This may now be substituted in the relations for the density of states and the Fermi energy.

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13. (1) During the process of this calculation, it will be desired to have the following relation:

$$\langle n'k' | f(H) | nk \rangle = f[E_n(k)]\, \delta_{nn'}\, \delta_{kk'}$$

(2) Now if $f(H)$ is analytic within a region of interest to us (that is, well behaved), it may be expanded in a uniformly convergent Taylor series about some point in this region and hence be term by term integrable. For convenience, we choose the limit point to be the origin of a suitable coordinate system giving for the expansion:

$$f(H) = f(0) + f'(1)\, H + \frac{f''(1)}{2} H^2 + \cdots$$

$$= \sum_{p=0}^{\infty} \frac{f^{(p)}(0)}{p!} H^p$$

(3) It is now clear that in order to prove (1) we merely have to show:

$$\langle n'k' | H^p | nk \rangle = E_n^p(k)\, \delta_{nn'}\, \delta_{kk'}$$

and resubstitute in the series to get $f[E_n(k)]$.

(4) It will be convenient now to digress and consider The Schroedinger equation involving the Bloch functions as eigen functions:

$$H\, b_n(k,r) = E_n(k)\, b_n(k,r)$$

where the Bloch functions are assumed to be normalized. Multiply by $\int b^*_{n'}(k',r)\, d^3r$:

$$\int b^*_{n'}(k',r)\, H\, b_n(k,r)\, d^3r = E_n(k) \int b^*_{n'}(k',r)\, b_n(k,r)\, d^3r$$

$$\| \qquad\qquad\qquad \| \qquad\qquad\qquad \|$$

$$\langle n'k' | H | nk \rangle = E_n(k)\, \delta_{nn'}\, \delta_{kk'}$$

(5) Returning to (3), it is possible to write using the well-known rule for the multiplication of matrix elements:

$$\langle n'k' | H^p | nk \rangle = \sum_{n''k''} \langle n'k' | H^{p-1} | n''k'' \rangle \langle n''k'' | H | nk \rangle$$

(6) $\langle n'k'|H^p|nk\rangle = \sum_{n''k''} \langle n'k'|H^{p-1}|n''k''\rangle E_n(k)\,\delta_{n''n}\,\delta_{k''k}$

$= E_n(k)\ \langle n'k'|H^{p-1}|nk\rangle$

It is obvious that this can be repeated until:

$\langle n'k'|H^p|nk\rangle = E_n^{p-2}(k) \sum_{n''k''} \langle n'k'|H|n''k''\rangle\langle n''k''|H|nk\rangle$

$= E_n^{p-1}(k)\ \langle n'k'|H|nk\rangle = E_n^p(k)\ \delta_{nn'}\,\delta_{kk'}$

Therefore $\langle n'k'|f(H)|nk\rangle = f[E_n(k)]\ \delta_{nn'}\,\delta_{kk'}$ ✓

(7) Consider now:

$\langle nk|[f(H), X_\alpha]|n'k'\rangle = \langle nk|f(H)\cdot X_\alpha - X_\alpha\cdot f(H)|n'k'\rangle$

$= \sum_{n''k''}\left\{\langle nk|f(H)|n''k''\rangle\langle n''k''|X_\alpha|n'k'\rangle - \langle nk|X_\alpha|n''k''\rangle\langle n''k''|f(H)|n'k'\rangle\right\}$

$= \sum_{n''k''}\left\{\delta_{nn''}\,\delta_{kk''}\,f[E_n(k)]\cdot\imath\frac{\partial}{\partial k_\alpha}\delta_{nn'}\,\delta_{kk'} - \delta_{nn''}\delta_{kk''}\,\imath\frac{\partial}{\partial k_\alpha}\cdot f[E_n(k)]\,\delta_{nn'}\delta_{kk'}\right\}$

$= \imath\left\{f[E_n(k)]\cdot\frac{\partial}{\partial k_\alpha} - \frac{\partial}{\partial k_\alpha}\cdot f[E_n(k)]\right\}$

Nonsense, $\langle 1|1\rangle$ is a number, not an operator.

considering X_α as an operator in the CMR; $\langle n'k'|X_\alpha|nk\rangle = \imath\frac{\partial}{\partial k_\alpha}\delta_{nn'}\,\delta_{kk'}$ as shown in lecture.

(8) Now let both sides of (7) operate on some suitable momentum wave function, say $\varphi_n(k)$:

$-\imath\langle nk|[f(H), X_\alpha]|n'k'\rangle\,\varphi_{n'}(k) = f[E_n(k)]\frac{\partial\varphi}{\partial k_\alpha} - \frac{\partial}{\partial k_\alpha}\left\{f[E_n(k)]\,\varphi\right\}$

$= -\frac{\partial}{\partial k_\alpha}\left\{f[E_n(k)]\right\}\varphi_n(k)$, or

(9) $\imath\langle nk|[f(H), X_\alpha]|n'k'\rangle = \frac{\partial}{\partial k_\alpha}\left\{f[E_n(k)]\right\}$ Q.E.D.

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14. (1) We begin with a discussion of second order degenerate perturbation theory as presented by Prof. Furry in P251a. We merely sketch the method and make no attempt to fill in the details. We begin with a set of "new" wave functions expanded as as set of "known" wave functions:

$$u_{k,\gamma} = \sum_{n,\beta} v_{n,\beta}\, S_{n,\beta;\,k,\gamma}$$

We hold that the v's form a complete orthonormal set. Substituting in the Schroedinger equation, $Hu = Eu$, and forming matrix elements, we have:

$$\sum_{n,\beta} \langle m,\alpha|H|n,\beta\rangle\, S_{n,\beta;\,k,\alpha} = E_{k,\gamma}\, S_{m,\alpha;\,k,\gamma}$$

α is the index of a degenerate wave function of the state m
β " " " " " " " " " " " " " " n
γ " " " " " " " " " " " " " " k

k is the state whose correction we wish to find.

(2) We make the usual expansion in terms of the dummy parameter λ:

$$S_{n,\beta;\,k,\gamma} = \delta_{nk}\, S_{\beta\gamma}(k) + \lambda\, C^{(1)}_{n,\beta;\,k,\gamma} + \lambda^2 C^{(2)}_{n,\beta;\,k,\gamma} + \cdots$$

$$E_{k,\gamma} = E^{(0)}_{k,\gamma} + \lambda\, E^{(1)}_{k,\gamma} + \lambda^2 E^{(2)}_{k,\gamma} + \cdots$$

$$\langle m,\alpha|H|n,\beta\rangle = E^{(0)}_m\, \delta_{mn}\, \delta_{\alpha\beta} + \lambda \langle m,\alpha|V|n,\beta\rangle$$

where V is the perturbing potential.

We plug in above and obtain the following three equations:

(3) 0th order: $E^{(0)}_m\, \delta_{mk}\, S_{\alpha\gamma}(k) = E^{(0)}_k\, \delta_{mk}\, S_{\beta\alpha}(k)$

(4) 1st order: $E^{(0)}_m\, C^{(1)}_{m,\alpha;\,k,\gamma} + \sum_\beta \langle m,\alpha|V|k,\beta\rangle\, S_{\beta\gamma}(k)$
$= E^{(0)}_k\, C^{(1)}_{m,\alpha;\,k,\gamma} + \delta_{mk}\, S_{\alpha\gamma}(k)\, E^{(1)}_{k,\gamma}$

(5) 2nd Order: $E^{(0)}_m\, C^{(2)}_{m,\alpha;\,k,\gamma} + \sum_{n\beta} \langle m,\alpha|V|n,\beta\rangle\, C^{(1)}_{n,\beta;\,k,\gamma}$
$= E^{(0)}_{k,\gamma}\, C^{(2)}_{m,\alpha;\,k,\gamma} + E^{(1)}_{k,\gamma}\, C^{(1)}_{m,\alpha;\,k,\gamma} + \delta_{mk}\, E^{(2)}_{k,\gamma}\, S_{\alpha\gamma}(k)$

(6) Putting $m = k$ in (4) we obtain the matrix leading to the secular equation for the first order corrections.

$$\sum_{\beta}^{g_k} \left\{ \langle k,\alpha | V | k,\beta \rangle - E^{(1)}_{k,r}\, \delta_{\alpha\beta} \right\} S_{\beta\gamma}(k) = 0 \quad ; \quad \alpha = 1, 2, 3, \cdots, g_k$$

(7) For $m \neq k$, we obtain:

$$C^{(1)}_{m,\alpha;\,k,\gamma} = \frac{\sum_{\beta} \langle m,\alpha | V | k,\beta \rangle \; S_{\beta\gamma}}{E^{(0)}_k - E^{(0)}_m}$$

Examine: $\sum_{\beta} \int \psi^{*}_{m,\alpha}\, V\, \psi_{k,\beta}\, d^3 r \; S_{\beta\gamma}$

We see that if we had chosen

$$\omega_{k,\gamma} = \sum_{\beta} \psi_{k,\beta}\, S_{\beta,\gamma}$$

to begin with, the secular equation would have been diagonal.

(8) Using much the same approach, putting $m = k$ in (5), along with some violent algebra, we obtain for the matrix equation of second order:

$$\sum_{\delta} \left\{ \sum_{\substack{n \neq k \\ \beta}} \frac{\langle k\alpha | V | n\beta \rangle \langle n\beta | V | k\delta \rangle}{E^{(0)}_k - E^{(0)}_n} - E_{2\gamma}\, \delta_{\alpha\delta} \right\} S_{\delta\gamma}(k) = 0$$

where δ was introduced in the calculation to couple between two wave functions of the same state. Also degeneracy indices run from 1 to g_k where g_k is the degree of degeneracy of the state k. Writing out in matrix notation:

(9)
$$\begin{bmatrix} \sum_{\substack{n\neq k \\ \beta}} \frac{\langle 1k | V | n\beta \rangle \langle n\beta | V | k1 \rangle}{E^{(0)}_k - E^{(0)}_n} & \sum_{\substack{n\neq k \\ \beta}} \frac{\langle 1k | V | n\beta \rangle \langle n\beta | V | k2 \rangle}{E^{(0)}_k - E^{(0)}_n} & \cdots \\ \sum_{\substack{n\neq k \\ \beta}} \frac{\langle 2k | V | n\beta \rangle \langle n\beta | V | k1 \rangle}{E^{(0)}_k - E^{(0)}_n} & \sum_{\substack{n\neq k \\ \beta}} \frac{\langle 2k | V | n\beta \rangle \langle n\beta | V | k2 \rangle}{E^{(0)}_k - E^{(0)}_n} & \cdots \\ \vdots & \vdots & \end{bmatrix} \begin{bmatrix} S_{1\gamma}(k) \\ S_{2\gamma}(k) \\ \vdots \end{bmatrix}$$

$$= E^{(2)}_{k\gamma} \, \mathbb{I} \begin{bmatrix} S_{1\gamma}(k) \\ S_{2\gamma}(k) \\ \vdots \end{bmatrix}$$

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14 Continued:

(10) We now transfer notation: As we are considering only degeneracy in the level under consideration and assuming no degeneracy in the other states, we have $\beta = 0$.

$n \to \nu$, the band index
$k \to o$, denoting the degenerate state

$\alpha, \delta \to 1, 2, 3$ or x, y, z, the index of the degenerate wave functions of the state o.

(11) Consider the following Schroedinger equation:

$$H\, b_n(k,r) = E_n\, b_n(k,r); \qquad \left[\frac{p^2}{2m} + V(r)\right] e^{ik\cdot r}\, u_n(k,r) = E_n\, e^{ik\cdot r}\, u_n(k,r)$$

$$p\, e^{ik\cdot r} = e^{ik\cdot r}(p + \hbar k)$$

$$\therefore \left[\frac{1}{2m}(p+\hbar k)^2 + V(r)\right] u_n(k,r) = E_n\, u_n(k,r)$$

(12) $$\left[\underbrace{\frac{1}{2m}p^2 + V(r)}_{H_o} + \underbrace{\frac{\hbar k\cdot p}{m}}_{V}\right] u_\nu(k,r) = \left[E_\nu(k) - \frac{\hbar^2 k^2}{2m}\right] u_\nu(k,r)$$

Consider V the perturbation and the unperturbed wave functions as the degenerate set of p functions at $k=0$ of the state $\nu = o$. Then, from consideration of zeroth order perturbation theory:

$$H_o\, u^{(\alpha)}(0,r) = E_o^{(0)}\, u^{(\alpha)}(0,r)$$

where $u^{(\alpha)}(0,r) = u^{(1)}(0,r), u^{(2)}(0,r), u^{(3)}(0,r) = x f(r), y f(r), z f(r)$

$= |x\rangle, |y\rangle, |z\rangle$.

We wish to show the equation that determines the correct linear combination of wave functions,

$$u^{(\delta)}(k,r) = \sum_\beta \alpha_{\gamma\beta}\, u^{(\beta)}(0,r)$$

which diagonalize the first order secular equation. We see that:

$$\alpha_{\gamma 1}, \text{ etc.} = S_{\gamma 1}, \text{ etc}$$

(13) By direct substitution into equation (9) from our definitions:

$$\begin{bmatrix} \sum_{\lambda\neq 0} \frac{\langle x|V|\lambda\rangle\langle\lambda|V|x\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle x|V|\lambda\rangle\langle\lambda|V|y\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle x|V|\lambda\rangle\langle\lambda|V|z\rangle}{E_0^{(0)}-E_\lambda^{(0)}} \\ \sum_{\lambda\neq 0} \frac{\langle y|V|\lambda\rangle\langle\lambda|V|x\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle y|V|\lambda\rangle\langle\lambda|V|y\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle y|V|\lambda\rangle\langle\lambda|V|z\rangle}{E_0^{(0)}-E_\lambda^{(0)}} \\ \sum_{\lambda\neq 0} \frac{\langle z|V|\lambda\rangle\langle\lambda|V|x\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle z|V|\lambda\rangle\langle\lambda|V|y\rangle}{E_0^{(0)}-E_\lambda^{(0)}} & \sum_{\lambda\neq 0} \frac{\langle z|V|\lambda\rangle\langle\lambda|V|z\rangle}{E_0^{(0)}-E_\lambda^{(0)}} \end{bmatrix} \begin{bmatrix} \alpha_{1\gamma} \\ \alpha_{2\gamma} \\ \alpha_{3\gamma} \end{bmatrix}$$

$$= E_0^{(2)} \mathbb{1} \begin{bmatrix} \alpha_{1\gamma} \\ \alpha_{2\gamma} \\ \alpha_{3\gamma} \end{bmatrix} \quad ; \text{ where:}$$

$$V = \frac{\hbar}{m} k\cdot p = k_x p_x + k_y p_y + k_z p_z$$

(14) For the elucidation of the symmetry argument, we will consider only two elements of the above matrix and extend the reasoning to the others by induction.

$$\langle x|V|\lambda\rangle\langle\lambda|V|x\rangle = \frac{\hbar^2}{m^2}\langle x|k_x p_x + k_y p_y + k_z p_z|\lambda\rangle\langle\lambda|k_x p_x + k_y p_y + k_z p_z|x\rangle$$

$$= \frac{\hbar^2}{m^2}(k_x\ k_y\ k_z)\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|x\rangle \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_z|x\rangle \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle \end{pmatrix}\begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}$$

$$\langle x|V|\lambda\rangle\langle\lambda|V|y\rangle$$

$$= \frac{\hbar^2}{m^2}(k_x\ k_y\ k_z)\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|y\rangle \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_z|y\rangle \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|y\rangle \end{pmatrix}\begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}$$

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14 Continued:

(15) Let us digress for a moment and consider the first order energy correction. Substituting in equation (6) and forming the secular equation:

$$\begin{vmatrix} \langle x|V|x\rangle - E_0^{(1)} & \langle x|V|y\rangle & \langle x|V|z\rangle \\ \langle y|V|x\rangle & \langle y|V|y\rangle - E_0^{(1)} & \langle y|V|z\rangle \\ \langle z|V|x\rangle & \langle z|V|y\rangle & \langle z|V|z\rangle - E_0^{(1)} \end{vmatrix} = 0$$

Consider two typical matrix elements:

$$\langle x|V|x\rangle = \frac{\hbar}{m}\left\{\langle x|p_x|x\rangle k_x + \langle x|p_y|x\rangle k_y + \langle x|p_z|x\rangle k_z\right\}$$

$$\langle x|V|y\rangle = \frac{\hbar}{m}\left\{\langle x|p_x|y\rangle k_x + \langle x|p_y|y\rangle k_y + \langle x|p_z|y\rangle k_z\right\}$$

It is seen that there are several types of sub-elements

$$\langle \xi|p_\xi|\xi\rangle,\ \langle \xi|p_\xi|\eta\rangle,\ \langle \xi|p_\eta|\gamma\rangle,\ \langle \xi|p_\eta|\xi\rangle$$

$$\langle \xi|p_\eta|\eta\rangle;\quad \xi = x,y,z;\quad \eta = x,y,z;\quad \gamma = x,y,z$$

$$|p_\xi|\xi\rangle \Rightarrow \frac{\partial}{\partial\xi}\left[\xi f(r)\right] = f(r) + \frac{\xi^2 f'(r)}{r}$$

$$|p_\xi|\eta\rangle \Rightarrow \frac{\partial}{\partial\xi}\left[\eta f(r)\right] = \frac{\eta\xi f'(r)}{r}$$

$$\langle \xi|p_\xi|\xi\rangle = \int\left\{\xi^2 f(r) + \frac{\xi^3 f(r) f'(r)}{r}\right\} d^3r = 0$$

$$\langle \gamma|p_\xi|\eta\rangle = \int\left\{\gamma\eta\xi\frac{f'(r)f(r)}{r}\right\} d^3r = 0$$

$$\langle \xi|p_\xi|\eta\rangle = \int\left\{\frac{\eta\xi^2 f(r) f'(r)}{r}\right\} d^3r = 0$$

and so on, so that the first order correction to the energy is zero and none of the degeneracy has been removed. Thus we have the second order degenerate perturbation appearing in its full glory.

(16) We now return to a consideration of equations (14). Because of the cubic symmetry of the problem (and also the spherical symmetry) we see that inversion symmetry exists. Therefore, the matrices of equations (14), which are typical of the elements of the secular equation, should be invariant under an inversion of the co-ordinates of the crystal. That is, when we let:

$$\begin{array}{lll} x \to -x, & p_x \to -p_x \\ \text{or} \quad y \to -y, & p_y \to -p_y \\ \text{or} \quad z \to -z, & p_z \to -p_z \end{array}$$

the results of the problem should be equal. This will only be true if the matrices of equations (14) undergo the transformation invariantly. That is, the matrices must be equal before and after the transformation. Thus;

No (K) matrices also change.

$$\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|x\rangle \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_z|x\rangle \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|x\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_y|x\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle \end{pmatrix}$$

we denote changes in sign only instead of repeating the entire matrix:

Subject to: $x \to -x,\ p_x \to -p_x$; $y \to y,\ p_y \to p_y$; $z \to z,\ p_z \to p_z$ $\Big\}$ $= \begin{pmatrix} + & - & - \\ - & + & + \\ - & + & + \end{pmatrix}$

$x \to x,\ p_x \to p_x$; $y \to -y,\ p_y \to -p_y$; $z \to z,\ p_z \to p_z$ $\Big\}$ $= \begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix}$

Thus we see that all non-diagonal elements vanish for this matrix and we are left with:

$$\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle & 0 & 0 \\ 0 & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle & 0 \\ 0 & 0 & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle \end{pmatrix}$$

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14. Continued:

(16) Consider:

$$\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|y\rangle \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_y|\lambda\rangle\langle\lambda|p_z|y\rangle \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|y\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_y|y\rangle & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|y\rangle \end{pmatrix}$$

Subject to:

$$\left.\begin{array}{l} x \to -x \;,\; p_x \to -p_x \\ y \to y \;,\; p_y \to p_y \\ z \to z \;,\; p_z \to p_z \end{array}\right\} = \begin{pmatrix} - & + & + \\ + & - & - \\ + & - & - \end{pmatrix}$$

$$\left.\begin{array}{l} x \to x \;,\; p_x \to p_x \\ y \to -y \;,\; p_y \to -p_y \\ z \to z \;,\; p_z \to p_z \end{array}\right\} = \begin{pmatrix} - & + & - \\ + & - & + \\ - & + & - \end{pmatrix}$$

$$\left.\begin{array}{l} x \to x \;,\; p_x \to p_x \\ y \to y \;,\; p_y \to p_y \\ z \to -z \;,\; p_z \to -p_z \end{array}\right\} = \begin{pmatrix} + & + & - \\ + & + & - \\ - & - & + \end{pmatrix}$$

Thus the matrix reduces to:

$$\begin{pmatrix} 0 & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle & 0 \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

It is now clear what the pattern is that has developed. Any element that contains an odd number of functions, be they position and/or momentum, will vanish under an inversion transformation. Thus, it would be foolish not to recognize this fact now and apply it by induction to the other elements of the secular equation and save ourselves tedious and trivial labor.

Also, the cubic symmetry dictates that a simultaneous interchange of co-ordinates and momenta should leave the result of the problem invariant as the original choice of the co-ordinate was purely arbitrary and the resultant energy should not be dependent on this choice. These transformations involve rotations and reflections of the coordinate system.

(17) Consider: $\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle & 0 & 0 \\ 0 & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle & 0 \\ 0 & 0 & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle \end{pmatrix}$

Subject to:

$x \leftrightarrow y,\ p_x \leftrightarrow p_y$
$z \to z,\ p_z \to p_z$
$\Bigg\}$ $\begin{pmatrix} \langle y|p_y|\lambda\rangle\langle\lambda|p_y|y\rangle & 0 & 0 \\ 0 & \langle y|p_x|\lambda\rangle\langle\lambda|p_x|y\rangle & 0 \\ 0 & 0 & \langle y|p_z|\lambda\rangle\langle\lambda|p_z|y\rangle \end{pmatrix}$

$x \leftrightarrow z,\ p_x \leftrightarrow p_z$
$y \to y,\ p_y \to p_y$
$\Bigg\}$ $\begin{pmatrix} \langle z|p_z|\lambda\rangle\langle\lambda|p_z|z\rangle & 0 & 0 \\ 0 & \langle z|p_y|\lambda\rangle\langle\lambda|p_y|z\rangle & 0 \\ 0 & 0 & \langle z|p_x|\lambda\rangle\langle\lambda|p_x|z\rangle \end{pmatrix}$

$y \leftrightarrow z,\ p_y \leftrightarrow p_z$
$x \to x,\ p_x \to p_x$
$\Bigg\}$ $\begin{pmatrix} \langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle & 0 & 0 \\ 0 & \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle & 0 \\ 0 & 0 & \langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle \end{pmatrix}$

Thus we have:

$$\langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle = \langle y|p_y|\lambda\rangle\langle\lambda|p_y|y\rangle = \langle z|p_z|\lambda\rangle\langle\lambda|p_z|z\rangle$$

and: $\langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle = \langle y|p_x|\lambda\rangle\langle\lambda|p_x|y\rangle = \langle z|p_y|\lambda\rangle\langle\lambda|p_y|z\rangle = \langle x|p_z|\lambda\rangle\langle\lambda|p_z|x\rangle$

$= \langle y|p_z|\lambda\rangle\langle\lambda|p_z|y\rangle = \langle z|p_x|\lambda\rangle\langle\lambda|p_x|z\rangle$

(18) Now consider: $\begin{pmatrix} 0 & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle & 0 \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

Subject to:

$x \leftrightarrow y,\ p_x \leftrightarrow p_y$
$z \to z,\ p_z \to p_z$
$\Bigg\}$ $\begin{pmatrix} 0 & \langle y|p_y|\lambda\rangle\langle\lambda|p_x|x\rangle & 0 \\ \langle y|p_x|\lambda\rangle\langle\lambda|p_y|x\rangle & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$x \leftrightarrow z,\ p_z \leftrightarrow p_x$
$y \to y,\ p_y \leftrightarrow p_y$
$\Bigg\}$ $\begin{pmatrix} 0 & \langle z|p_z|\lambda\rangle\langle\lambda|p_y|y\rangle & 0 \\ \langle z|p_y|\lambda\rangle\langle\lambda|p_z|y\rangle & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

$y \leftrightarrow z,\ p_y \leftrightarrow p_z$
$x \to x,\ p_x \to p_x$
$\Bigg\}$ $\begin{pmatrix} 0 & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|z\rangle & 0 \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|z\rangle & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

Thus we have:

$$\langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle = \langle y|p_x|\lambda\rangle\langle\lambda|p_y|x\rangle = \langle z|p_y|\lambda\rangle\langle\lambda|p_z|y\rangle = \langle x|p_z|\lambda\rangle\langle\lambda|p_x|z\rangle$$

and $\langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle = \langle y|p_y|\lambda\rangle\langle\lambda|p_x|x\rangle = \langle z|p_z|\lambda\rangle\langle\lambda|p_y|y\rangle = \langle x|p_x|\lambda\rangle\langle\lambda|p_z|z\rangle$

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14. Continued

(19) Consider:

$$\begin{pmatrix} 0 & 0 & \langle x|p_x|\lambda\rangle\langle\lambda|p_z|z\rangle \\ 0 & 0 & 0 \\ \langle x|p_z|\lambda\rangle\langle\lambda|p_x|z\rangle & 0 & 0 \end{pmatrix}$$

Subject to:

$$\left.\begin{matrix} x \leftrightarrow y\,,\ p_x \leftrightarrow p_y \\ z \to z\,,\ p_z \to p_z \end{matrix}\right\} \begin{pmatrix} 0 & 0 & \langle y|p_y|\lambda\rangle\langle\lambda|p_z|z\rangle \\ 0 & 0 & 0 \\ \langle y|p_z|\lambda\rangle\langle\lambda|p_y|z\rangle & 0 & 0 \end{pmatrix}$$

$$\left.\begin{matrix} x \leftrightarrow z\,,\ p_x \leftrightarrow p_z \\ y \to y\,,\ p_y \to p_y \end{matrix}\right\} \begin{pmatrix} 0 & 0 & \langle z|p_z|\lambda\rangle\langle\lambda|p_x|x\rangle \\ 0 & 0 & 0 \\ \langle z|p_x|\lambda\rangle\langle\lambda|p_z|x\rangle & 0 & 0 \end{pmatrix}$$

$$\left.\begin{matrix} z \leftrightarrow y\,,\ p_y \leftrightarrow p_z \\ x \to x\,,\ p_x \to p_x \end{matrix}\right\} \begin{pmatrix} 0 & 0 & \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle \\ 0 & 0 & 0 \\ \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle & 0 & 0 \end{pmatrix}$$

Thus we have:

$$\langle x|p_z|\lambda\rangle\langle\lambda|p_x|z\rangle = \langle y|p_z|\lambda\rangle\langle\lambda|p_y|z\rangle = \langle z|p_x|\lambda\rangle\langle\lambda|p_z|x\rangle = \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle$$

and: $\langle x|p_x|\lambda\rangle\langle\lambda|p_z|z\rangle = \langle y|p_y|\lambda\rangle\langle\lambda|p_z|z\rangle = \langle z|p_z|\lambda\rangle\langle\lambda|p_x|x\rangle = \langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle$

The upshot is, when we combine this with the result of of (17) and (18), that only four independent matrix elements exist, viz.,

$\langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle$ $\quad$ $\langle x|p_z|\lambda\rangle\langle\lambda|p_x|y\rangle$ and $\langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle$

$\langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle$

(20) Let us now define the following quantities:

$$L = \frac{\hbar^2}{m^2} \sum_{\lambda\neq 0}' \frac{\langle x|p_x|\lambda\rangle\langle\lambda|p_x|x\rangle}{E_0^{(0)} - E_\lambda^{(0)}}$$

$$M = \frac{\hbar^2}{m^2} \sum_{\lambda\neq 0}' \frac{\langle x|p_y|\lambda\rangle\langle\lambda|p_y|x\rangle}{E_0^{(0)} - E_\lambda^{(0)}}$$

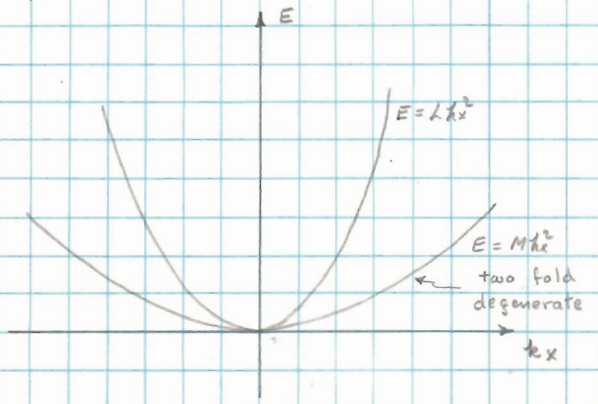
$$N = \frac{\hbar^2}{m^2} \sum_{\lambda\neq 0}' \frac{\langle x|p_x|\lambda\rangle\langle\lambda|p_y|y\rangle + \langle x|p_y|\lambda\rangle\langle\lambda|p_x|y\rangle}{E_0^{(0)} - E_\lambda^{(0)}}$$

(21) Hence, it is now clear from the last definition, our symmetry results, and equations (14) that our matrix equation (13) becomes:

$$\begin{bmatrix} L k_x^2 + M(k_y^2 + k_z^2) & N k_y k_x & N k_x k_z \\ N k_y k_x & L k_y^2 + M(k_x^2 + k_z^2) & N k_y k_z \\ N k_x k_z & N k_y k_z & L k_z^2 + M(k_x^2 + k_y^2) \end{bmatrix} \begin{bmatrix} \alpha_{1\delta} \\ \alpha_{2\delta} \\ \alpha_{3\delta} \end{bmatrix} = E_0^{(2)} \mathbb{I} \begin{bmatrix} \alpha_{1\delta} \\ \alpha_{2\delta} \\ \alpha_{3\delta} \end{bmatrix}$$

(22) Let us consider E vs k in the k_x direction ($k_y, k_z = 0$)

$$\begin{vmatrix} L k_x^2 - E & 0 & 0 \\ 0 & M k_x^2 - E & 0 \\ 0 & 0 & M k_x^2 - E \end{vmatrix} = 0 \quad ; \quad E = L k_x^2 \quad E = M k_x^2$$



Consider $L > M$: The same curves will also obviously be obtained along k_y, k_z. The E vs k curves along the principal axes are simple parabolas. Notice that even in the second order the degeneracy has not been completely removed in these directions.

(23) Consider the intersection of the constant energy surface with the k_x-k_y plane:

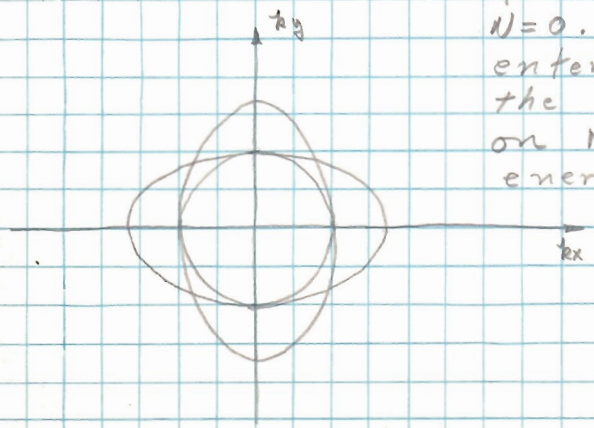
$$\begin{vmatrix} L k_x^2 + M k_y^2 - E & N k_x k_y & 0 \\ N k_x k_y & L k_y^2 + M k_x^2 - E & 0 \\ 0 & 0 & M(k_x^2 + k_y^2) - E \end{vmatrix} = 0$$

$$E = M(k_x^2 + k_y^2)$$

$$E = \frac{(L+M)(k_x^2 + k_y^2)}{2} \pm \frac{1}{2}\left\{ (L-M)^2 (k_x^4 + k_y^4) + 2\left[2N^2 - (L-M)^2 k_x^2 k_y^2 \right] \right\}^{1/2}$$

For $N = 0$, we have a circle bounded by two $\perp$ ellipses:

$E = M(k_x^2 + k_y^2)$
$E = L k_x^2 + M k_y^2$
$E = M k_x^2 + L k_y^2$



It is evident that the same will occur on the other two plane projections, so that the constant energy surfaces will be ellipsoids of revolution about the principle axes for $N = 0$. For $N \neq 0$, the mixing term $k_x k_y$ enters which tilts the ellipsoids off the major axis by an amount depending on N, so that generally, the 3 constant energy surfaces are ellipsoids, not of revolution, rotated from the principle axes (k_x, k_y, k_z) with degeneracys at their lines of intersection.

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15. (1) We begin with the usual general Schroedinger Equation:

$$H\Psi(r,t) - i\hbar \frac{\partial}{\partial t}\Psi(r,t) = 0$$

with the stipulation that Ψ is expanded in terms of Bloch functions:

$$\Psi(r,t) = \sum_{n'k'} \varphi_{n'}(k',t)\, b_{n'}(k',r)$$

Hereafter, the time dependence of $\varphi(k,t)$ will be understood implicitly and we will write $\varphi(k)$.

(2) The complete Hamiltonian is:

$$H = \frac{p^2}{2m} + V(r) + U(r)$$

where $H_0 = \frac{p^2}{2m} + V(r)$ is regarded as the unperturbed Hamiltonian whose result of operation on the Bloch functions is well-known. $U(r)$ is considered as the perturbing potential.

(3) We now operate on $\Psi(r,t)$, making $n,k \to n',k'$

$$\sum_{n'k'} H_0\, b_{n'}(k',r)\, \varphi_{n'}(k') + \sum_{n'k'} U(r)\, b_{n'}(k',r)\, \varphi_{n'}(k')$$

$$- i\hbar \sum_{n'k'} b_{n'}(k',r)\, \frac{\partial}{\partial t}\varphi_{n'}(k') = 0$$

(4) Multiplying by $\int b^*_{n}(k,r)\, d^3r$ in order to form matrix elements:

$$\sum_{n'k'} \langle nk|H_0|n'k'\rangle \varphi_{n'}(k') + \sum_{n'k'} \langle nk|U(r)|n'k'\rangle \varphi_{n'}(k')$$

$$- i\hbar \sum_{n'k'} \langle nk|n'k'\rangle \frac{\partial}{\partial t}\varphi_{n'}(k') = 0$$

(5) Consider the unperturbed Hamiltonian operating on the time independent Bloch functions yielding stationary states:

$$H_0\, b_{n'}(k',r) = E_{n'}(k')\, b_{n'}(k',r)$$

giving $\langle nk|H_0|n'k'\rangle = E_{n'}(k')\langle nk|n'k'\rangle = E_{n'}(k')\,\delta_{nn'}\,\delta_{kk'}$

as the Bloch functions were shown in lecture to be orthonormal in n and k. This shows that the $E_n(k)$'s are diagonal.

(6) Now consider $\langle nk|U(r)|n'k'\rangle$. We would like to show:

$$\langle nk|U(r)|n'k'\rangle \rightarrow \mathcal{U}\ (\text{CMR operators})$$

A way to show this, although not completely general, is to consider $U(r)$ as rather well behaved, as most perturbations are, and expand it in a Taylor series. Even if $U(r)$ is not very well behaved, as long as its discontinuities are simple and isolated (as an example, $\sin x^{-1}$ does not satisfy this requirement; however, staircase, step, and finite impulse functions and their like do), we may expand in a ~~Taylor~~ Fourier series with reasonable hope that it will converge to the function. The point is that the exponential terms of the Fourier series could in turn be expanded in their power series and anything to be shown about r^p will be true about $U(r)$. Thus we consider:

$$\langle nk|r^p|n'k'\rangle$$

(7) $$\langle nk|r^p|n'k'\rangle = \langle nk|r\cdot r^{p-1}|n'k'\rangle = \cdot \sum_{n''k''} \langle nk|r^{p-1}|n''k''\rangle\langle n''k''|r|n'k'\rangle$$

Now it was shown in lecture that:

$$\langle nk|r|n'k'\rangle = i\nabla_k \delta_{nn'}\delta_{kk'} + \chi_{nn'}(k)\delta_{kk'}$$

where $$\chi_{nn'}(k) \equiv i\frac{1}{V_a}\int u_n^*(k,r)\nabla_k u_{n'}(k,r)\, d^3r$$

However, we will repeat the argument for completeness.

(8) As $\langle nk|r|n'k'\rangle$ is non-quadratically integrable, we will consider $r \rightarrow \frac{\sin q\cdot r}{q}$, seeing that $r = \lim_{q\to 0}\frac{\sin q\cdot r}{q}$.

$$\langle nk|\frac{\sin qr}{q}|n'k'\rangle = \frac{1}{2iq}\int\left[e^{iq\cdot r} - e^{-iq\cdot r}\right]e^{i(k-k')\cdot r}\, u_n^*(k,r)\, u_{n'}(k',r)\, d^3r$$

$$= \frac{1}{2iq}\int\left[e^{i(k-k'+q)\cdot r} - e^{i(k-k'-q)\cdot r}\right]u_n^*(k,r)\, u_{n'}(k',r)\, d^3r$$

(9) Consider: $$\frac{1}{\Omega}\int u_n^*(k,r)\, u_{n'}(k',r)\, e^{i(k'-k\pm q)\cdot r}\, d^3r$$

As the Bloch functions and the sine are periodic, we can replace the above integral with a sum of integrals over one cell:

$$\underbrace{\frac{1}{\Omega}\sum_R e^{i(k'-k\pm q)\cdot R}}_{G^3\delta_{k',k\pm q}}\int_0 u_n^*(k,r)\, u_{n'}(k',r)\, e^{i(k'-k\pm q)\cdot r}\, d^3r$$

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15 continued:

(10) Put $k' \to k \mp q$:

$$(9) = \delta_{k',\,k\mp q}\,\frac{1}{v_a}\int_0 u_{n'}^*(k,r)\,u_{n'}(k\mp q,r)\,d^3r$$

Expand $u_{n'}(k\mp q,r)$ in a Taylor series considering only the component k_x:

$$(9) = \delta_{k',\,k\mp q}\,\frac{1}{v_a}\int_0 \underbrace{u_{n'}^*(k,r)\,u_{n'}(k,r)}_{\delta_{nn'}} \mp q\,\frac{\partial u_{n'}(k,r)}{\partial k_x} + q^2\,\frac{\partial^2 u}{\partial k_x^2} \mp \cdots\Big]d^3r$$

$$= \delta_{k';\,k\mp q}\left\{\delta_{nn'} \mp \frac{1}{v_a}\int_0 u_n^*(k,r)\left[q\,\frac{\partial}{\partial k_x} \pm q^2\,\frac{\partial^2}{\partial k_x^2} \mp \cdots\right]u_{n'}(k,r)\,d^3r\right\}$$

(11) Therefore:

$$\langle nk\,|\,\frac{\sin q\cdot r}{q}\,|\,n'k'\rangle = \delta_{nn'}\cdot\frac{1}{2iq}\left[\delta_{k',\,k-q} - \delta_{k',\,k+q}\right]$$

$$-\frac{1}{2iq}\left[\delta_{k',\,k-q} + \delta_{k',\,k+q}\right]\cdot\frac{1}{v_a}\int_0 u_n^*(k,r)\left[q\,\frac{\partial}{\partial k_x} \pm q^2\,\frac{\partial^2}{\partial k_x^2} \mp \cdots\right]u_{n'}(k,r)\,d^3r$$

(12) Consider: $\lim_{q\to 0}\langle nk\,|\,\frac{\sin q\cdot r}{q}\,|\,n'k'\rangle\,\varphi_n(k')$; then:

$$\lim_{q\to 0}\frac{\varphi(k-q) - \varphi(k+q)}{q} = -\lim_{\Delta q\to 0}\frac{2\,\Delta\varphi(k)}{\Delta q} = -2\,\frac{\partial\varphi(k)}{\partial k_x}$$

$$\Rightarrow -2\,\nabla_k\,\varphi(k)\,, \text{ considering } \Delta q = (k+q) - (k-q)$$

$$\lim_{q\to 0}\left[\delta_{k',\,k-q} + \delta_{k',\,k+q}\right]\cdot\frac{1}{v_a}\int_0 u_n^*(k,r)\left[\frac{\partial}{\partial k_x} \pm q\,\frac{\partial^2}{\partial k_x^2} \mp \cdots\right]u_{n'}(k,r)\,d^3r$$

$$= \delta_{k'k}\,\frac{2}{v_a}\int_0 u_n^*(k,r)\,\frac{\partial}{\partial k_x}\,u_{n'}(k,r)\,d^3r \Rightarrow \delta_{k'k}\,\frac{2}{v_a}\int_0 u_n^*(k,r)\,\nabla_k\,u_{n'}(k,r)\,d^3r$$

$\frac{\sin(q\cdot r)}{|q|} = \frac{\sin(|q||r|\cos\theta)}{|q|} \to |r|\cos\theta$

(13) $\therefore$ $\lim_{q\to 0}\langle nk\,|\,\frac{\sin q\cdot r}{|q|}\,|\,n'k'\rangle = \langle nk\,|\,r\,|\,n'k'\rangle$

$$= \delta_{k'k}\,\delta_{nn'}\,i\,\nabla_k + \frac{i}{v_a}\int_0 u_n^*(k,r)\,\nabla_k\,u_{n'}(k,r)\,d^3r\;\delta_{k'k}$$

(14) Define: $\chi_{nn'}(k) \equiv i\,\frac{1}{v_a}\int_0 u_n^*(k,r)\,\nabla_k\,u_{n'}(k,r)\,d^3r$

as per lecture.

Then: $\langle nk\,|\,r\,|\,n'k'\rangle = \delta_{k'k}\,\delta_{nn'}\,i\,\nabla_k + \delta_{k'k}\,\chi_{nn'}$

(15) Returning to (7):

We consider the repeated zone scheme. In this case, the band number n is independent of the wave vector k. We then think of a matrix formed from $\langle nk|r^p|n'k'\rangle$ as indexed on k only for two fixed bands n and n'. We can then form, via the product rule for multiplication of matrix elements:

$$\langle nk|r^p|n'k'\rangle = \sum_{k''} \langle nk|r^{p-1}|n'k''\rangle\langle nk''|r|n'k'\rangle$$

$$= \sum_{k''} \langle nk|r^{p-1}|n'k''\rangle \left[\delta_{nn'}\delta_{k'k''}\, i\nabla_{k'} + \delta_{k'k''}\chi_{nn'}\right]$$

$$= \langle nk|r^{p-1}|n'k'\rangle \left[\delta_{nn'}\, i\nabla_{k'} + \chi_{nn'}\right]$$

Obviously this procedure can be repeated until:

$$\langle nk|r^p|n'k'\rangle = \left[\delta_{nn'}\, i\nabla_{k'} + \chi_{nn'}\right]^{p-1}\langle nk|r|n'k'\rangle$$

$$= \delta_{kk'}\left[\delta_{nn'}\, i\nabla_{k'} + \chi_{nn'}\right]^p$$

(16) Therefore, we can say with reasonable assurance

$$\langle nk|U(r)|n'k'\rangle = \delta_{kk'}\, U\left[\delta_{nn'}\, i\nabla_{k'} + \chi_{nn'}\right]$$

Putting this result, along with (5), back into (4) and summing on k', we have:

$$\sum_{n'}\left\{E_{n'}(k)\,\delta_{nn'} + U\left[\delta_{nn'}\, i\nabla_k + \chi_{nn'}\right] - i\hbar\,\delta_{nn'}\frac{\partial}{\partial t}\right\}\varphi_{n'}(k) = 0$$

This equation can now be easily thrown into matrix form by inspection:

$$\left[\mathbb{E} + U(\mathbb{R} + \mathbb{X}) - i\hbar\frac{\partial}{\partial t}\mathbb{I}\right]\underline{\Phi}(k) = 0$$

where $\mathbb{E} = \begin{bmatrix} E_1(k) & 0 & 0 & \cdots \\ 0 & E_2(k) & 0 & \\ 0 & 0 & E_3(k) & \\ \vdots & & & \ddots \end{bmatrix}$; $\mathbb{X} = \begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} & \cdots \\ \chi_{21} & \chi_{22} & \chi_{23} & \\ \vdots & & & \ddots \end{bmatrix}$

$\mathbb{R} = i\nabla_k\,\mathbb{I}$; $\underline{\Phi}(k) = \begin{bmatrix} \varphi_1(k) \\ \varphi_2(k) \\ \varphi_3(k) \\ \vdots \end{bmatrix}$

Insufficient explanation where noted. If you can explain, see me.

(8)

Assignment #3
Problems VI

Paul Grant
DEAP-AP-16
AP 295
1-14-61

16. (1) For the purposes of this problem, we may take over the results of the Kohn-Luttinger treatment of a homogeneous magnetic field in a solid.

$$E_n(-i\nabla - \frac{e}{\hbar c}A)F_n(r) = E F_n(r)$$

with $A = (-Hy, 0, 0)$ and using the effective mass approximation:

$$\left[\frac{-\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2} + 2isy\frac{\partial}{\partial x} + i^2s^2y^2\right)\right]F_n(r)$$

$$= [E - E_n(0)]F_n(r)$$

where $s = \frac{eH}{\hbar c}$

The solution of this eigenvalue equation is:

$$E = E_n(0) + \frac{\hbar^2 k_z^2}{2m^*} + (n + \tfrac{1}{2})\hbar\omega$$

or, for a gas of free particles:

$$E = \frac{\hbar^2 k_z^2}{2m} + (n + \tfrac{1}{2})\hbar\omega \quad , \quad \omega = \frac{eH}{mc}$$

(2) We now take over the lecture result for the density of states in a uniform magnetic field suitably modified for the free particle:

$$\rho(E)\,dE = \frac{\Omega}{4\pi^2}\hbar\omega\left(\frac{2m}{\hbar^2}\right)^{3/2}\sum_{n=0}^{n_{max}}{}' \frac{1}{[E - \hbar\omega(n+\frac{1}{2})]^{1/2}}\,dE$$

where n_{max} is determined by the vanishing value of $[E - \hbar\omega(n+1/2)]$.

(3) The definition of the Fermi level at $T=0$ follows:

$$N = \int_0^{E_F}\rho(E)\,dE$$

where N is the totality of electrons and n will be the number per unit volume, N/Ω.

(4) $$n = \frac{\hbar\omega}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sum_{\nu=0}^{\nu_{max}} \int_{\frac{1}{2}\hbar\omega + \nu\hbar\omega}^{E_F} \left[E - \hbar\omega(\nu+1/2)\right]^{-1/2} dE$$

We replace the lower limit by the zero-point energy, $\frac{1}{2}\hbar\omega$, as this is the lowest energy the system will have. When the integral is evaluated, this lower limit will vanish since now $\nu_{max} = 0$.

You've screwed up here. Limit (lower) changes for each term.

(5) $$n = \frac{\hbar\omega}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \left\{ \sum_{\nu=0}^{\nu_{max}} \left[E_F - \hbar\omega(\nu+1/2)\right]^{1/2} - \left(\left[\tfrac{1}{2}\hbar\omega - \hbar\omega(\nu+1/2)\right]^{1/2} \right)_{\nu=0} \right\}$$

You had to reset to ⟶ to cure it.

$$= \frac{\hbar\omega}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sum_{\nu=0}^{\nu_{max}} \left[E_F - \hbar\omega(\nu+1/2)\right]^{1/2}, \quad \nu_{max} = \frac{E_F}{\hbar\omega} - \frac{1}{2}$$

(6) We recall that the Fermi level at $T=0$ for an unperturbed free electron gas is given by:

$$E_F^0 = \frac{\hbar^2 k_F^2}{2m}, \quad k_F^3 = 3\pi^2 n$$

$$E_F^0 = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}, \quad 3n\pi^2 = \left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E_F^0\right)^{3/2}$$

$$\text{or} \quad n = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E_F^0\right)^{3/2}$$

(7) $$\therefore \quad \frac{2}{3}\left(\frac{E_F^0}{\hbar\omega}\right)^{3/2} = \sum_{\nu=0}^{\nu_{max}} \left[E_F/\hbar\omega - (\nu+1/2)\right]^{1/2}$$

A few values of $E_F/\hbar\omega$ vs. $E_F^0/\hbar\omega$ are plotted below. Note that ν_{max} depends on $E_F/\hbar\omega$.

$E_F/\hbar\omega - 1/2$	$E_F^0/\hbar\omega$	$E_F/\hbar\omega$
0	0	.5
1	1.3	1.5
2	2.35	2.5
3	3.4	3.5
4	4.4	4.5
5	5.4	5.5
6	6.4	6.5
7	7.4	7.5
8	8.5	8.5

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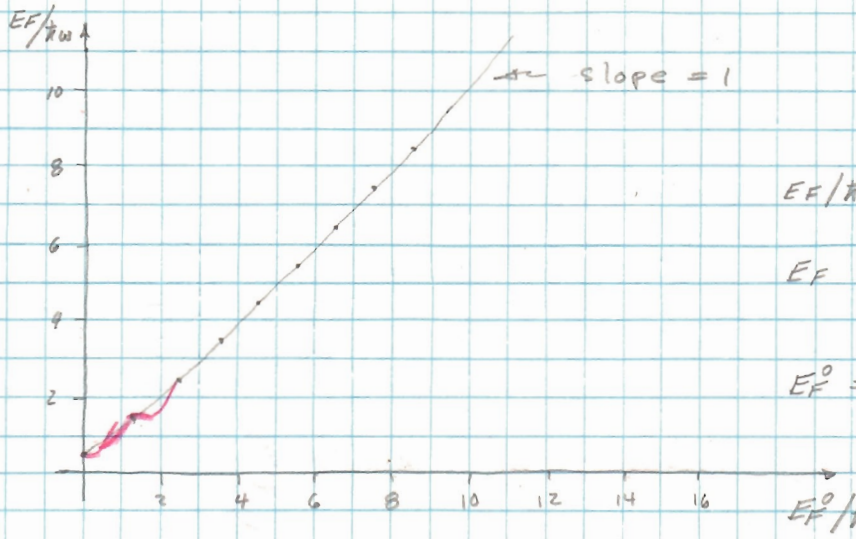
16 Continued



$E_F/\hbar\omega$ vs. $E_F^\circ/\hbar\omega$

E_F = fermi level in magnetic field

E_F° = fermi level without magnetic field.

we see that for low fields (high ν_{max}), there is only a slight shift in the fermi level from that in the absence of a magnetic field. In fact, for high ν_{max}, we can change the sum into an integral and find in the limit:

$$\frac{E_F^\circ}{\hbar\omega} = \frac{E_F}{\hbar\omega} - 1/2 \quad , \text{or} \quad E_F = E_F^\circ + 1/2\,\hbar\omega$$

That this is a fact can be seen from the graph. Thus the Fermi level is shifted by an amount equal to the zero point energy of the harmonic oscillator for weak magnetic fields. If $E_F^\circ \gg 1/2\,\hbar\omega$ to begin with, then the shift will be hardly noticable. One's physical intuition would lead one to expect that the effect of applying a weak field would only shift the fermi level by an amount $1/2\,\hbar\omega$ because the energy of Larmour orbits are of this order of magnitude. In a typical metal, Na, $E_F^\circ \approx 3$ ev while for a field as large as 10^4 gauss, $1/2\,\hbar\omega \approx 10^{-4}$ ev, so that the shift is really negligible.

On the other hand, for high fields, ν_{max} is low and we can take the first term of the sum as an approximation.

Here we have:

$$\frac{2}{3}\left(\frac{E_F^\circ}{\hbar\omega}\right)^{3/2} = \left[E_F/\hbar\omega - 1/2\right]^{1/2}$$

or $$\frac{E_F}{\hbar\omega} = 1/2 + \frac{4}{9}\left(\frac{E_F^\circ}{\hbar\omega}\right)^3$$

or $$E_F = 1/2\,\hbar\omega + \frac{4}{9}\frac{(E_F^\circ)^3}{(\hbar\omega)^2}$$

Here we have the complete collapse of the gas into the zero point energy of the harmonic oscillator in the high field limit. For this to happen, however, the field would have to be tremendously high, well above the order of 10^8 gauss. In this limit, the fermi energy is $1/2\,\hbar\omega$ and the density of states is infinite.

You missed whole point of problem! See posted solution on me.

A. B.

Sorry! (#7)

Assignment #3
Problems VI
Continued

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17. (1) We approach this problem via the following procedure:

a) Write the Helmholtz free energy for an electron gas obeying Fermi-Dirac statistics:

$$F = U - TS$$

b) Assume the Fermi distribution varies linearly about its characteristic Fermi energy and write it in terms of two parameters describing the equation of a straight line.

c) Eliminate one of the parameters via the constraint that the number of electrons remain constant.

d) Minimize the free energy with respect to the remaining parameter such that equilibrium is established and a relation between the parameter and temperature found.

e) Use $C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$ to find formally the specific heat in terms of the parameter which may be eliminated with the use of d.

(2) The entropy of an electron gas is given by (Mott & Jones, p. 204)

$$S = \kappa \log \prod_k \frac{z_k!}{n_k!\,(z_k - n_k)!}$$

where κ = Boltzmann's constant
z_k = no. of states with energy $E(k)$
n_k = no. of electrons in these states

when S is a maximum:

$$\frac{n_k}{z_k} = f(k)\,,$$ the Fermi-Dirac distribution.

(3) Using Stirlings Approximation, $\log N! \simeq N \log N$, we find:

$$S = \kappa \sum_k \{ \log Z_k! - \log n_k! - \log (Z_k - n_k)! \}$$

$$\simeq -\kappa \sum_k Z_k \{ f \log f + (1-f) \log (1-f) \}$$

$$\longrightarrow -\kappa \frac{\Omega}{8\pi^3} \int d^3k \; Z(k) \{ f \log f + (1-f) \log (1-f) \}$$

↑ continuum of states

$$= -\kappa \frac{\Omega}{2\pi^2} \int Z(k) \{ f \log f + (1-f) \log (1-f) \} k^2 \, dk$$

We take $Z(k) = 1$ because of the exclusion principle, then:

$$S = -\kappa \frac{\Omega}{2\pi^2} \int_0^\infty \{ f \log f + (1-f) \log (1-f) \} k^2 \, dk$$

(4) We now follow the treatment given by Wohlfarth and write for the internal energy:

$$\mathcal{U} = \overline{\epsilon(k)} - \overline{I_x(k)} = \frac{\hbar^2 \Omega}{4\pi^2 m} \int_0^\infty f(k) \, k^4 \, dk$$

$$- \frac{e^2 \Omega}{4\pi^3} \int_0^\infty \int_0^\infty f(k_1) f(k_2) \, k_1 k_2 \ln \left| \frac{k_1 + k_2}{k_1 - k_2} \right| dk_1 \, dk_2$$

The first term is merely the statistical average of the usual free electron energy:

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$$

and the second term is the average over the interaction - exchange energy as found by Hartree-Fock methods.

(5) We now choose an approximation to the Fermi distribution as follows:

$$f(k) = 1 \; ; \quad 0 \le k \le a$$

$$f(k) = \alpha - \beta k \; ; \quad a \le k \le b$$

$$f(k) = 0 \; ; \quad k \ge b$$

Assignment #3
Problems VI
Continued

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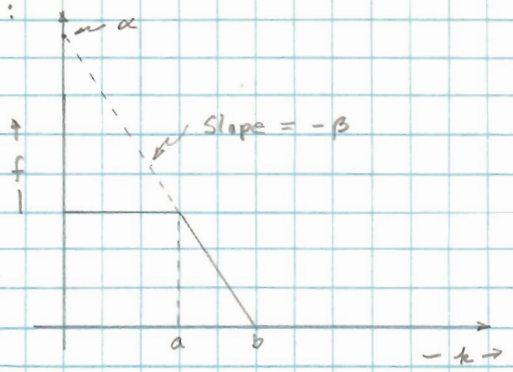
Problem 17
Continued:



$$a = \frac{1-\alpha}{\beta} \qquad b = \frac{\alpha}{\beta}$$

Note that as $T \to 0$, $\alpha \to \infty$

(6) We now compute the free electron term of the internal energy:

$$\overline{\epsilon(k)} = \frac{\hbar^2 \Omega}{4\pi^2 m} \left\{ \int_0^a k^4\,dk + \int_a^b (\alpha - \beta k)\, k^4\,dk \right\}$$

$$\int_0^a k^4\,dk = \frac{a^5}{5} \qquad \int_a^b (\alpha - \beta k)\, k^4\,dk = \frac{\alpha}{5}(b^5 - a^5) - \frac{\beta}{6}(b^6 - a^6)$$

$$a^6 = \frac{1}{\beta^6}\left(1 - 6\alpha + 15\alpha^2 - 20\alpha^3 + 15\alpha^4 - 6\alpha^5 + \alpha^6\right)$$

$$a^5 = \frac{(1-\alpha)^5}{\beta^5} = \frac{1}{\beta^5}\left(1 - 5\alpha + 10\alpha^2 - 10\alpha^3 + 5\alpha^4 - \alpha^5\right)$$

Noting that as $T \to 0$, $\alpha \to \infty$, it would be advisable to put these terms in reciprocal powers of α and then cut-off at a reasonable order for a low temperature approximation.

$$a^6 = \left(\frac{\alpha^5}{\beta^5}\right)\left(\alpha - 6 + 15\alpha^{-1} - 20\alpha^{-2} + 15\alpha^{-3} - 6\alpha^{-4} + \alpha^{-5}\right)$$

$$a^5 = \left(\frac{\alpha^5}{\beta^5}\right)\left(-1 + 5\alpha^{-1} - 10\alpha^{-2} + 10\alpha^{-3} - 5\alpha^{-4} + \alpha^{-5}\right)$$

$$\{\} = \frac{1}{5}\left(\frac{\alpha^5}{\beta^5}\right)\left(-1 + 5\alpha^{-1} - 10\alpha^{-2}\right) + \frac{1}{5}\left(\frac{\alpha^5}{\beta^5}\right)\left(\alpha + \alpha - 5 + 10\alpha^{-1} - 10\alpha^{-2}\right)$$

$$- \frac{1}{6}\left(\frac{\alpha^5}{\beta^5}\right)\left(\alpha - \alpha + 6 - 15\alpha^{-1} + 20\alpha^{-2}\right)$$

$$= \frac{1}{30}\left(\frac{\alpha^5}{\beta^5}\right)\left(-6 + 30\alpha^{-1} - 60\alpha^{-2} + 12\alpha - 30 + 60\alpha^{-1} - 60\alpha^{-2}\right.$$

$$\left. - 30 + 75\alpha^{-1} - 100\alpha^{-2}\right)$$

$$= \frac{1}{30}\left(\frac{\alpha^5}{\beta^5}\right)\left(12\alpha - 66 + 165\alpha^{-1} - 220\alpha^{-2}\right)$$

(7) We can eliminate $\left(\frac{\alpha}{\beta}\right)$ by the use of the constancy of the totality of the particles of the system.

$$N = \frac{\Omega}{\pi^2}\int_0^\infty k^2 f(k)\,dk \quad \text{, counting spin.}$$

$$\text{or } \frac{N\pi^2}{\Omega} = \int_0^a k^2 dk + \alpha\int_a^b k^2 dk - \beta\int_a^b k^3 dk$$

$$= \frac{1}{3}a^3 + \frac{\alpha}{3}(b^3-a^3) - \frac{\beta}{4}(b^4-a^4)$$

$$a^3 = (1 - 3\alpha + 3\alpha^2 - \alpha^3)\frac{1}{\beta^3} = \frac{\alpha^3}{\beta^3}(-1 + 3\alpha^{-1} - 3\alpha^{-2} + \alpha^{-3})$$

$$a^4 = (1 - 4\alpha + 6\alpha^2 - 4\alpha^3 + \alpha^4)\frac{1}{\beta^4} = \frac{\alpha^3}{\beta^4}(\alpha - 4 + 6\alpha^{-1} - 4\alpha^{-2} + \alpha^{-3})$$

$$\frac{N\pi^2}{\Omega} = \left(\frac{\alpha^3}{\beta^3}\right)\left[\left\{-1 + 3\alpha^{-1} - 3\alpha^{-2} + \alpha^{-3} + 2\alpha - 3 + 3\alpha^{-1} - \alpha^{-2}\right\}\frac{1}{3}\right.$$

$$\left. - \frac{1}{4}\left\{4 - 6\alpha^{-1} + 4\alpha^{-2} - \alpha^{-3}\right\}\right]$$

$$[\ ] = \frac{1}{12}\left\{8\alpha - 16 + 24\alpha^{-1} - 16\alpha^{-2} + 4\alpha^{-3} - 12 + 18\alpha^{-1} - 12\alpha^{-2} + 3\alpha^{-3}\right\}$$

$$= \frac{1}{12}\left\{8\alpha - 28 + 42\alpha^{-1} - 28\alpha^{-2} + 7\alpha^{-3}\right\}$$

(8) Upon considerable manipulation, we obtain:

$$\overline{\epsilon(k)} = \frac{3}{5}N\left(\frac{\hbar^2}{2m}\right)\left(\frac{3N}{\pi^2\Omega}\right)^{2/3}\left\{1 + \frac{5}{12}\alpha^{-2}\right\}$$

where we have only kept terms to order α^{-2}.

(9) Further lengthy algebraic operation gives, to the order α^{-2}:

$$\overline{I_x(k)} = \frac{3}{4}N\,e^2\left(\frac{3N}{\pi V}\right)^{1/3}\left(1 - \frac{13}{72}\alpha^{-2} + \frac{1}{6}\alpha^{-2}\ln\frac{1}{2\alpha}\right)$$

$$TS = \frac{3}{2}\kappa T\alpha^{-1}$$

(10) Making the proper substitutions, we obtain Wohlfarth's results:

$$\frac{F}{N} = \frac{3}{5}\epsilon_0\left(1 + \frac{5}{12}x^2\right) - \frac{3}{4}\epsilon_1\left(1 - \frac{13}{72}x^2 + \frac{1}{6}x^2\ln\frac{x}{2}\right) - \frac{3}{2}\kappa Tx$$

where $x = \frac{1}{\alpha}$; $\epsilon_0 = \left(\frac{\hbar^2}{2m}\right)\left(\frac{3N}{\pi^2\Omega}\right)^{2/3}$

$$\epsilon_1 = e^2\left(\frac{3N}{\pi V}\right)^{1/3}$$

Assignment # 3
Problem Set VI
Continued

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Problem 17
Continued

(11) To find the desired relation between x and T, we minimize the free energy at a constant temperature with respect to the parameter of the distribution, x.

$$\frac{1}{2}\epsilon_0 x + \frac{13}{48}\epsilon_1 x - \epsilon_1 \frac{1}{4} x \ln\frac{x}{2} - \frac{1}{8}\epsilon_1 x - \frac{3}{2} n T = 0$$

$$\text{or } \frac{3nT}{\epsilon_0} = x + \frac{13}{24}\frac{\epsilon_1}{\epsilon_0} x - \frac{1}{4}\frac{\epsilon_1}{\epsilon_0} x - \frac{1}{2}\frac{\epsilon_1}{\epsilon_0} \ln\frac{x}{2}$$

$$\therefore \frac{3nT}{\epsilon_0} = \left(1 + \frac{7}{24}\frac{\epsilon_1}{\epsilon_0}\right) x - \frac{1}{2}\frac{\epsilon_1}{\epsilon_0} \ln\frac{x}{2}$$

(12) From the Maxwell relations and the definition of the Helmholtz free energy, we have:

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$\text{or } C_v = \frac{3}{2} N n T \frac{dx}{dT} = \frac{9/2\, N n (n T/\epsilon_0)}{\frac{d}{dx}(3 n T/\epsilon_0)}$$

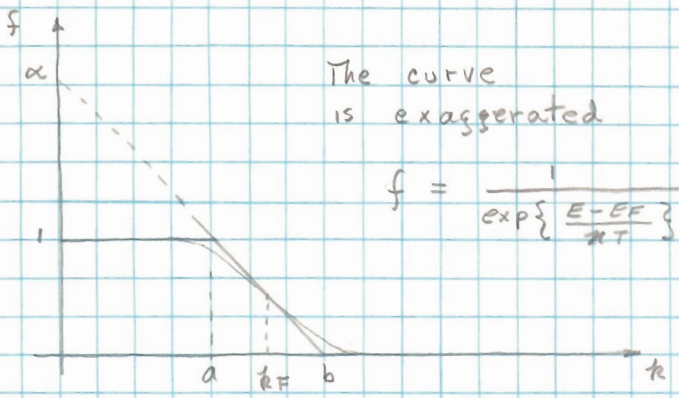
(13) We substitute the derivative of (11):

$$C_v = \frac{9/2\, N n (n T/\epsilon_0)}{\left\{1 - \frac{5}{24}\frac{\epsilon_1}{\epsilon_0} - \frac{1}{2}\frac{\epsilon_1}{\epsilon_0}\ln\frac{x}{2}\right\}}$$

We see that $C_v \sim \frac{T}{\log \frac{x}{k}}$

we now need a relation between x and T for clearly they are dependent on each other. This relation may be had by simultaneous solution of (13) and (11). However, these are transcendental functions and an explicit solution is unlikely.

To show that x depends on T more explicitly, let us consider the linearization of the Fermi function about k_F which should be a good approximation for low temperatures. The resulting equation will then be of the form of (5), $f = \alpha - \beta k$



The curve is exaggerated

$$f = \frac{1}{\exp\left\{\frac{E-E_F}{\kappa T}\right\}+1} = \frac{1}{\exp\left\{\frac{\hbar^2}{2m\kappa T}(k^2-k_F^2)\right\}+1}$$

$$(14)\quad \left(\frac{d f(k)}{dk}\right)_{k=k_F} = \left[-\left(\exp\{\}+1\right)^{-2}\cdot\frac{\hbar^2}{2m\kappa T}\cdot 2k\ \exp\{\}\right]_{k=k_F}$$

$$= -\frac{\hbar^2}{4m\kappa T}k_F = \beta$$

$$(15)\quad 1/2 = -\frac{\hbar^2 k_F^2}{4m\kappa T} + \alpha\ ;\ \alpha = 1/2 + \frac{\hbar^2 k_F^2}{4m\kappa T}$$

$$\therefore\ f = -\frac{\hbar^2 k_F}{4m\kappa T}k + \left\{1/2 + \frac{\hbar^2 k_F^2}{4m\kappa T}\right\}$$

where $a = \frac{2m\kappa T}{\hbar^2 k_F} - k_F$, $b = \frac{2m\kappa T}{\hbar^2 k_F} + k_F$

Now, for low temperatures, it is clear that the $1/2$ in α can be neglected. Thus we have shown for low temperatures that:

$$\alpha \sim \frac{1}{T}$$

Now, since $x \equiv \frac{1}{\alpha}$, then $x \sim T$

Substituting in (13): $C_V \sim \frac{T}{\ln \frac{T}{K}}$

where K is a constant of the material analogous to the Debeye or Einstein temperatures. If $T/K < 1$, then we use the absolute value as C_V is positive.

$$\therefore\ C_V \sim \frac{T}{|\ln T/K|}$$

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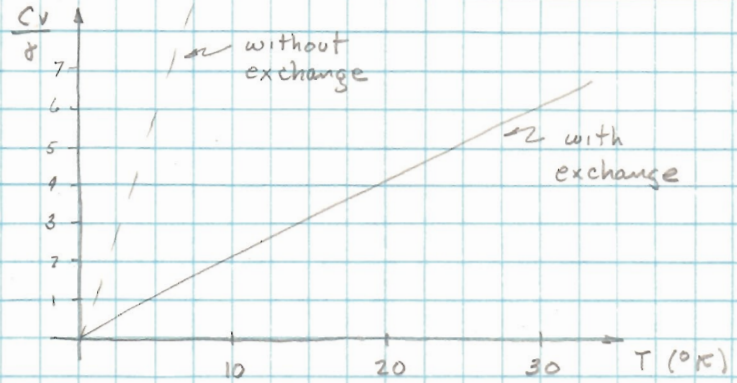
17 Continued.

(16) Discussion:

The inclusion of exchange leads to anomalous results in that it disagrees to rather high ($10^{\circ}K$) with the Sommerfeld specific heat based on a no-exchange, free-electron model. Note the following graph sketched roughly from Wohlfarth.



γ = sommerfeld constant.

$\frac{Cv}{\gamma}$ vs T

for Na

The Sommerfeld result has been established without doubt for a large number of free electron metals. The anomaly that exists is due to the neglect of correlation forces, ie, coulombic interaction between electrons. These forces may be simulated by replacing the coulomb potential used in calculating the exchange term with a screened potential (Hartree-Fock) and thus retain the one electron model. Such an arrangement can be shown to regain agreement with the simple free electron theory.

(10)

Applied Physics 295

Final Examination

Please answer 5 of the following questions, and indicate on the front cover of your examination book which questions you have answered. The credit assigned each question is indicated in the right-hand margin.

1

a) Give the following information about Brillouin zones for electrons in a solid.

(i) How is the first zone constructed?

(ii) What is its volume?

(iii) How many states does it contain?

(iv) Which symmetry properties of the crystal lattice determine the Brillouin zone structure? 8

b) Calculate numerical orders of magnitude for the quantities that follow. In some cases you will have to choose reasonable (although not necessarily unique) input data. Be sure to state these numbers and the basic equations clearly. Useful (approximate) constants: $m = 10^{-27}$ gm, $\hbar = 10^{-27}$ erg-sec, $e = 5 \times 10^{-10}$ esu, K (Boltzmann constant) $= 10^{-16}$ erg/^{o}K, Rydberg $= \frac{e^4 m}{2\hbar^2} = 13$ eV Bohr orbit $= \frac{\hbar^2}{me^2} = 0.5$ Å, 1 eV $= 2 \times 10^{-12}$ ergs. Express energies in electron volts.

(i) Plasma energy of a typical "free electron" metal.

(ii) Fermi energy of the metal considered in (i).

(iii) Bohr orbit of a hydrogenic impurity in a semiconductor characterized by an effective mass of 0.1m and a dielectric constant $\epsilon = 10$.

(continued)

1b continued

(iv) Binding energy of the electron in the ground state of the hydrogenic impurity considered in (iii).

(v) Debye temperature of a typical metal.

(vi) Average sound velocity of the metal considered in (v) 12

2

a) Define and find an explicit representation for the crystal translation operator. 3

b) Define Bloch functions $b_n(k, r)$ and show that they are solutions of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]b_n(k,r) = E_n(k)b_n(k, r). \qquad 7$$

c) State whether each of the following statements concerning functions appearing in the preceding Schrödinger equation is true or false:

(i) $b_n(k, r + R) = b_n(k, r)$

(ii) $b_n(k + K, r) = b_n(k, r)$

(iii) $b_n(-k, r) = b_n(k, r)$

(iv) $E_n(-k) = E_n(k)$

(v) $E_n(k) = E_n(k - K)$ 5

Here R and K respectively are ordinary and reciprocal lattice vectors.

d) Prove your answer to part c) (iv). 5

3

a) Discuss the dispersion relations satisfied by (i) electrons in solids, (ii) phonons, and (iii) plasmons, indicating briefly how they are calculated and sketching typical behavior for the three cases on clearly labelled diagrams. A complete derivation is not necessary. 18

b) Mention two experiments that give information concerning the preceding dispersion relations, indicating to which particles they apply. 2

4

a) Describe physically the meaning and behavior of the two-particle density matrix $\Gamma(x_1 x_2 | x_1 x_2)$ for a free electron gas treated in the Hartree-Fock approximation. 6

b) Which function of the frequency and wave-number dependent dielectric constant $\epsilon(\omega, q)$ is involved in the expression for the energy loss of a fast electron? Show why and under what conditions the energy loss in a given energy region may be discrete. 6

c) The quantum mechanical expression for $\epsilon(0,q)$ of a free electron gas obeying Fermi statistics at zero absolute temperature is:

$$\epsilon(0, q) = 1 + \frac{1}{q^2\lambda^2}\left[\frac{1}{4\sigma}\left\{2\sigma + (1 - \sigma^2)\log\left|\frac{1 + \sigma}{1 - \sigma}\right|\right\}\right]$$

where $\lambda = [E_F/6\pi ne^2]^{1/2}$ is the Thomas-Fermi screening length, $E_F = \hbar^2 k_F^2/2m$ is the Fermi energy, n is the particle density and $\sigma = q/2k_F$. Discuss this result physically in connection with the screening of a point charge

(continued)

4c continued

immersed in the gas. [Do not try to calculate the modified screening length explicitly]. 8

5

a) State and prove the orthogonality conditions for Wannier functions. 5

b) Calculate the Wannier function for an electron in an empty simple cubic lattice having lattice constant a. 5

c) Discuss how the results of part (b) reflect two characteristic properties of Wannier functions. 4

d) Prove that, aside from normalization constants, the Wannier functions are the Fourier transforms of the momentum eigenfunctions $\chi_n(k)$ defined by

$$b_n(k, r) = \sum_K \chi_n(k + K) e^{i(k + K)\cdot r}$$ 4

e) Under what condition do Wannier functions reduce to atomic wave functions satisfying the Schrödinger equation for an atom in the solid? 2

6

a) Explain why the specific heat of a free electron gas at very low temperatures is much smaller than that of a gas of purely classical particles. What, approximately, is the factor by which the specific heat is reduced from the classical value? 8

b) State the temperature dependences of the lattice specific heat at low temperatures for one, two, and three dimensional lattices. Give simple arguments that substantiate these statements. 8

(continued)

6 continued

c) Explain why the number of branches (or bands) in the lattice vibration spectrum is finite, whereas it is unbounded for an electron in a periodic potential. 4

7

a) Explain why the motion of a Bloch electron in a uniform electric field is periodic (Ignore interband effects). 4

b) Calculate an expression for the period of the motion. 4

c) Find the relationship between the Larmor orbits in r and k space for a free electron in a uniform magnetic field. 4

d) Show by means of a diagram and accompanying explanation how the Fermi sphere for a free electron gas is modified when a uniform magnetic field is applied to the system. 4

e) Using the expression for the cyclotron frequency

$$\omega_c = \frac{2\pi eH}{\hbar^2 c} \left(\frac{dA}{dE}\right)^{-1},$$

where A is the area of the orbit in k-space, and Onsager's theorem

$$A = \frac{2\pi eH}{\hbar c} (n + \phi),$$

show that for large quantum numbers n, the separation of permitted energy levels of an electron in a uniform magnetic field H is given by $\hbar\omega_c$. 4

AP 295

PROBLEM SET # 1 : SPECIAL

PROBLEMS 1 & 3

AP295: PROBLEM SET #1 : SPECIAL

Problem 1

A Translation of the notation used here to the notation used in class will be given at the end of the problem. In most cases the correspondence will be obvious. We will work initially with a general 3-dimensional crystal, one atom per unit cell, with inversion symmetry. The crystal potential energy, neglecting constant terms, can be written:

$$V = \frac{1}{2} \sum_{ll'} \vec{u}_l \cdot \mathbb{C}(l-l') \cdot \vec{u}_{l'}$$

Here $\mathbb{C}(l-l')$ is the interaction tensor, and $\vec{R}_l = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3$ is the direct lattice vector. Using the "cosmological" principle, we may write:

$$V = \frac{1}{2} \sum_{ll'} \vec{u}_l \cdot \mathbb{C}(l-l') \cdot \vec{u}_{l'} = \frac{1}{2} \sum_{ll''} \vec{u}_l \cdot \mathbb{C}(l'') \cdot u_{l-l''}$$

$l'' = l - l'$, $l' = l - l''$; $l'' \to -l'$; $\mathbb{C}(l) = \mathbb{C}(-l)$

Then:

$$V = \frac{1}{2} \sum_{ll'} \vec{u}_l \cdot \mathbb{C}(l') \cdot \vec{u}_{l+l'}$$

$$= \frac{1}{2} \sum_{ll'} u_{l,\sigma}\, C_{\sigma\alpha}(l')\, u_{l+l',\alpha}$$

By Taylor's theorem, we have:

$$M_{l+l',\alpha} = M_{l,\alpha} + \frac{\partial M_{l,\alpha}}{\partial R_{l,\beta}} R_{l',\beta} + \frac{1}{2} \frac{\partial^2 M_{l,\alpha}}{\partial R_{l,\gamma} \partial R_{l,\delta}} R_{l'\gamma} R_{l'\delta} + \cdots$$

considering that if $M_{l,i}$ varies slowly enough, $\frac{\partial}{\partial R_{l,i}}$ has a meaning. Upon resubstituting in V, we see that the first term vanishes because $\sum_{l} C(l') = 0$ (rigid displacement). The second term vanishes as $M_{l,\sigma} \frac{\partial M_{l,\alpha}}{\partial R_{l,\beta}}$ forms an odd function. Hence:
Also $\sum_{l'} C(l') R_{l'} = 0$ when inversion symmetry is present.

$$V = \frac{1}{2} \sum_{ll'} M_{l,\sigma} C_{\sigma\alpha}(l') \left\{ \frac{1}{2} \frac{\partial^2 M_{l,\alpha}}{\partial R_{l,\gamma} \partial R_{l,\delta}} R_{l'\gamma} R_{l's} \right\}$$

We drop higher order terms in the hope they are small and in the spirit of the harmonic approximation to V in the first place. We now stipulate that as we proceed to the continuum picture, $\vec{M}_l$ and $\frac{\partial^2 M_{l,\alpha}}{\partial R_{l,\gamma} \partial R_{l,\delta}}$ are slowly varying with respect to R_l. This permits us to change the $\sum_l$ to an integration over continuous space. In doing this, we must remember to weight the integral with respect to the sum interval to bring about dimensional correctness and to preserve the total number of atoms:

$$\sum_l \rightarrow \frac{1}{v_a} \int d^3r \quad ; \quad v_a = \text{cellular volume.}$$

Hence:

$$V = \left\{ \frac{1}{2v_a} \sum_{l'} C_{\sigma\alpha}(l') R_{l'\gamma} R_{l's} \right\} \cdot \frac{1}{2} \int u_\sigma \frac{\partial^2 u_\alpha}{\partial r_\gamma \partial r_s} d^3r$$

Integrating by parts: $\int u_\sigma \frac{\partial^2 u_\alpha}{\partial r_\gamma \partial r_s} d^3r$

$$= \int u_\sigma \frac{\partial}{\partial r_\gamma} \left(\frac{\partial u_\alpha}{\partial r_s} \right) dr_\gamma \cdots$$

$$= u_\sigma \frac{\partial u_\alpha}{\partial r_s} \Bigg|_{\text{crystal}} - \int \left(\frac{\partial u_\sigma}{\partial r_\gamma} \right) \left(\frac{\partial u_\alpha}{\partial r_s} \right) d^3r$$

If we impose the BVK boundary condition, the constant term vanishes and we have:

$$V = \frac{1}{2} \int \frac{\partial u_\sigma}{\partial r_\gamma} \left\{ -\frac{1}{2v_a} \sum_{l'} C_{\sigma\alpha}(l') R_{l'\gamma} R_{l's} \right\} \frac{\partial u_\alpha}{\partial r_s} d^3r \qquad (A)$$

From the classical theory of elasticity, we use the fact that the crystal potential energy is the integrated potential energy density which is a quadratic function of the local strain:

$$V = \frac{1}{2} \int \frac{\partial \vec{u}}{\partial \vec{r}} : \mathbb{E} : \frac{\partial \vec{u}}{\partial \vec{r}} d^3r = \frac{1}{2} \int \frac{\partial u_\sigma}{\partial r_\gamma} E_{\sigma\alpha}^{\gamma s} \frac{\partial u_\alpha}{\partial r_s} d^3r \qquad (B)$$

(See Ziman)

We may also write the potential energy in Voigt's notation (used by Kittel) where we have:

$$\sum_{\sigma\gamma\alpha\delta=1}^{3} \frac{\partial \mathcal{U}_\sigma}{\partial \lambda_\gamma} E_{\sigma\alpha}^{\gamma\delta} \frac{\partial \mathcal{U}_\alpha}{\partial \lambda_\delta} = \sum_{i,j=1}^{6} e_i C_{ij} e_j$$

where i, j are "double" indices, that is, we could write $\sum_{i,j=1}^{6} e_i C_{ij} e_j = \sum_{klmn=1}^{3} e_{kl} C_{kl,mn} e_{mn}$. The usual definition of the stain tensor is: $e_{kl} = \frac{1}{2}\left(\frac{\partial \mathcal{U}_k}{\partial x_l} + \frac{\partial \mathcal{U}_l}{\partial x_k}\right)$. We can then identify:

$$\boxed{C_{ij} = E_{\sigma\alpha}^{\gamma\delta}} \quad (C)$$

providing we match indices according to the following table:

i or j:	1 : xx	2 : yy	3 : zz	4 : yz	5 : zx	6 : xy
γ or δ:	1 : x	2 : y	3 : z	3 : z	1 : x	2 : y
σ or α:	1 : x	2 : y	3 : z	2 : y	3 : z	1 : x

(D)

We now match coefficients in (A) and (B). However, (A) possesses a symmetry in γ and δ which (B) does not. Hence we must have:

$$\boxed{E_{\sigma\alpha}^{\gamma\delta} + E_{\sigma\alpha}^{\delta\gamma} = -\frac{1}{v_a} \sum_{l} C_{\sigma\alpha}(l) R_{l\gamma} R_{ls}} \quad (E)$$

Relations (E) and (C) together with table (D) relate the elastic constants C_{ij} with the atomic force constants $C_{\sigma\alpha}(l)$ as requested in the problem.

We now proceed to find the explicit relation between the C_{ij} and the components of $\mathbb{C}(l)$ for interactions in a simple cubic lattice up to and including next nearest neighbors, not necessarily with central forces. We must first find the form of the $\mathbb{C}(l)$ Tensor.

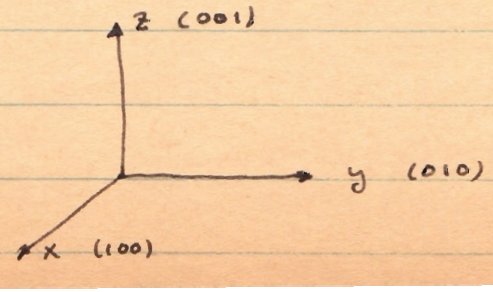
We know that the potential should be invariant under a symmetry operation of the crystal. From the equation for V it is implied that there is a matrix S such that:

$$\boxed{\mathbb{C}(l) = \tilde{S}\,\mathbb{C}(l)\,S \quad ; \quad \tilde{S}S = 1}$$

Consider first nearest neighbor interaction along the principle axes of the lattice, that is, $\mathbb{C}(100) = \mathbb{C}(\bar{1}00)$, $\mathbb{C}(010) = \mathbb{C}(0\bar{1}0)$, $\mathbb{C}(001) = \mathbb{C}(00\bar{1})$. Now let:

$$\mathbb{C}(100) = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

What are the symmetry operations that leave 100 invariant?



We ask what S performs the following operations and find S by inspection:

I. $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \to \begin{pmatrix} x \\ z \\ y \end{pmatrix}$; $S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$; since $\begin{pmatrix} x \\ y \\ z \end{pmatrix} = S \begin{pmatrix} x \\ z \\ y \end{pmatrix}$

II. $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \to \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$; $S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

III. $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \to \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$; $S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

For I we have: $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{33} & a_{23} \\ a_{31} & a_{32} & a_{22} \end{pmatrix}$

We conclude: $a_{33} = a_{22}$.

II. $\tilde{S}\, C(100)\, S = \begin{pmatrix} a_{11} & -a_{12} & a_{13} \\ -a_{21} & a_{22} & -a_{23} \\ a_{31} & -a_{32} & a_{33} \end{pmatrix}$; hence: $a_{12} = a_{21} = a_{23} = a_{32} = 0$

III. $S\, C(100)\, S$ gives: $a_{13} = a_{31} = 0$

We choose $a_{11} = \alpha$, $a_{22} = a_{33} = \beta$ and have:

$$C(100) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

Finding an S that gives $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \to \begin{pmatrix} y \\ x \\ z \end{pmatrix}$, we get:

$$C(010) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix} \quad ; \text{ similarly, } \quad C(001) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}$$

We should note that there is an ambiguity of sign involved in the interaction constants. That is, there is no reason why α, β must be positive and we saw in the case of the monoatomic linear lattice that indeed they must be negative for real frequencies to be propagated in the crystal (Recall $C(0) = -\frac{1}{2} C(1)$).

The finding of the $C(l)$ for the next nearest neighbor interaction, along the face diagonals, is trivial and may be handled as before or looked up in Leibfried's article in the Handbuch der Physik. We have altogether:

Nearest neighbor: $C(100) = C(\bar{1}00) = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \beta \end{pmatrix}$

$C(010) = C(0\bar{1}0) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$; $C(001) = C(00\bar{1}) = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}$

Next nearest neighbor:

$C(110) = C(\bar{1}\bar{1}0) = \begin{pmatrix} \gamma & \varkappa & 0 \\ \varkappa & \gamma & 0 \\ 0 & 0 & \delta \end{pmatrix}$; $C(011) = C(0\bar{1}\bar{1}) = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \gamma & \varkappa \\ 0 & \varkappa & \gamma \end{pmatrix}$

$C(101) = C(\bar{1}0\bar{1}) = \begin{pmatrix} \gamma & 0 & \varkappa \\ 0 & \delta & 0 \\ \varkappa & 0 & \gamma \end{pmatrix}$; $C(1\bar{1}0) = C(\bar{1}10) = \begin{pmatrix} \gamma & -\varkappa & 0 \\ -\varkappa & \gamma & 0 \\ 0 & 0 & \delta \end{pmatrix}$

$C(01\bar{1}) = C(0\bar{1}1) = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \gamma & -\varkappa \\ 0 & -\varkappa & \gamma \end{pmatrix}$; $C(10\bar{1}) = C(\bar{1}01) = \begin{pmatrix} \gamma & 0 & -\varkappa \\ 0 & \delta & 0 \\ -\varkappa & 0 & \gamma \end{pmatrix}$

We could get $C(0)$ from $\sum_l C(l) = 0$, but we do not need it.

In order to escape undue calculation, we examine the effect of cubic symmetry on the form of the matrix $\| C_{ij} \|$:

$$\| C_{ij} \| = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix}$$

Under the symmetry operations of the cube, we have:

$$\| C_{ij} \| = \tilde{\mathcal{S}} \, \| C_{ij} \| \, \mathcal{S} \qquad (\mathcal{S} \neq \mathcal{S} \text{ of before})$$

Suppose we have the symmetry operation $\begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$.
Let:

$$\begin{pmatrix} xx \\ yy \\ zz \\ yz \\ zx \\ xy \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{pmatrix}; \quad \text{then} \quad \begin{pmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{pmatrix} \rightarrow \begin{pmatrix} 1 \\ 2 \\ 3 \\ -4 \\ 5 \\ -6 \end{pmatrix}$$

and:

$$\mathcal{S} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix}$$

It becomes clear that repeated inversion operations will clear the off-diagonal lower half of $\| C_{ij} \|$, that is.

$C_{41} = C_{42} = C_{43} = 0$

$C_{51} = C_{52} = C_{53} = C_{54} = 0$

$C_{61} = C_{62} = C_{63} = C_{64} = C_{65} = 0$

Rotation symmetry operations (proper and improper) about each principle axis reflects this lower half and also leads to the fact that there are only 3 independent elastic constants. Hence we can write for cubic symmetry:

$$\| C_{ij} \| = \begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{11} & C_{12} & & 0 & \\ C_{12} & C_{12} & C_{11} & & & \\ & & & C_{44} & & \\ & 0 & & & C_{44} & \\ & & & & & C_{44} \end{pmatrix}$$

The rest of the calculation is now very nearly trivial. For aid in computation we construct a table of values for $R_{\alpha\beta}/a$ for the simple cubic:

$R_{\alpha\beta}/a$

	γ	1	2	3	
l		x	y	z	
(100), (1̄00)		1, -1	0, 0	0, 0	} nearest neighbours
(010), (01̄0)		0, 0	1, -1	0, 0	
(001), (00 1̄)		0, 0	0, 0	1, -1	
(110), (1̄1̄0)		1, -1	1, -1	0, 0	} next nearest neighbours
(101), (1̄01̄)		1, -1	0, 0	1, -1	
(011), (01̄1̄)		0, 0	1, -1	1, -1	
(1 1̄0), (1̄10)		1, -1	-1, 1	0, 0	
(10 1̄), (1̄01)		1, -1	0, 0	-1, 1	
(01 1̄), (01̄1)		0, 0	1, -1	-1, 1	

We proceed, using relations © and (E).

$$C_{11} = E''_{11} = -\frac{1}{2a^3} \sum_{\ell} C_{11}(\ell)\, R_{\ell 1} R_{\ell 1}$$

$$= -\frac{1}{2a} \left\{ 2 \underbrace{C_{11}(100)}_{\alpha} + 2 \underbrace{C_{11}(110)}_{\gamma} + 2 \underbrace{C_{11}(101)}_{\gamma} + 2 \underbrace{C_{11}(1\bar{1}0)}_{\gamma} + 2 \underbrace{C_{11}(10\bar{1})}_{\gamma} \right\}$$

$$= -\frac{1}{a} \left\{ \alpha + 4\gamma \right\}$$

$$C_{44} = E^{33}_{22} = -\frac{1}{2a^3} \sum_{\ell} C_{22}(\ell)\, R_{\ell 3} R_{\ell 3}$$

$$= -\frac{1}{2a} \left\{ 2 \underbrace{C_{22}(001)}_{\beta} + 2 \underbrace{C_{22}(101)}_{\delta} + 2 \underbrace{C_{22}(011)}_{\gamma} + 2 \underbrace{C_{22}(01\bar{1})}_{\gamma} + 2 \underbrace{C_{22}(10\bar{1})}_{\delta} \right\}$$

$$= -\frac{1}{a} \left\{ \beta + 2\gamma + 2\delta \right\}$$

$$E^{12}_{12} + E^{21}_{12} = C_{12} + C_{44} = -\frac{1}{a^3} \sum_{\ell} C_{12}(\ell)\, R_{\ell 1} R_{\ell 2}$$

$$= -\frac{1}{a} \left\{ 2 \underbrace{C_{12}(110)}_{\kappa} - 2 \underbrace{C_{12}(1\bar{1}0)}_{-\kappa} \right\} = -\frac{4\kappa}{a}$$

Recapitulating:

$$C_{11} = -\frac{1}{a} \left\{ \alpha + 4\gamma \right\}$$

$$C_{44} = -\frac{1}{a} \left\{ \beta + 2\gamma + 2\delta \right\}$$

$$C_{12} + C_{44} = -\frac{4\kappa}{a}$$

Except for sign, this checks with Kittel's (4.37). It is shown in texts on elasticity that the elastic constants C_{11}, C_{44}, C_{12} are positive and hence our $\alpha, \beta, \gamma, \delta, \kappa$ must be negative (recall the ambiguity in sign when they were defined). That the atomic force constants are negative can be clinched by writing the secular equation (derived in lecture) for interactions up to next nearest neighbours and for various appropriate directions of wave propagation and observing that $\alpha, \beta, \gamma, \delta, \kappa$ must be negative in order that real eigenvalues exist.

Relation between notations used here and that in lecture:

$$C(l) \rightarrow A(\vec{m})$$

$$C\alpha\gamma(l) \rightarrow A^{\alpha\gamma}(\vec{m})$$

$$\vec{Re} \rightarrow l \rightarrow \vec{m}$$

AP 295: SPECIAL PROBLEM SET #1

Problem 3:

The most general partition function based on the canonical ensemble is:

$$Z = \sum_{\{n_i\}} e^{-\sum_i \frac{E_{n_i}}{kT}}$$

where $\{n_i\}$ denotes the set $n_1, \ldots\ldots$. For a system of phonons, we have from lecture:

$$E_{n_{fs}} = (n_{fs} + 1/2)\, \hbar\, \omega(fs) .$$

Hence:

$$Z = \sum_{\{n_{fs}\}} \exp\left[- \sum_{fs} \frac{(n_{fs} + 1/2)\, \hbar\, \omega(fs)}{kT} \right]$$

$$= \sum_{\{n_{fs}\}} \prod_{fs} \exp\left[- \frac{(n_{fs} + 1/2)\, \hbar\, \omega(fs)}{kT} \right]$$

$$= \prod_{fs} \sum_{n_{fs}} e^{- \frac{(n_{fs} + 1/2)\, \hbar\, \omega(fs)}{kT}}$$

$$= \prod_{fs} \frac{e^{-1/2 \frac{\hbar\, \omega(fs)}{kT}}}{1 - e^{- \frac{\hbar\, \omega(fs)}{kT}}}$$

In regard to interchanging $\prod$ and $\sum_i$, mathematical questions of convergence can be disregarded as the results are physically meaningful.

We use the well-known relation connecting thermodynamics and statistical mechanics, namely, $F = -kT \log Z$ where F is the Helmholtz free energy. We find:

$$F = \sum_{fs} \frac{\hbar\omega(fs)}{2} + kT \sum_{fs} \log\left(1 - e^{-\frac{\hbar\omega(fs)}{kT}}\right)$$

We see that the first term represents the internal energy at $T=0$, hence we may define: $U_0 = \sum_{fs} \frac{\hbar\omega(fs)}{2}$. Note that in a crystal this is finite, but increases with its size.

We are interested in the classical limit. Physically this means the limit in which the thermal energy per normal mode kT (from $E = 3NkT$, the classical value) is much greater than the quantum energy of the mode $\hbar\omega(fs)$ (for phonons of all wave vectors and polarizations). Hence we can write:

$$e^{-\frac{\hbar\omega(fs)}{kT}} \approx 1 - \frac{\hbar\omega(fs)}{kT}$$

and finally:

$$F = U_0 + kT \sum_{fs} \log \frac{\hbar\omega(fs)}{kT}$$

A COURSE OUTLINE FOR AP. PHYS. 295

R. ORBACH - FALL, 1961

I. Phonons

A. The diatomic linear chain

1. The frequency spectrum

2. The concept of zone

a. Extended

b. Reduced

3. The density of states

4. The band width

B. The three dimensional lattice. Classical treatment.

1. Potential energy function

2. Symmetry properties of the interaction constants

3. Expansion of the displacements in running waves

4. The secular equation

a. Symmetry properties of the solutions (time invar.)

b. Limiting values (small wave vector)

c. Wave description of eigenstates

1) Lack of plane polarization in general crystals

2) Effect of center of inversion

5. The Reciprocal Lattice

a. Brillouin Zones

b. Extended zone scheme

c. Reduced zone scheme

d. Proof of symmetry relations on energy at zone boundary

C. The Quantization of the vibrational modes

1. Definition of time dependent operators

2. Expansion of vibration in terms of quantum mechanical operators

3. Commutation properties of operators

4. Total energy in terms of quantum operators

5. Generation of ladder equations using commutation relations

a. Energy spectrum

b. Allowed matrix elements

6. Matrix formulation of quantum mechanical operators

D. The partition function for the three dimensional lattice

1. The internal energy

2. The free energy

3. The entropy

4. Einstein-Bose statistics

5. The specific heat

a. High temperature limit

b. Low temperature limit

1) Debye relationship

2) Density of states

3) Born's treatment

4) Einstein assumptions

c. General features of real density of state curves

1) Generalized minima in the dispersion law

2) Generalized maxima in the dispersion law

3) Saddle points in the dispersion law

4) Effects on density of states and specific heats

II. Electrons - Energy Bands

A. The Bloch Theorem

1. Proof in absence of degeneracy

2. Proof in presence of degeneracy

B. The Kronig-Penney model

1. Concept of bands

2. General form of wave functions in periodic structures

C. The symmetry properties of Bloch functions

D. The case of nearly free electrons

1. Fourier expansion of Bloch waves, and lattice potential

2. The energy spectrum

3. Matrix elements of the potential

4. Band gaps and widths

a. Brillouins zones

b. Structure factor

1) Jones zones

2) Example of F.c.c. lattice

5. Density of states formula

a. Definition of Fermi energy

b. Free electron case

c. Electrons near top of band case

E. Tight binding

1. Band width assumptions

2. Energy surfaces for s states

3. Energy surfaces and solutions for p states

4. Energy surfaces and solutions for mixtures of s and p states

5. Density of states

F. The effects of external fields on Bloch functions

1. The group velocity

a. Wave packet argument

b. Ehrenfests relation for force

1) The effective mass tensor

2) dk/dt relation

c. Exact proof of group velocity for Bloch waves

2. The Bohm-Bloch theoram on minimum current flow

3. The Adams Argyres proof of the effective mass relation

a. Elimination of interband terms

b. Exact proof of dk/dt relation

G. The k.p. approximation

1. The Wigner-Seitz cell

2. The Wigner-Seitz computation for wave functions

3. The correction of Bardeen

a. The effective mass

b. The form of the k.p. wave functions at the cell boundary

H. The OPW approximation

1. Derivation of the wave function---core orthogonalization

2. Properties of OPW functions

I. The Empty lattice test

1. Form of wave functions

2. Example for (100) directions in a SC lattice

J. The splitting of the valence bands in germanium and silicon

1. Application of k.p. approximation

a. Form of wave function at k=0.

b. Symmetry of matrix elements of p.

2. Secular equation

   a. Splitting for different directions in k space

   b. The effective mass of holes

   c. The form of the energy surfaces

3. Cyclotron resonance of holes

   a. Resonance condition

   b. Experimental observations

K. The Effective Mass Formula: Proof of its validity

1. Use of k.p. approach. Equivalance to Luttinger and Kohn.

2. Form of wave functions (electric field only)

   a. The elimination of interband terms

   b. The treatment of the "weak" potential

3. The transformation from momentum to real space

   a. The equivalence with the Wannier approach

   b. The form of the envelope function in the conduction band of germanium and silicon

4. Treatment of the degenerate case

5. Indication of proof when a magnetic field is present

6. Case of shallow donors in silicon

   a. Form of effective mass equation

   b. Ionization energy computation

   c. Troubles with effective mass treatment

L. Exciton states

1. Generation of the effective Hamiltonian

2. Use of the effective mass theorem

   a. Form of the envelope function

   b. Shape of exciton bands

III. Electrons--many body effects

A. The one-electron approximation: Hartree fields

1. The Hartree wave function

2. The Hartree self consistent potential

B. The one-electron approximation: Hartree-Fock-Slater treatment

1. Determinental wave functions

a. Matrix element of one electron operators

b. Matrix element of two electron operators

c. Computation of probability P $(r_1 r_2)$.

1) Trick of simple two electron function

2) Form of probability curve

3) Effect on coulomb energy

d. Diagonal Matrix elements of the one electron Hamiltonian

1) Exchange terms, source

2) Shape of exchange hole, significance

3) Comparison with the Hartree solution

4) Computation of the exchange energy for a free electron gas.

5) Discussion of ferromagnetism in a free electron gas

2. Effects of correlation

a. Built into determinental wave function

b. Additional terms omitted in HFS treatment

c. Comparison with Gell-Mann Bruckner formula

C. Plasma Oscillations

1. Classical treatment

2. Observation in Insb.

D. Screening

1. Classical Fermi-Thomas treatment
2. Derivation of screening length

E. The Bohm-Pines Treatment of Electron Correlation

1. Derivation of Fourier transform of one electron Hamiltonian
2. The introduction of the generating function
   a. The cut-off
   b. The transformation of all coordinates and momenta
   c. The form of the new terms- longitudinal fluctuations
   d. The transformed Hamiltonian
3. The additional terms added to the Hamiltonian
   a. The final form of the Hamiltonian
   b. The subsidiary condition
   c. The transformation of the subsidiary condition
4. The separation of the final Hamiltonian
   a. The computation of the short range coulomb interaction
      1) Similarity with screened term
      2) Computation of its magnitude
   b. The computation of the plasma and self energy terms
   c. Minimization of the energy with respect to cut-off parameter
   d. Computation of the correlation energy
5. The effect of cut-off on the exchange interaction
   a. The new total system energy
   b. The new cut-off
   c. The new correlation energy
6. The second order contribution of the short range coulomb interaction
   a. Description of the virtual process
   b. Computation and comparison with Gell-Mass and Bruckner
7. The form of the system wave function
   a. Separation of coordinates
   b. Effect of the subsidiary conditions

c. Shape at long and short distances--effect of correlation

d. Comparison of screening length with cut-off wave vector

8. The electronic specific heat

a. The usual one electron treatment

b. The change of Fermi level with temperature

c. The temperature dependence of the electronic specific heat, and the dependence on the density of states

d. The Hartree-Fock corrections to the simple picture

1) The HF density of states

2) The lack of agreement with experiment

e. The Bohm-Pines corrections

1) Form of density of states

2) Comparison with experiment

9. The electronic susceptibility

a. The usual one electron treatment

b. The corrections due to currelation and exchange

c. Comparison with experiment

d. The disaster of using the HF exchange term alone

IV. The Electron-Phonon Interaction

A. The adiabatic approximation

1. Separation of coordinates

2. Estimate of non-adiabatic terms

B. Bloch form of the electron-phonon interaction

1. Introduction of phonon coordinates

2. Matrix elements between phonon states

a. Momentum conservation

b. Umklapp processes

c. Distribution functions

C. The Rigid Ion Approximation

1. The form of the matrix element between electronic states

a. Manipulation of Shroedinger's equation

b. Condition on polarization direction of phonon

2. Estimate of energy coefficient
    a. Wigner-Seitz approximation
    b. Connection with Fermi energy
3. The interference condition

D. The deformable ion
1. Change in the assumed potential
2. Computation of the matrix element between electron states
3. Comparison with rigid ion matrix elements
4. Criticism of the deformable ion treatment

E. The Bardeen self-consistent treatment of the electron-phonon interaction
1. Change in state of interacting electrons
2. Effect of uniform background of electronic charge
    a. Change of electron potential
    b. Addition to rigid ion scattering matrix element
3. Allowance for change in electron distribution
    a. Self consistency condition
    b. Fourier expansion of charge fluctuations and wave function
    c. Computation of scattering potential from Poisson's eqn.
    d. Satisfying self-consistency requirement
    e. Final form of scattering matrix element
4. Discussion of screening effects
    a. Effect on energy factor
    b. Final form of interaction

V. Transport properties

9/27/61

Books on reserve for AP 295

1) Elements of Solid State Theory, G. Wannier

2) Introduction to Solid State Physics, C. Kittel

3) Electrons and Phonons, J. M. Ziman

4) The Theory of Metals, A. H . Wilson

5) Quantum Theory of Solids, R. E. Pierls

6) Quantum Theory of Fields, G. Wentzel

7) The Modern Theory of Solids, F. Seitz

If you do not possess any of these books, could you please obtain them? They are all of rather wide interest.

Raymond Orbach

APPLIED PHYSICS 295

QUANTUM THEORY OF SOLIDS

INSTRUCTOR: OHRBACH — ROOM 307 : MWF 11

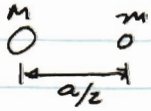
LECTURE 1 : 9-25-61

Course Outline:

Phonons (two weeks)
Electrons (4 weeks)
Electron - Phonon Interaction (4 weeks)
Transport Properties (remainder)

Look at Wentzel's book on the Q. Th. of Fields.

Phonons: 1-dimensional, 2 atoms per cell.



Assume nearest neighbor interaction with "force constant" field.

Equations of Motion:

(m) $$m \frac{d^2}{dt^2} x_{2n+1} = -\mu \left[(x_{2n+1} - x_{2n}) - (x_{2n+2} - x_{2n+1}) \right]$$

(M) $$M \frac{d^2}{dt^2} x_{2n} = -\mu \left[(x_{2n} - x_{2n-1}) - (x_{2n+1} - x_{2n}) \right]$$

Impose BVK Condition: $2N$ masses in all, N of m and N of M. Thus:

$$x_\ell = x_\ell + 2N$$

Although these boundary conditions are not the only ones to use, they are the most convenient. We assume a solution of the form

$$x_{2n+1} = A \exp\left\{ i \left[2\pi \ell \frac{2n+1}{2N} - \omega t \right] \right\}$$

$$X_{2m} = B \exp\left\{ i \left[2\pi l \frac{2u}{2N} - \omega t \right] \right\}$$

l is an integer which will eventually determine the reciprocal lattice vector. We usually write travelling waves as $e^{i(k\cdot r - \omega t)}$. Then here, $r = \frac{na}{2}$; $k = \frac{4\pi l}{Na}$ where l is arbitrary. Resubstituting determines A and B. Set for the set which determines the secular equation:

$$(m\omega^2 - 2\mu) A + 2\mu B \cos(2\pi l/2N) = 0$$
$$2\mu A \cos(2\pi l/2N) + (M\omega^2 - 2\mu) B = 0$$

$$\begin{vmatrix} m\omega^2 - 2\mu & 2\mu \cos(2\pi l/2N) \\ 2\mu \cos(2\pi l/2N) & M\omega^2 - 2\mu \end{vmatrix} = 0$$

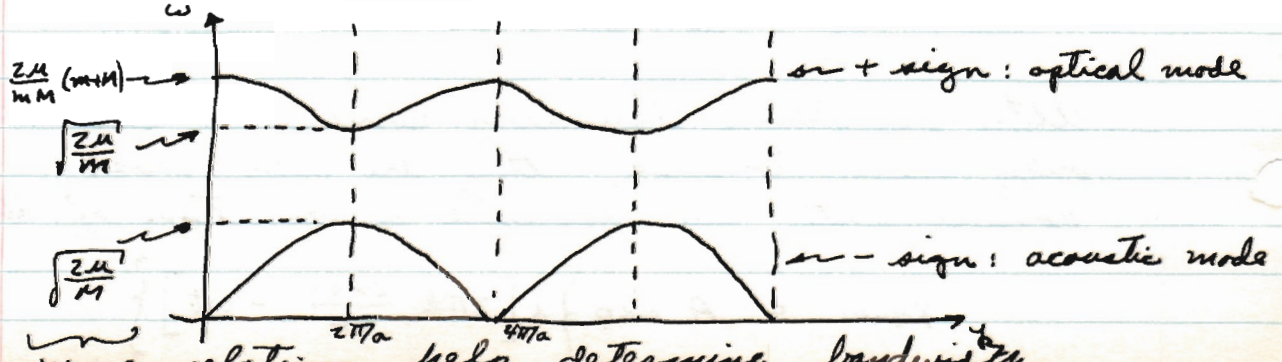
Finally:

$$\omega^2 = \frac{\mu}{mM}\left[M + m \pm \sqrt{M^2 + m^2 + 2Mm\cos(2\pi l/N)} \right]$$

Note that while the eigenvectors are periodic in $2N$, the eigenvalue ω is periodic in N. Also:

$$\frac{A}{B} = \frac{2M\cos(2\pi l/2N)}{\left[M - m \pm \sqrt{\quad} \right]}$$

Periodicity on ω: $0 < l < N$
Periodicity on eigenvectors: $0 < l < 2N$
This means that we have twice as many solutions as needed. Plot ω versus k:



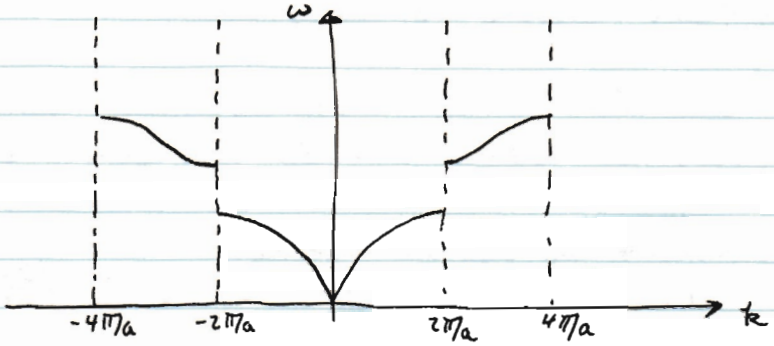
These relations help determine bandwidth.

Recall group velocity: $v = \frac{\partial \omega}{\partial k}$, as $k \to 0$, $\omega \to vk$ in the acoustic band or mode.

What about difficulties involved in the multi-valued function above? Could consider only one mode to exist each period:

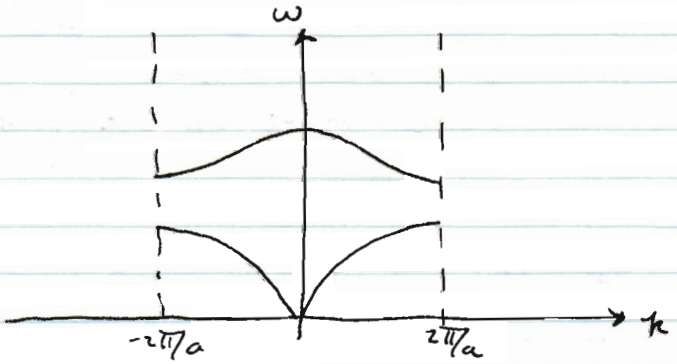
This provides complete discription.

Another way is called the extended zone scheme:



We see that this gives use the right number of solutions.

Reduced Zone Scheme:



Looks a lot like the energy band scheme of the electron theory of solids.

Note that $k = \pm \pi/a$, $l = \pm N/2$ at the zone boundary. At this point, substitution into the secular equation will find the coefficients independent of each other. This means that in acoustic or optical modes we have either big atoms vibrating and little still, or the reverse.

For $0 < k < \pi/a$, $\frac{A}{B} > 0$

$\pi/a < k < 2\pi/a$, $\frac{A}{B} < 0$

This is the reason for the terms optical and acoustical.

Acoustic: vibrate in phase

Optical: vibrate out of phase

If we let $m \to M$, we change periodicity such that optical mode disappears.

What is relative width of bands when one mass becomes very much larger than the other?

Bandwidth of Optical mode:

$$\left(1 + \tfrac{1}{2}\tfrac{m}{M}\right)\sqrt{\tfrac{2\mu}{M}} - \sqrt{\tfrac{2\mu}{m}} \approx \tfrac{1}{2}\tfrac{m}{M}\sqrt{\tfrac{2\mu}{M}}$$

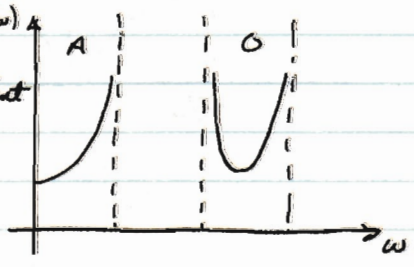
Acoustical: $\sqrt{\frac{2\mu}{M}}$

$$\therefore \quad \frac{OBW}{ABW} = \sqrt{\frac{m}{2\mu}}$$

The significance is that in complicated lattices, we can determine something about dispersion heuristically. What happens is narrowing of optical band.

Mode Density: Total # modes / band = N

$$f(\omega) = \frac{Na}{2\pi}\left(\frac{d\omega}{dk}\right)^{-1}$$



Can see why BW is important because if $OBW \to 0$, can use δ function for $f(\omega)$

LECTURE 2 : 9-27-61

Errata : $f(\omega) = \frac{Na}{2\pi} \left(\frac{d\omega}{dz}\right)^{-1}$

Important : if mass is in imbalance, optical mode approaches a single frequency oscillator. Model might apply to large molecules where one of the atoms is loosely coupled.

Clearly the number of modes per unit k is constant, however, this is not true for ω, hence $f(\omega)$.

Suppose 3 atoms / cell, then in extended zone scheme take on new zone for each atom. In reduced zone scheme, get new band for each atom per unit cell.

Three Dimensional Lattice Vibrations :

Lattice Vector : $\underline{n}$

Position to atom : $\underline{R_n} = \underline{n} + \underline{u_n}$

Expand potential energy :

$$V - V_0 = \sum_{nn'} \frac{1}{2} A_{nn'}^{\alpha\beta} u_n^\alpha u_{n'}^\beta + \sum_{nn'n''} \frac{1}{6} B_{nn'n''}^{\alpha\beta\delta} u_n^\alpha u_{n'}^\beta u_{n''}^\delta$$

$+ \cdots$

no linear term because at equilibrium. We will only diagonalize the harmonic term.

Classical equations of motion : N cells, M = mass

$$M \ddot{u}_n^\alpha = -\frac{\partial}{\partial u_n^\alpha} V$$

$$= -\sum_{n'} A_{nn'}^{\alpha\beta} u_{n'}^\beta \equiv F_n^\alpha$$

Since :

$$\frac{\partial F_n^\alpha}{\partial u_{n'}^\beta} = \frac{\partial F_{n'}^\beta}{\partial u_n^\alpha}$$

This implies : $A_{nn'}^{\alpha\beta} = A_{n'n}^{\beta\alpha}$

and: $A^{\alpha\beta}_{nn'} = A^{\alpha\beta}(n-n') = A^{\beta\alpha}(n'-n)$

What about inversion symmetry? If this exists,

$$A^{\alpha\beta}_{nn'} = A^{\alpha\beta}_{n'n} \quad \text{or} \quad A^{\alpha\beta}(n-n') = A^{\alpha\beta}(n'-n)$$

Note that the potential or rather the kinetic energy is:

$$T = \sum_n \frac{1}{2} M \dot{u}_n^2$$

From the equation of motion, we see under a rigid displacement:

$$\sum_{n'} A^{\alpha\beta}_{nn'} = 0$$

Assume a solution of the form:

$$u_n = v \exp\left[-i\omega t + i f \cdot n\right]$$

f is the phonon wave vector. Substitution gives:

$$M\omega^2 v^\alpha = \sum_{n'} A^{\alpha\beta}_{nn'} e^{if\cdot(n'-n)} v^\beta$$

Making $m = n - n'$ and using tensors:

$$M\omega^2 v^\alpha \equiv G^{\alpha\beta}(f)\, v^\beta$$

where: $G^{\alpha\beta}(f) = \sum_m A^{\alpha\beta}(m) e^{-if\cdot m}$

The secular equation can then be constructed to solve for ω. The solution is a function of f, and the position in the zone determines things like degeneracy. For more than one atom / cell, use appropriate subscripts.

Properties of $G^{\alpha\beta}(f)$:

Hermiticity: $G^{\beta\alpha}(f) = G^{\alpha\beta}(f)^*$

This gives reason for 3 real solutions of ω^2.
We label solutions by index s:
We take highest slope as $\lim_{f\to 0} \omega(f,s) = v_s |f|$
as the longitudinal mode.

Actually, in 3-D lattice, transverse and longitudinal directions are not apparent.

Further Properties: $G^{\alpha\beta}(-f) = G^{\alpha\beta}(f)^*$

$$M\omega^2 v^\alpha = G^{\alpha\beta}(f) v^\beta$$
$$M\omega^2 v^\alpha(f)^* = \left[G^{\alpha\beta}(f)\right]^* v^\beta(f)^* = G^{\alpha\beta}(-f) v^\beta(f)^*$$

$$M\omega^2 v^\alpha(-f) = G^{\alpha\beta}(-f)\, v^\beta(f)$$

Using above relations, we find:

$$v(-f,s) = v^*(f,s)$$

If only we have a center of inversion, we have further:

$$v(f,s) = v^*(f,s)$$

which implies v real.

If center of inversion is in real lattice, exists in reciprocal lattice also, then at zone boundaries, we must have: $\frac{\partial \omega}{\partial k} = 0$.

LECTURE 3 : 9-29-61

Last time we did not prove vanishing of $\nabla_f \omega$ at BZ edges, we instead have proved symmetry in the BZ under inversion symmetry.

It is a general rule, regardless of inversion symmetry that:

$$\omega(f, s) = \omega(-f, s) \qquad \text{(even function)}$$

This is a result of taking complex conjugate of secular equation and using:

$$G^{\alpha\beta}(f)^* = G^{\alpha\beta}(-f)$$

Proof of $\nabla_f \omega = 0$ and BZ edges: Recall:

$$M\omega^2 v^\alpha = \sum_m A^{\alpha\beta}(m)\, e^{-i f\cdot m}\, v^\beta$$

Differentiate with respect to f:

$$2M\omega \frac{\partial \omega}{\partial f} v^\alpha = \sum_m A^{\alpha\beta}(m)(-im)\, e^{-if\cdot m} v^\beta$$

$$= \sum_m \Big[A^{\alpha\beta}(m)(-im)\, e^{-if\cdot m} v^\beta + A^{\alpha\beta}(-m)(im)\, e^{if\cdot m} v^\beta \Big]$$

$A^{\alpha\beta}(-m) = A^{\alpha\beta}(m)$ if inversion center exists.

$$= \sum_m A^{\alpha\beta}(m)\, 2m \sin(f\cdot m)\, v^\beta$$

However, if we sum along a zone boundary $\sin(f\cdot m) = 0$ at BZ edge, hence either $\omega = 0$ or $\left(\frac{\partial \omega}{\partial f}\right)_\perp = 0$ at BZ edge. Given a symmetry direction the symmetry is a $\perp$ plane.

When degeneracies are present, we must write:

$$\sum \left(\frac{\partial \omega}{\partial f}\right)_\perp = 0$$

at center of BZ, either $\omega = 0$ or $\frac{\partial \omega}{\partial f} = 0$.

Recall that the eigenvectors are real only if inversion symmetry exists.

$$u_n = v\, e^{-i(\omega t + f\cdot n)}$$

$$\therefore \quad u_n^\alpha = a^\alpha \sin(f\cdot n - \omega t) + b^\alpha \cos(f\cdot n - \omega t)$$

$$b^\alpha = \mathrm{Re}\, v^\alpha \quad ; \quad a^\alpha = -\mathrm{Im}\, v^\alpha$$

If v^α is complex, have bad situation where can not determine plane polarization, have elliptic polarization or otherwise. Only have plane polarization when v^α is real. Zeman is wrong on this point.

Brillouin Zones:

Impose BVK conditions: $u_n = u_{n+N}$, which gives:

$$e^{if\cdot n} = 1$$

Recall primitive lattice vectors, N_1, N_2, N_3, calls along the three directions respectively. Define primitive vectors τ_1, τ_2, τ_3. Then from BVK:

$$N_1 f\cdot\tau_1 = 2\pi p_1$$
$$N_2 f\cdot\tau_2 = 2\pi p_2$$
$$N_3 f\cdot\tau_3 = 2\pi p_3$$

We define a vector f in the reciprocal space as:

$$f = 2\pi\left[\frac{p_1}{N_1}\frac{\tau_2\times\tau_3}{\tau_1\tau_2\tau_3} + \frac{p_2}{N_2}\frac{\tau_3\times\tau_1}{\tau_1\tau_2\tau_3} + \frac{p_3}{N_3}\frac{\tau_1\times\tau_2}{\tau_1\tau_2\tau_3}\right]$$

This is the solution for f of the three equations above. We take as principle value of p.

$$-\frac{N_2}{2} \le p_2 < \frac{N_2}{2}$$

This gives as the boundary of the BZ:

$$f_{BZ} = \pm\pi\left[\underbrace{\frac{\tau_2\times\tau_3}{V}} + \underbrace{\frac{\tau_3\times\tau_1}{V}} + \underbrace{\frac{\tau_1\times\tau_2}{V}}\right]$$

defined as the primitive vectors of the reciprocal lattice.

This shows bisection of reciprocal lattice vector to construct 1st BZ.

LECTURE 4: 10-2-61

Brillouin Zones:

We calculate the BZ for the fcc.

Recall: $\underbrace{\frac{\tau_2\times\tau_3}{\tau_1\tau_2\tau_3}}_{g_1}, \ldots, g = \alpha g_1 + \beta g_2 + \gamma g_3$

$$f = 2\pi\left[\frac{p_1}{N_1}g_1 + \frac{p_2}{N_2}g_2 + \frac{p_3}{N_3}g_3\right]$$

$-\frac{N}{2} < p_1 < \frac{N}{2}$, etc., to get number of solutions right.

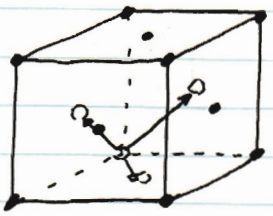
Functions of f are periodic in f space:

$$\omega(f,s) = \omega(f+2\pi g, s)$$

We have defined a reciprocal lattice space, the first period is called the first BZ.

Now for the fcc:

$$\tau_1 = a\left(0,\tfrac{1}{2},\tfrac{1}{2}\right);\quad \tau_2 = a\left(\tfrac{1}{2},0,\tfrac{1}{2}\right);\quad \tau_3 = a\left(\tfrac{1}{2},\tfrac{1}{2},0\right)$$



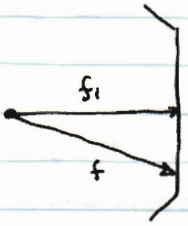
Direct cell of the fcc.

For the reciprocal lattice:

$$g_1 = a^{-1}(-1,1,1) \;;\; g_2 = a^{-1}(1,-1,1) \;;\; g_3 = a^{-1}(1,1,-1)$$

which is the bcc. We can construct the BZ by bisecting $\perp$ planes to the nearest neighbor distances.

Prove $\frac{\partial \omega}{\partial f} = 0$ at BZ boundary. Calculate in g_1 direction.



$$f = f_1 + a f_2 + b f_3$$

Then we want to show:

$$\left.\frac{\partial G^{\alpha\beta}(f)}{\partial f_1}\right|_{f_1 = i\pi g_1} = 0$$

Recall: $G^{\alpha\beta} = \sum_m A^{\alpha\beta}(m)\, e^{-i f\cdot m}$

$$m = m_1\tau_1 + m_2\tau_2 + m_3\tau_3$$

$$\therefore \quad \frac{\partial G^{\alpha\beta}}{\partial f_1} = \sum_{m_1 m_2 m_3} A^{\alpha\beta}(m_1\tau_1 + m_2\tau_2 + m_3\tau_3) \cdot \underbrace{\frac{\partial}{\partial f_1}\left[e^{i(f_1\cdot\tau_1 m_1 + a f_2\cdot\tau_2 m_2 + b f_3\cdot\tau_3 m_3)}\right]}_{i\tau_{f_1} m_1 \; e^{i f_1\cdot\tau_1 m_1}\left[e^{i a f_2\cdot\tau_2 m_2 + i b f_3\cdot\tau_3 m_3}\right]}$$

sum over m_1, positive m_1.

Then this becomes:

$$\sum_{m,i} f_i \cdot \tau_i \left[\cdots \right]$$

since $f = \pi \dfrac{\tau_2 \times \tau_3}{\tau_1 \tau_2 \tau_3}$

Then we have $\sum_{m,i} \pi$ which is zero. We have assumed a mirror plane so $A^{\alpha\beta}$ has symmetry.

Quantization of the lattice vibrations:

$$u_n = \sum_{f,s} q_{fs}(t)\, e^{i f \cdot n}\, v(fs)$$

We consider u_n, $q_{fs}(t)$ as QM operators. We write:

$$q_{fs}(t) = Q_{fs}(0)\, e^{-i\omega(fs)t} + P_{fs}(0)\, e^{i\omega(fs)t}$$

(Heisenberg representation)

$$u_n = \sum_{fs} Q_{fs}(0)\, e^{i f\cdot n - i\omega(fs)t}\, v(fs) + P_{fs}(0)\, e^{-i f\cdot n + i\omega(fs)t}\, v(fs)$$

since u_n is real, $u_n^+ = u_n$ obviously.

$$u_n^* = \sum_{fs} Q_{fs}^+(0)\, e^{-i f\cdot n + i\omega t}\, v^+(fs) + P_{fs}^+(0)\, e^{-i f\cdot n - i\omega t}\, v^+(fs)$$

$$v^+(f,s) = v(-fs)$$

Set: $Q_{f,}(0) = P_{-fs}^+(0)$

$$Q_{-fs}^+(0) = P_{ss}(0)$$

LECTURE 5 : 10-4-61

We can write u_n now:

$$u_n = \sum_{fs} Q_{fs}(0)\, e^{i f\cdot n - i\omega_{fs} t}\, v(fs) + \sum_{fs} Q^*_{fs}(0)\, e^{-if\cdot n + i\omega(fs)t}\, v^*(fs)$$

Define: $Q_{fs}(t) = Q_{fs}(0)\, e^{-i\omega(fs)t}$

Then:

$$\boxed{u_n = \sum_{fs} Q_{fs}(t)\, e^{i f\cdot n}\, v(fs) + \sum_{fs} Q^*_{fs}(t)\, e^{-if\cdot n}\, v^*(fs)}$$

Commutation rules on u's:

$$\left[\dot{u}^\alpha_{n'},\, u^\beta_n\right] = \frac{-i\hbar}{M}\,\delta_{nn'}\,\delta_{\alpha\beta}$$

Now want to find commutation rule for Q's:
Operate with:

$$\sum_n e^{-if'\cdot n}\, v^*(fs) \qquad \text{on } u_n$$

$$\sum_n e^{i(f-f')\cdot n} \qquad \text{must be evaluated.}$$

$$n = n_1\tau_1 + \cdots \qquad , \; 0 < n_i \le N_i$$

$$f = 2\pi\left[\frac{p_1}{N_1}g_1 + \cdots\right]$$

$$f' = 2\pi\left[\frac{p_1'}{N_1}g_1 + \cdots\right]$$

Then:

$$\sum_{n_1} e^{i\frac{2\pi n_1}{N_1}(p_1 - p_1')} = \frac{1 - e^{2\pi i (p_1 - p_1')}}{1 - e^{2\pi i (p_1 - p_1')/N_1}}$$

$$= N_1\,\delta_{p_1 p_1'}$$

$$\therefore \sum_n e^{i(f-f')\cdot n} = N\,\delta_{ff'}$$

now v's are orthogonal. So that we get:

$$Q_{fs}(t) + Q^*_{-fs}(t) = \frac{1}{N} \sum_n e^{-i f\cdot n} u_n \cdot v^*(fs)$$

and for the derivatives:

$$i\omega(fs)\left[Q^*_{-fs}(t) - Q_{fs}(t)\right] = \frac{1}{N} \sum_n e^{-i f\cdot n} v^*(fs)\cdot \dot{u}_n$$

Solve this for $Q_{fs}(t)$, $Q^*_{fs}(t)$ and then take the commutator bracket and get:

$$\left[Q_{fs}(t),\ Q^*_{f's'}(t)\right] = \frac{\hbar}{2NM\omega(fs)}\ \delta_{ff'}\,\delta_{ss'}$$

Compute the kinetic energy:

$$T = \frac{1}{2}\sum_n M \dot{u}_n^2$$

$$= \frac{1}{2} MN \sum_{fs} \omega^2(fs)\left[Q_{fs}(t)\,Q^*_{fs}(t) + Q^*_{fs}(t)\,Q_{fs}(t)\right]$$

$$- \frac{1}{2} MN \sum_{fs} \omega^2(fs)\left[Q_{fs}(t)\,Q_{-fs}(t) + Q^*_{fs}(t)\,Q^*_{-fs}(t)\right]$$

Because of the time dependence of Q, we have a wild oscillatory behaviour in time. However, we will see that the potential energy will cause cancellation of these terms.

LECTURE 6 : 10-6-61

Computation of Potential Energy:

$$V - V_0 = \frac{1}{2} \sum_{nn'} A_{nn'}^{\alpha\beta} u_{n'}^{\alpha} u_n^{\beta}$$

$$= \frac{1}{2} \sum_{nn'} A_{nn'}^{\alpha\beta} \sum_{\substack{fs \\ f's'}} \left\{ Q_{fs}(t) e^{i f\cdot n} v^{\alpha}(fs) + Q_{fs}^{*}(t) e^{-i f\cdot n} v^{\alpha *}(fs) \right\}$$

$$\left\{ Q_{f's'}(t) e^{i f'\cdot n'} v^{\beta}(f's') + Q_{f's'}^{*}(t) e^{-i f'\cdot n'} v^{\beta *}(f's') \right\}$$

Recall secular equation:

$$M \omega^2 v^{\beta} = \sum_{n} A_{n'n}^{\alpha\beta} e^{i f\cdot(n-n')} v^{\alpha}$$

We get for the potential energy in terms of the Q's and P's:

$$V - V_0 = \frac{1}{2} MN \sum_{fs} \omega^2(fs) \left\{ Q_{fs}(t) Q_{fs}^{*}(t) + Q_{fs}^{*}(t) Q_{fs}(t) \right\}$$

$$+ \frac{1}{2} MN \sum_{fs} \omega^2(fs) \left\{ Q_{fs}(t) Q_{-fs}(t) + Q_{fs}^{*}(t) Q_{-fs}^{*}(t) \right\}$$

This last term exactly cancels the term in the KE and removes the oscillatory term. Then:

$$\mathcal{H} = T + V - V_0 = MN \sum_{fs} \omega^2(fs) \left\{ Q_{fs}(t) Q_{fs}^{*}(t) + Q_{fs}^{*}(t) Q_{fs}(t) \right\}$$

We now introduce second quantization. There is no term in $\mathcal{H}$ which connects f and f' hence we can write it for only one state f. Thus:

$$\mathcal{H} = MN \omega^2 \left[Q Q^{+} + Q^{+} Q \right]$$

Recall: $\left[Q, Q^{+} \right] = \dfrac{\hbar}{2NM\omega}$

Now $\dot{Q} = \frac{1}{\hbar}[\mathcal{H}, Q]$ giving:

$$\dot{Q} = -i\omega Q \quad ; \quad Q = \frac{1}{\hbar\omega}[Q, \mathcal{H}]$$

as could be seen from the definition.
We now construct states that diagonalize the Hamiltonian so that:

$$\mathcal{H}|n\rangle = E_n|n\rangle$$

Calculate the matrix element:

$$\langle m|Q|n\rangle = -\frac{1}{\hbar\omega}\langle m|[\mathcal{H}, Q]|n\rangle$$

$$= -\frac{E_m - E_n}{\hbar\omega}\langle m|Q|n\rangle$$

and: $E_n = \hbar\omega + E_m$

hence Q is a destruction operator in that it lowers the energy of the system.
similarly:

$$\langle m|Q^*|n\rangle = \frac{E_m - E_n}{\hbar\omega}\langle m|Q^*|n\rangle$$

$E_n = -\hbar\omega + E_m$; hence $E_n = n\hbar\omega + E_0$

so that Q^* is a creation operator.

Recall: $\mathcal{H} = NM\omega^2\left[qq^* + q^*q\right]$

Then in the commutators above:

$$QQ^* = [q, q^*] + Q^*Q$$

$$\therefore \quad \mathcal{H} = \frac{2NM\omega^2}{\hbar\omega}Q^*Q + \frac{\hbar\omega}{2}$$

Therefore: $Q|0\rangle = 0$ since n is positive definite. We cannot destroy a state that doesn't exist.

We now find the representation of the Q's. Change all c.c. to $\dagger$. Recall:

$$\langle n|Q|m\rangle^\dagger = \langle m|Q^\dagger|n\rangle$$

Recall the unit operator: $1 = \sum_m |m\rangle\langle m|$

Then:

$$\langle n|\mathcal{H}|n\rangle = 2NM\omega^2 \langle n|Q^\dagger Q|n\rangle + \tfrac{1}{2}\hbar\omega$$

and using unit operator:

$$\langle n|\mathcal{H}|n\rangle = 2NM\omega^2 \langle n|Q^\dagger|n-1\rangle\langle n-1|Q|n\rangle + \tfrac{1}{2}\hbar\omega$$

$$= 2NM\omega^2 \left|\langle n-1|Q|n\rangle\right|^2 + \tfrac{1}{2}\hbar\omega$$

$$= n\hbar\omega + \tfrac{1}{2}\hbar\omega$$

Finally: $2NM\omega^2 \left|\langle n-1|Q|n\rangle\right|^2 = n\hbar\omega$

or $\langle n-1|Q|n\rangle = \sqrt{\dfrac{n\hbar}{2NM\omega}}$

Also: $\langle n+1|Q^\dagger|n\rangle = \sqrt{\dfrac{\hbar(n+1)}{2NM\omega}}$

} Einstein Relations

Or: $\mathcal{H} = \sum_{ss} \hbar\omega_{fs}\left(n_{ss} + \tfrac{1}{2}\right)$

Also can identify:

$$n = \frac{2NM\omega}{\hbar} Q^* Q$$

Matrix Formulation:

Definition:

$$\begin{pmatrix} 1 \\ 0 \\ \vdots \\ \vdots \\ \cdot \end{pmatrix}_{fs} = |0\rangle_{fs} \qquad \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ \vdots \\ 1 \end{pmatrix}_{fs} = |1\rangle_{fs} \qquad \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}_{fs} = |4\rangle_{fs}$$

Then the Q's are:

$$Q = \sqrt{\frac{\hbar}{2MN\omega}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \cdots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$$Q^{\dagger} = \sqrt{\frac{\hbar}{2MN\omega}} \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

Can show that this satisfies

$$\frac{2NM\omega}{\hbar} Q^{\dagger} Q = n$$

LECTURE 7 : 10-9-61

Properties of Phonon states:

Phonon state is written : $|n_{fs}\rangle$

The probability of occupation of a state is given by:

$$e^{-E_{fs}/kT} = e^{-(n_{fs}+\frac{1}{2})\hbar\omega(fs)/kT}$$

$$\bar{n}_{fs} = \frac{1}{e^{\hbar\omega(fs)/kT} - 1}$$ by the usual method.

This is the Bose-Einstein distribution, hence phonons are Bosons.

We now calculate the partition function Z:

$$Z = \sum_{fs}\sum_{n_{fs}} e^{-E_{fs}/kT} = \prod_{fs}\sum_{n_{fs}} e^{-\hbar\omega(fs)(n_{fs}+\frac{1}{2})/kT}$$

$$= \prod_{fs} e^{-\hbar\omega(fs)/kT} \sum_{n_{fs}} e^{-\hbar\omega(fs)\,n_{fs}/kT}$$

$$= \prod_{fs} \frac{e^{-\hbar\omega(fs)/2kT}}{1 - e^{-\hbar\omega(fs)/kT}}$$

Define $\theta = e^{-1/kT}$:

$$Z = \prod_{fs} \frac{\theta^{\hbar\omega(fs)/2}}{1 - \theta^{\hbar\omega(fs)}}$$

Calculate the internal energy:

$$\mathcal{U} = kT^2 \frac{\partial}{\partial T} \log Z = \theta \frac{\partial}{\partial \theta} \log Z$$

$$= \theta \frac{\partial}{\partial \theta} \sum_{fs} \left[\log \theta^{\hbar\omega(fs)/2} - \log\left(1 - \theta^{\hbar\omega(fs)}\right) \right]$$

Then: $$U = \sum_{fs} \left[\frac{\hbar\omega(fs)}{2} + \frac{\hbar\omega(fs)}{e^{\hbar\omega(fs)/kT} - 1} \right]$$

Compute the free energy of the system:

$$F = -kT \log Z$$

$$= -kT \sum_{fs} \log \left[\frac{e^{-\hbar\omega(fs)/kT 2}}{1 - e^{-\hbar\omega(fs)/kT}} \right]$$

$$= \sum_{fs} \left[\frac{\hbar\omega(fs)}{2} + kT \log \left(1 - e^{-\hbar\omega(fs)/kT} \right) \right]$$

Now: $F = U - TS$, or $S = \frac{U - F}{T}$

What is entropy? We see that zero point energy drops out.

$$S = -\frac{1}{T} \sum_{fs} \left[kT \log \left(1 - e^{-\hbar\omega(fs)/kT} \right) - \frac{\hbar\omega(fs)}{e^{\hbar\omega(fs)/kT} - 1} \right]$$

$$= k \sum_{fs} \left[(\bar{n}_{fs} + 1) \log (\bar{n}_{fs} + 1) - \bar{n}_{fs} \log \bar{n}_{fs} \right]$$

This equation is used for thermal conduction problems.

Specific Heat:

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \sum_{fs} \frac{\hbar\omega(fs)}{e^{\hbar\omega(fs)/kT} - 1}$$

$$C_v = \sum_{fs} \frac{\hbar^2 \omega^2(fs)}{k T^2} \frac{e^{\hbar\omega(fs)/kT}}{\left(e^{\hbar\omega(fs)/kT} - 1\right)^2}$$

Assume that: $T >> \frac{\hbar \omega(fs)}{k}$

$$C_v = \sum_{fs} \frac{\hbar^2 \omega^2(fs)}{k T^2} \left[1 - \frac{\hbar\omega(fs)}{kT} + \cdots\right] \Bigg/ \frac{\hbar^2 \omega^2(fs)}{k^2 T^2} \left[1 + \frac{\hbar\omega(fs)}{2kT} + \cdots\right]$$

$$= k \sum_{fs} \left[1 - \frac{\hbar^2 \omega^2(fs)}{12 k^2 T^2}\right] = 3Nk$$

to the first order. The second order term can be gotten from the secular equation or the trace of $A^{\alpha\beta}_{nn'}$. Then to the second order:

$$C_v = 3Nk - \frac{Nk}{12M(kT)^2} \operatorname{Tr} A(0)$$

Low temperature Approximations: Cannot expand in usual sense because some value in the sum $\hbar\omega(fs)$ will be less than kT.

We can write: $\sum_f \rightarrow \frac{V}{8\pi^3} \int df$

LECTURE 8 : 10-11-61

Debye Specific Heat :

$$C_v = \sum_s \int \frac{\hbar^2 \omega^2(f_s)}{k T^2} \frac{e^{\hbar\omega(f_s)/kT}}{\left(e^{\hbar\omega(f_s)/kT} - 1\right)^2} \frac{V}{(2\pi)^3} \, df$$

It is convenient to transform the integration space from f to ω.

$$df = dS \left(\frac{df}{d\omega}\right) d\omega$$

where $dS = f^2(\omega, \theta, \varphi) \, d\Omega$

$$\frac{df}{d\omega} = \frac{1}{|\nabla_f \omega(f_s)|}$$

Then:

$$C_v = \sum_s \int \frac{\hbar^2 \omega^2(f_s)}{k T^2} \frac{e^{\hbar\omega(f_s)/kT}}{\left(e^{\hbar\omega(f_s)/kT} - 1\right)^2} \frac{V}{(2\pi)^3} \frac{dS \, d\omega}{|\nabla_f \omega(f_s)|}$$

Define:

$$g_s(\omega) = \frac{V}{(2\pi)^3} \int_S \frac{dS}{|\nabla_f \omega(f_s)|}$$

with $\int g_s(\omega) \, d\omega = N$

Consider : $\omega^2 = \omega_0^2 + v^2 \left(f_1^2 + f_2^2 + f_3^2\right)$

Suppose $\omega_0 = 0$, Then : $\omega_s = v_s f$

If we assume this true over entire Brillouin zone , this is the Debye approximation

$$g_s(\omega) = \frac{4\pi V}{(2\pi)^3} \frac{\omega^2}{v_s^3}$$

To get in the first BZ, we demand:

$$\int_0^{\omega_D} g_s(\omega)\, d\omega = N$$

and find: $\omega_D = \left(\frac{6\pi^2 v_s^3 N}{V} \right)^{1/3} = \frac{k\Theta_D}{\hbar}$

Putting $x = \frac{\hbar\omega}{kT}$; $x_{s\,max} = \frac{k\Theta_s}{\hbar}$

$$C_V = \sum_s \frac{V\hbar^2}{2\pi^2 kT^2 v_s^3} \left(\frac{kT}{\hbar}\right)^5 \int_0^{x_{s\,max}} \frac{e^x x^4 dx}{(e^x-1)^2}$$

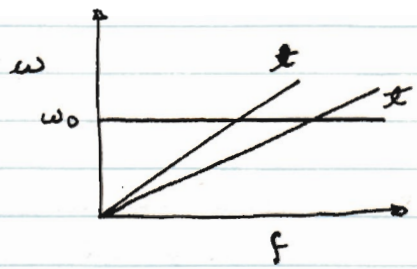
$$= \sum_s 3Nk \left(\frac{T}{\Theta_D(s)}\right)^3 \int_0^{x_{s\,max}} \frac{e^x x^4 dx}{(e^x-1)^2}$$

If $T < .1\Theta_D$, then we can replace $x_{s\,max}$ by ∞.

$$C_V = 3NkT^3 \left(\frac{1}{\Theta_D^3(l)} + \frac{2}{\Theta_D^3(t)} \right) \int_0^{\infty} \frac{e^x x^4 dx}{(e^x-1)^2}$$

Debye actually wrote:

$$\frac{3}{\Theta_D^3} = \frac{1}{\Theta_D^3(l)} + \frac{2}{\Theta_D^3(t)}$$



Lose much of longitudinal mode.

Born approximation:

$$\frac{3}{\bar{v}^3} = \frac{1}{v_e^3} + \frac{2}{v_t^3}$$, choose f cutoff from $\frac{k\Theta_D}{\hbar} = \bar{v} f$

What about optical bands?
Recall that optical band gets flat when one mass becomes much less than other. Thus we can take a constant frequency for the entire optical band and write:

$$g_s(\omega) = N\,\delta(\omega - \omega_s^{opt})$$

Then:

$$C_v = \sum_s N \frac{\hbar^2 \omega_s^{2\,opt}}{kT^2} \frac{e^{\hbar\omega_s^{opt}/kT}}{\left(e^{\hbar\omega_s^{opt}/kT} - 1\right)^2}$$

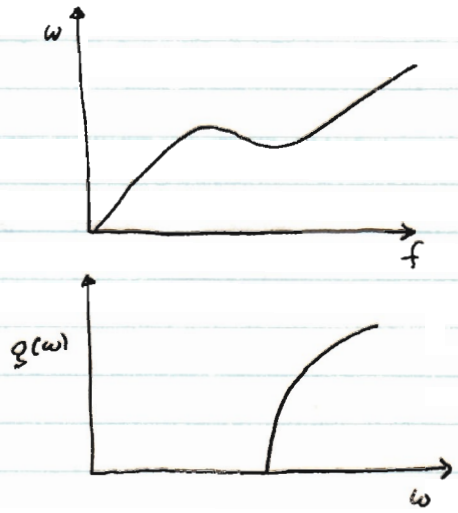
Today arguments can be made from group theory about the symmetry of $g(\omega)$. That is, where the critical points occur.

Assume a minimum in the dispersion. We can expand around ω_0, the minimum:

$$\omega = \omega_0 + \frac{v^2 f^2}{2\omega_0}$$

Then:

$$g(\omega) \propto (\omega - \omega_0)^{1/2}$$



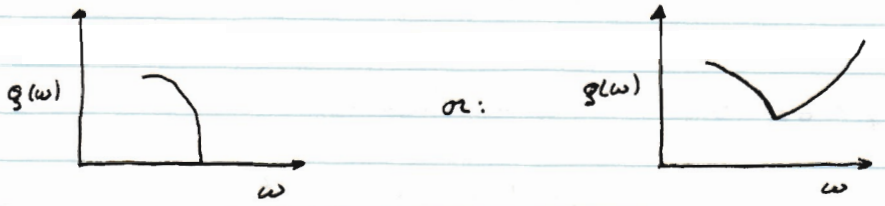
This is really superposed on usual $g(\omega)$.

LECTURE 9: 10-13-61

Case of maximum in dispersion curve:

$$\omega = \omega_0 - \frac{v^2}{2\omega_0} f^2$$

$$\therefore \quad g(\omega) \propto (\omega_0 - \omega)^{1/2}$$



Reference: L. Van Hove, PR 89, 1189 (1953).

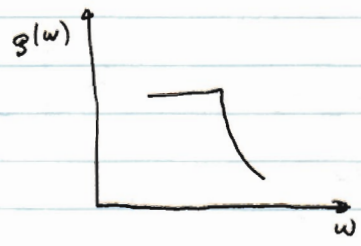
Case of Saddle Point:

$$\omega = \omega_0 + \frac{v^2}{2\omega_0} \left\{ f_z^2 - (f_x^2 + f_y^2) \right\}$$

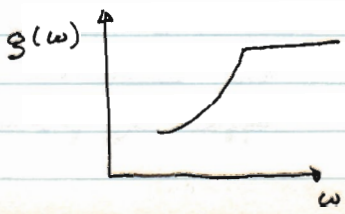
See discussion in Wannier on saddle points, and Van Hove.
Set:

$$g(\omega) \propto \left[(C^2 + \omega - \omega_0)^{1/2} \right] \qquad \omega < \omega_0$$

$$g(\omega) \propto \left[(C^2 + \omega - \omega_0)^{1/2} - 2(\omega - \omega_0)^{1/2} \right] \qquad \omega > \omega_0$$



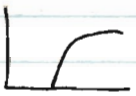
For $\omega = \omega_0 + \frac{v^2}{2\omega_0} \left\{ (f_x^2 + f_y^2) - f_z^2 \right\}$

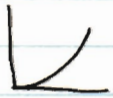


Can generalize this to:

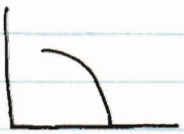
$$\omega = \omega_0 + \frac{v^2}{2\omega_0}\left[\epsilon_x f_x^2 + \epsilon_y f_y^2 + \epsilon_z f_z^2\right]$$

(0) $\epsilon_x = \epsilon_y = \epsilon_z = 1$: minimum

$g(\omega) \propto (\omega - \omega_0)^{1/2}$  $\omega_0 \neq 0$

$g(\omega) \propto \omega^2$  $\omega_0 = 0$

(1) $\epsilon_x = \epsilon_y = \epsilon_z = -1$: maximum

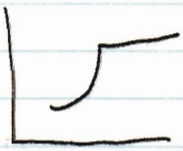
$g(\omega) \propto (\omega_0 - \omega)^{1/2}$ 

(2) $\epsilon_x = \epsilon_y = -\epsilon_z = -1$: saddle point

$$\omega = \omega_0 + \frac{v^2}{2\omega_0}\left(f_z^2 - f_x^2 - f_y^2\right)$$

$$g(\omega) \propto \left[(c^2 + \omega - \omega_0)^{1/2}\right] \quad \omega < \omega_0$$

$$\propto \left[(c^2 + \omega - \omega_0)^{1/2} - 2(\omega - \omega_0)^{1/2}\right] \quad \omega > \omega_0$$

(3) $\epsilon_x = \epsilon_y = -\epsilon_z = 1$: saddle point 

$$\omega = \omega_0 + \frac{v^2}{2\omega_0}\left(f_x^2 + f_y^2 - f_z^2\right)$$

$$g(\omega) \propto \left[(c^2 + \omega_0 - \omega)^{1/2} - 2(\omega_0 - \omega)^{1/2}\right] \quad \omega < \omega_0$$

$$\propto \left[(c^2 + \omega_0 - \omega)^{1/2}\right] \quad \omega > \omega_0$$

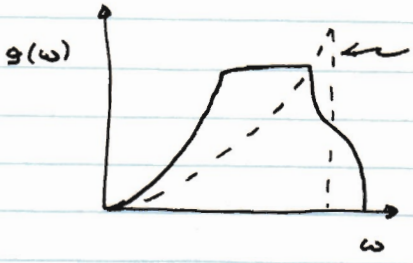
Can be shown by group theory:

$N_1 \geq 1$
$N_2 - N_1 \geq 2$
$N_3 - N_2 + N_1 \geq 1$
$N_0 - N_3 + N_2 - N_1 = 0$

} where N denotes the number of each type of point.

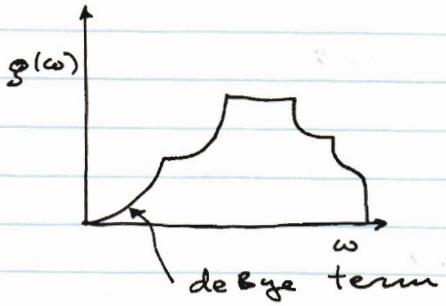
For a simple crystal, take $N_1 = 1$, then:
$N_2 = 3$, $N_3 = 3$, $N_0 = 1$

Then the simplest possible in 3 dimension

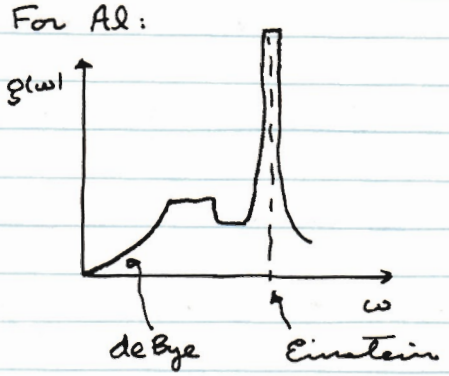


See how bad Debye approximation really is.

For fcc:



For Al:



Can fit Al to specific heat to both deBye and Einstein theories. Adjustable parameters are deBye cutoff and Einstein temperature.

Note: $\frac{1}{|\text{grad}_S\, \omega|} = \infty$ only when a symmetry direction intersects the BZ normally.

deBye spectrum is not correct at high temperatures, must use expansion as done before.

LECTURE 10 : 10-16-61

Elections:

Schroedinger Equation: Bloch Theorem:

$$\left\{ \frac{-\hbar^2}{2m} \nabla^2 + V \right\} \psi = E \psi$$

We have periodic potential in crystal:

$$V(\underline{r}) = V(\underline{r} + n_1 \underline{T}_1 + n_2 \underline{T}_2 + n_3 \underline{T}_3)$$

Form: $\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$

Assume l degenerate solutions:

$$\psi_1(\underline{r}, E), \ldots, \psi_l(\underline{r} E)$$

Then upon translation, we form linear combinations:

$$\psi_\lambda(\underline{r} + \underline{T}_i, E) = \sum_{\kappa=1}^{l} a_{\kappa\lambda} \psi_\kappa(\underline{r} E) \quad , \text{etc.}$$

Impose BVK conditions: First consider:

$$\psi_\lambda' = \sum_{\kappa=1}^{l} t_{\kappa\lambda} \psi_\kappa \quad ; \quad a'_{\kappa\lambda} = t\, a_{\kappa\lambda}\, t^{-1}$$

where $t_{\kappa\lambda}$ diagonalizes $a_{\kappa\lambda}$, etc. simultaneously. Then the BVK condition demands:

$$(a'_{\kappa\lambda})^{N_1} = (b'_{\kappa\lambda})^{N_2} = \cdots = \delta_{\kappa\lambda}$$

NB: a, b, c commute.

From intuition and group theory, we pick for a, b, c:

$$a'_{\lambda\lambda} = e^{2\pi i \lambda / N_1}$$

Now form:

$$t\,\psi_\lambda(\underline{r}+\underline{T}_i, E) = \sum_{\kappa=1}^{\ell} t\, a_{\kappa\lambda}\, t^{-1}\, t\, \psi_\kappa(r, E)$$

Then:

$$\psi'_\lambda(\underline{r}+\underline{T}_i, E) = a'_{\lambda\lambda}\, \psi'_\lambda(\underline{r}, E)$$

$$= e^{2\pi i p_{i\lambda}/N_i}\, \psi'_\lambda(r, E), \text{ etc.}$$

The most general wave that obeys this relation is:

$$\psi'(\underline{r}) = e^{i\underline{b}\cdot\underline{r}}\, u_{p_1 p_2 p_3}(\underline{r})$$

$$\underline{r} = r_1 \hat{e}_{r_1} + \cdots$$

$$\underline{k} = 2\pi \left[\frac{p_1}{N_1} \frac{\underline{T}_2 \times \underline{T}_3}{\underline{T}_1 \underline{T}_2 \underline{T}_3} + \cdots \right]$$

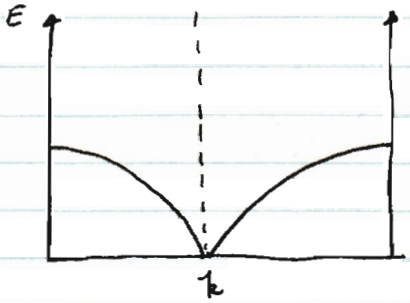
Thus: $\psi(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\underline{r})$

For bands: $\psi_{n\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{n\underline{k}}(\underline{r})$

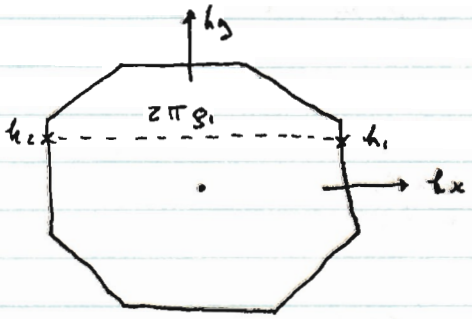
Kronig-Penney Model by method in Kittel.

LECTURE 11 : 10-18-61

Behaviour of grad$_k$ E at BZ Boundary.



Consider a two-dimensional model with mirror plane or better (inversion symmetry).



$\psi_{nk} = e^{ik\cdot r} u_{nk}$ given for u_{nk} :

$$\left[\frac{\hbar^2}{2m}(\nabla - ik)^2 + E_n(k) - V(r)\right] u_{nk}(r) = 0$$

with : $u^*_{kn}(r) = u_{-kn}(r)$

For center of symmetry $V(r) = V(-r)$ which leads to :

$$u^*_{kn}(r) = u_{kn}(r)$$

and : $E_n(k) = E_n(-k)$

Now $E_n(k_1) = E_n(k_2)$

and : grad$_k$ $E_n(k_1)$ = grad $E_n(k_2)$
on the repeated zone scheme.

Assume mirror symmetry about $x=0$ plane:

Then: $E_n(k_1) = E_n(k_2)$

$$\frac{\partial E_n(k_1)}{\partial k_y} = \frac{\partial E_n(k_2)}{\partial k_y}$$

$$\frac{\partial E_n(k_1)}{\partial k_x} = -\frac{\partial E_n(k_2)}{\partial k_x} = 0$$

Weak Binding Limit (Mott and Jones)

$$V(x) = V(x+a) \quad ; \quad \int_0^a V(x)\,dx = 0$$

In one band: $\psi_k = e^{ikx}\,u(x) \quad ; \quad u(x) = u(x+a)$

$$u(x) = \sum_{n=-\infty}^{\infty} A_n e^{-2\pi i n x/a}$$

Plug-in: $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$ and get:

$$\sum_{n=-\infty}^{\infty}\left[-\left(k-\frac{2\pi n}{a}\right)^2 + \frac{2m}{\hbar^2}(E-V)\right] A_n e^{-2\pi i n x/a} = 0$$

Assume for perturbation reasons: $A_0 \gg A_n$, $n \neq 0$ so that we can neglect terms with products of $A_n V$. Get:

$$\sum_{n=-\infty}^{\infty}\left[-\left(k-\frac{2\pi n}{a}\right)^2 + \frac{2mE}{\hbar^2}\right] A_n e^{-2\pi i n x/a} = \frac{2m}{\hbar^2} A_0 V$$

Operate with $\int_0^a e^{2\pi i n' x/a}\,dx$:

$$\left[-\left(k-\frac{2\pi n}{a}\right)^2+\frac{2mE}{\hbar^2}\right] a A_n = \frac{2m}{\hbar^2} A_0 \int_0^a V e^{2\pi i n x/a}\, dx$$

We get: $-k^2+\frac{2mE}{\hbar^2}=0$ so there is no first order correction to the energy, or:

$$\langle k|V|k\rangle = 0$$

This is only true in weak perturbing limit.

$$\langle k|V|k\rangle = \int_0^a \psi^* V \psi\, dx = \frac{1}{a}\int_0^a u^*(x)\, V\, u(x)\, dx$$

$=0$ on expanding each term in its Fourier series and considering:

$$\sum_{nn'} A_n^* A_{n'} V_{n-n'}$$

and neglecting terms like VA_n.

LECTURE 12 : 10-20-61

Weak Binding Case:

Recall:

$$u(x) = \sum_n A_n e^{-i 2\pi n a/x}$$

$$A_n = \frac{2m}{a\hbar^2} A_0 \frac{\int_0^a V e^{i 2\pi n x/a}}{\frac{2mE}{\hbar^2} - \left(k - \frac{2\pi n}{a}\right)^2}$$

$\langle k | V | k \rangle = 0$

$\langle n | V | n' \rangle = V_m \quad ; \quad V = \sum V_m e^{-i 2\pi m x/a}$

$E = \frac{\hbar^2 k^2}{2m} \quad ; \quad m = \frac{a(k-k')}{2\pi}$

$$A_n = \frac{2m V_n A_0}{\hbar^2 \left[\hbar^2 - \left(k - \frac{2\pi n}{a}\right)^2\right]} = \frac{A_0 V_n}{E_n^0 - E^0_{n - \frac{2\pi n}{a}}}, \quad n \neq 0$$

$$\psi = \frac{1}{\sqrt{a}} e^{ikx} u(x) = \frac{A_0}{a} e^{ikx} \left[1 + \frac{\sum_{n\neq 0} V_n e^{-i 2\pi n x/a}}{E_n^0 - E^0_{n - \frac{2\pi n}{a}}}\right]$$

$$E_n^{(2)} = E_n^0 + \sum_n \frac{|V_n|^2}{E_n^0 - E^0_{n - \frac{2\pi n}{a}}}$$

For $k = \frac{\pi n}{a}$, set vanishing denominator at BZ edge. Due to assumption that KE >> PE.

We now assume we can write for ψ:

$$\psi = \frac{1}{\sqrt{a}} e^{ikx} \left[A_0 + A_n e^{-i 2\pi n x/a}\right]$$

Substitute in Schroedinger equation, operate with $\int e^{-ikx} dx$ and $\int e^{-ikux} dx$ and get secular equation.

$$A_0 (E - E_n^0) - A_n V_n^* = 0$$
$$-A_0 V_n + A_n (E - E_{n-2\pi n/a}^0) = 0$$

$$\begin{vmatrix} E - E_n^0 & -V_n^* \\ -V_n & E - E_{n-2\pi n/a}^0 \end{vmatrix} = 0$$

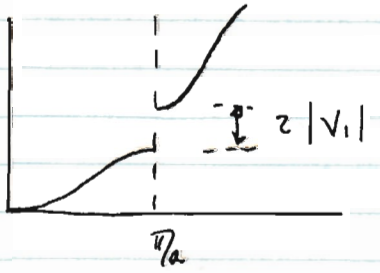
Waves drive each other apart as splitting occurs at BZ edge:

$$E = \frac{1}{2}\left[E_n^0 + E_{n-\frac{2\pi n}{a}}^0 \pm \sqrt{(E_n^0 - E_{n-2\pi n/a})^2 + 4\left(\frac{2m}{n}\right)^2 V_n V_n^*} \right]$$

$-$: $E_n^0 < E_{n-2\pi n/a}^0$

$+$: $E_n^0 > E_{n-2\pi n/a}^0$

At π/a :



Can see the generation of bands by periodic potentials.

At BZ edge, secular equation gives $A_0 \pm A_n = 0$ and the wave function becomes:

$$\psi = A \cos(kx + \kappa a)$$

or we get standing waves for k values at the BZ edge. We have energy discontinuities when:

$$k^2 = (k + 2\pi n/a)^2 \quad \text{in 1-D}$$

or in 3-D: $\underline{k}^2 = (\underline{k} + 2\pi \underline{g})^2$

or: $\vec{k} \cdot \vec{g} = \pi g^2$

LECTURE 13 : 10-23-61

Recall:

$$\sum_{\underline{k}} = \frac{V}{(2\pi)^3} \int d\underline{k} = N$$

Same holds for electrons, but these particles have spin, Thus:

$$\sum_{\underline{k}} = \frac{2V}{(2\pi)^3} \int d\underline{k} = 2N$$

For nearly free electrons: $E = \frac{\hbar^2 k^2}{2m}$. Assume first BZ is a sphere.

Fill up BZ with electrons to Fermi level denoted by E_F and k_F. Then:

$$\frac{2V}{(2\pi)^3} \int_0^{k_F} dk = N = \frac{2V}{(2\pi)^3} 4\pi \frac{k_F^3}{3} \quad , \quad \therefore \quad k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/2}$$

The total or average energy (kinetic) is:

$$\bar{E}_{KE} = \frac{\int_0^{k_F} E k^2 dk}{\int_0^{k_F} k^2 dk} = \frac{3}{10} \frac{\hbar^2}{m} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

now, $\int dk = \iiint \frac{dS\, dE}{|\text{grad}_k E|} = \int N(E) dE$

$$dS = \frac{V}{(2\pi)^3} \left[k(\theta, \varphi, E)\right]^2 d\Omega$$

Then: $N(E) = \frac{1}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$

If: $E = \frac{\hbar^2}{2m} \left[\alpha_1 k_x^2 + \alpha_2 k_y^2 + \alpha_3 k_z^2\right]$

$$N(E) = \frac{1}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{E^{1/2}}{(\alpha_1 \alpha_2 \alpha_3)^{1/2}}$$

near a band edge: $N(E) \propto (E_0 - E)^{1/2}$

The Tight-Binding Method:

Consider atomic case:

$$\nabla^2 \phi + \frac{2m}{\hbar^2}(E - U)\phi = 0$$

and take the case of s states. Write the Bloch function as a linear combination of the atomic wave functions:

$$\psi_k(r) = \sum_l C_{kl}\, \phi(r - R_l)$$

$$C_{kl} = e^{ik \cdot R_l}$$

Then: $\psi_k(r+\tau) = \sum_l e^{ik \cdot R_l} \phi(r + \tau - R_l)$

$$= e^{ik \cdot \tau} \sum_l e^{ik \cdot (R_l - \tau)} \phi(r + \tau - R_l)$$

which satisfies Bloch condition. Therefore:

$$\psi_k = \sum_l e^{ik \cdot R_l} \phi(r - R_l)$$

$$\mathcal{H} = -\frac{\hbar^2 \nabla^2}{2m} + V$$

where V is now the crystalline potential. Form:

$$E = \frac{\int \psi_k^* \mathcal{H} \psi_k \, d\tau}{\int \psi_k^* \psi_k \, d\tau}$$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$$

$$\left.\begin{aligned} \mathcal{H}_1 &= -\frac{\hbar^2 \nabla^2}{2m} + U(r - R_l) \\ \mathcal{H}_2 &= V(r) - U(r - R_l) \end{aligned}\right\} \quad \begin{aligned} \mathcal{H}_1 &= \mathcal{H}_2 \\ \mathcal{H}_2 &= \mathcal{H} - \mathcal{H}_2 \end{aligned}$$

Then:

$$E = E_0 + \frac{\int \psi_k^* \sum_l e^{ik\cdot R_l} [\mathcal{H} - \mathcal{H}_l] \phi(r - R_l)\, d\tau}{N}$$

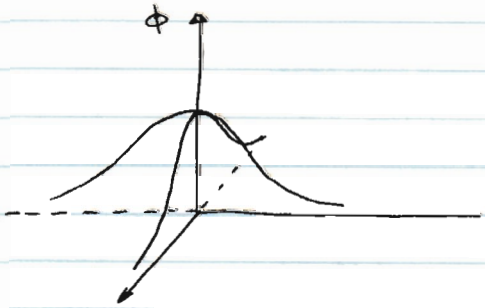
Tight Binding is good for insulators and the valence bands of conductors.

$$E = E_0 + \frac{1}{N} \sum_l \sum_m e^{ik\cdot(R_l - R_m)} \int \phi^*(r - R_m) \left[V(r) - U(r - R_l)\right] \phi(r - R_l)\, d\tau$$

$$= E_0 + \sum_l e^{ik\cdot\rho_l} \int \phi^*(r - \rho_l) \left[V(r) - U(r)\right] \phi(r)\, d\tau$$

$$\rho_l = R_m - R_l$$

For s functions:



This function is invariant under all rotations of the unit cell.

For nearest neighbor (only one where TB applies):

$$\int \phi^*(r) \left\{ V(r) - U(r) \right\} \phi(r)\, d\tau = -\alpha$$

$$\int \phi^*(r - a) \left\{ V(r) - U(r) \right\} \phi(r)\, d\tau = -\gamma$$

$$E = E_0 - \alpha - \gamma \sum_l e^{ik\cdot\rho_l}$$

$$E = E_0 - \alpha - 2\gamma \left(\cos k_x a + \cos k_y a + \cos k_z a \right) \quad (sc)$$

For small k, $E \propto k^2$

The bandwidth here is 12γ

LECTURE 14: 10-25-61

p states in the tight binding approximation:
Write for the p functions:

$$\left.\begin{aligned} \phi_0 &= g(r) \\ \phi_1 &= x f(r) \\ \phi_2 &= y f(r) \\ \phi_3 &= z f(r) \end{aligned}\right\} E_1$$

Cubic field does not remove the degeneracy

P function:

different sign in overlap region.

S function

We write for the lattice wave functions (cubic case)

$$\psi_{nk} = \sum_l e^{i a (k \cdot l)} \phi_n (r - al)$$

Then for the energy:

$$E = E_1 + \sum_l e^{-i (k \cdot l) a} \int \phi_n^* (r - al) \{ V(r) - U(r) \} \phi_n (r) \, d\tau$$

The integrals are:

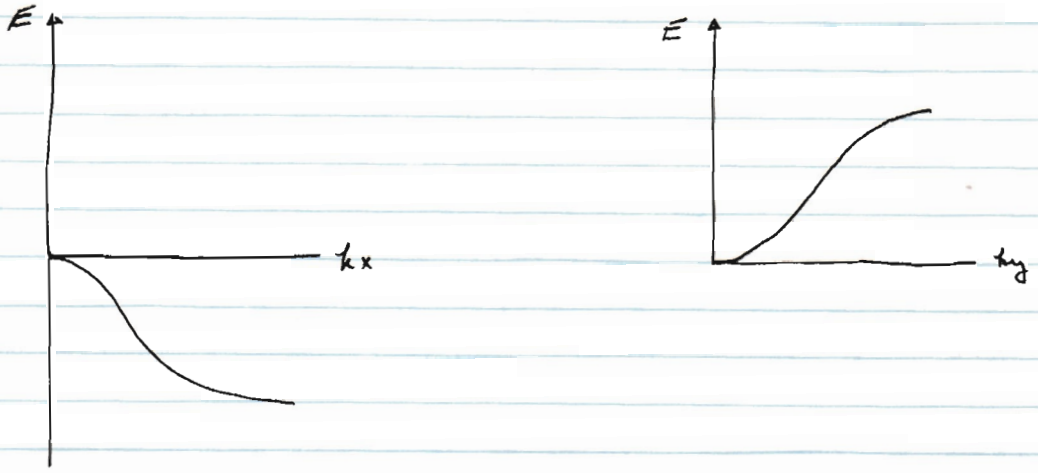
$$\left.\begin{aligned} \alpha_1 &= \int \phi_1^* (r) \{ V(r) - U(r) \} \phi_1 (r) \, d\tau < 0 \\ \gamma_1 &= \int \phi_1^* (x+a, y, z) (V - U) \phi_1 (xyz) \, d\tau > 0 \\ \gamma_1' &= \int \phi_1^* (x, y+a, z) (V - U) \phi_1 (xyz) \, d\tau < 0 \end{aligned}\right\}$$

Only 3 possible distinct integrals

To get signs and magnitudes, use arguments about signs in overlap region.

Hence: $\alpha_1 < 0$, $\gamma_1 > 0$, $\gamma_1' < 0$

$$E = E_1 - \alpha_1 + 2\gamma_1 \cos a k_x + 2\gamma_1' (\cos a k_y + \cos a k_z)$$



For around $k = 0$: $E \sim -\gamma_1 k_x^2 a^2 - \gamma_1' (k_y^2 + k_z^2) a^2$
see that bands are anisotropic.

What about p and s states that are close together in energy? That is, spin-orbit coupling may be weak. This leads to overlap of bands.

Call energy of s: $E_0(k)$, for p: $E_1(k)$

We have: $\psi_{nk} = \sum_l e^{ia(k \cdot l)} \phi_n(r - al)$; $n = 0, 1, 2, 3$

The most general wave function will be some linear combination of ψ_{nk}:

$$\psi_q(k,r) = \sum_n a_{qn}(k) \psi_{nk}$$

We will be considered with the special points of the BZ like $k = 0$, π/a and k along a symmetry direction.

The total problem resolves to the secular equation:

$$| H_{nm} - E S_{nm} | = 0$$

We will assume that matrix elements between ϕ functions like H_{12} are zero.

Thus we can write:

$$\begin{vmatrix} E_0(k)-E & x & x & x \\ x & E_1(k)-E & 0 & 0 \\ x & 0 & E_1(k)-E & 0 \\ x & 0 & 0 & E_1(k)-E \end{vmatrix} = 0$$

Calculate the matrix element $\mathcal{H}_{ox}$:

$$\mathcal{H}_{ox} = \frac{1}{N} \sum_{ll'} e^{-ika(l-l')} \int \phi_o^*(r-al)(V-U_l)\phi_x(r-al')\,dr$$

Taking nearest neighbors, we get terms like:

$$\int \phi_o^*(x+a,y,z)(V-U)\phi_1(xyz)\,dr = \beta$$

$$\int \phi_o^{p*}(x-a,y,z)(V-U)\phi_1(xyz)\,dr$$

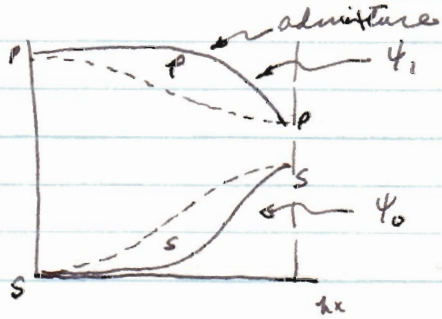
These are equal but opposite in sign. Then:

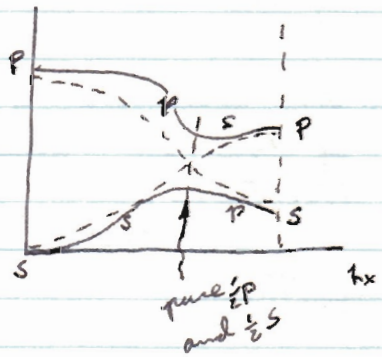
$$\mathcal{H}_{ox} = 2i\beta \sin kxa$$

Plugging into determinant gives:

$$2E = E_o(k) + E_1(k) \pm \left[(E_o - E_1)^2 + 16\beta^2 \sin^2 a k_x \right]^{1/2}$$

We now have situation, 2 cases:





- - - - - $E_o(k)$, $E_1(k)$

——— E from above.

NB: This is wrong: see Matt and Jones.

Now, for the wavefunctions:

$$\psi_0(k_x,0,0) = (\cos\tfrac{1}{2}\theta)\,\psi_{0z} + i(\sin\tfrac{1}{2}\theta)\,\psi_{1z}$$

$$\psi_1(k_x,0,0) = (\sin\tfrac{1}{2}\theta)\,\psi_{0z} - i(\cos\tfrac{1}{2}\theta)\,\psi_{1z}$$

where: $$\cot\theta = \frac{E_1(k) - E_0(k)}{4\beta \sin k_x a}$$

For non-crossing bands: s at $k=0$ and π/a but admixture inbetween. Same for ϕ.

For crossing bands, change in symmetry where crosses: see diagrams.

LECTURE 15: 10-27-61

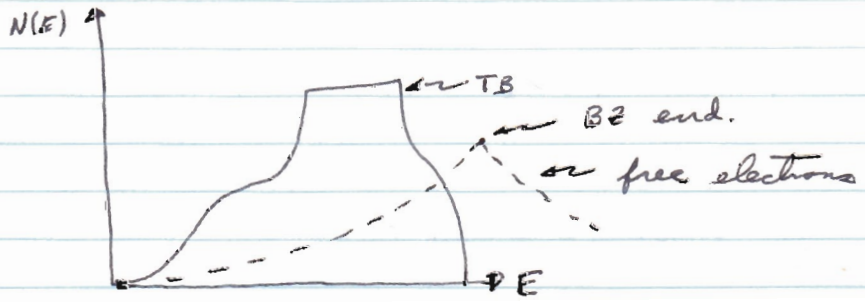
We continue on to find density of states $N(E)$:

$$N(E) = \iint \frac{2\,dS}{|\nabla_k E|}$$

$$dS = \frac{V}{8\pi^3}\,k^2(\theta,\phi,E)\,d\Omega$$

$$E = E_0 - \alpha - 2\gamma\,(\cos k_x a + \cos k_y a + \cos k_z a)$$

Given for TB then:



Usually can only find energy relations at BZ symmetry points. Can use computers to get other points: just coming into use.

Effective Mass in 1-Band Model:

The most general Block function is:

$$\psi_k = e^{i k \cdot r} u_k(r)\, e^{-2\pi i E(k) t/h}$$

Expand: $f_k(r,t) = \int a(k')\, e^{i(k' \cdot r - E(k')t/\hbar}\, u_{k'}(r)\, dk'$

Make $k' = k + \Delta k$ Then:

$$E(k') = E(k) + \Delta k \cdot \text{grad}_k E(k) + \cdots$$

Then:

$$f_k(r,t) = e^{i(k \cdot r - E(k)t/\hbar)} \int a(\Delta k)\, e^{i\Delta k \cdot (r - \text{grad}_k \frac{E(k)t}{\hbar})}$$

$$\cdot\, u_{k'}(r)\, d(\Delta k)$$

Take $u_k(r)$ out. Then we can identify the group velocity:

$$v_g = \frac{\text{grad}_k E(k)}{\hbar}$$

For free electrons: $v_g = \frac{\langle p \rangle}{m}$

Now: $\frac{dE}{dt} = F \cdot \langle v_g \rangle$

$$\frac{dv}{dt} = \frac{1}{\hbar} \text{grad}_k \frac{\partial E_k}{\partial t} = \frac{1}{\hbar} \text{grad}_k F \cdot v$$

$$= \frac{1}{\hbar^2} \left[\text{grad}_k \text{grad}_k E(k) \right] \cdot F$$

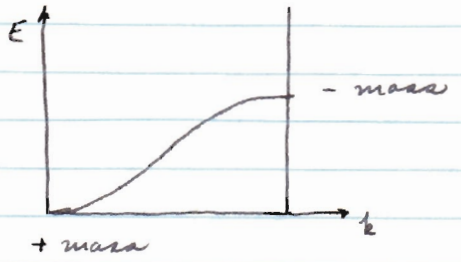
We then define the effective mass tensor:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \text{grad}_k \text{grad}_k E(k)$$

or:

$$\hbar^2 \ddot{x}^\alpha = \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} F^\beta$$

In one dimension: $m^* = \dfrac{\hbar^2}{\dfrac{d^2 E}{dk^2}}$



Also get: $\dfrac{dk}{dt} = \dfrac{eE}{\hbar}$

Group Velocity: $\psi_k = e^{ik\cdot r} u_k(r)$

$\nabla^2 \psi_k + \frac{2m}{\hbar^2}(E_k - V)\psi_k = 0$, operate on Schroedinger equation with ∇_k.

$\nabla_k \psi_k = \nabla_k (e^{ik\cdot r} u_k(r))$

$\nabla^2 \nabla_k \psi_k = ir\, \nabla^2 \psi_k + 2r \nabla \psi + \nabla^2 [e^{ik\cdot r} \nabla_k u_k]$

$\nabla^2 \nabla_k \psi_k + \frac{2m}{\hbar^2}(\nabla_k E_k)\psi_k + \frac{2m}{\hbar^2}(E_k - V)\nabla_k \psi_k = 0$

$2r \nabla \psi_k + \frac{2m}{\hbar^2}(\nabla_k E_k)\psi_k + ir\left[\nabla^2 \psi_k + \frac{2m}{\hbar^2}(E_k - V)\psi_k\right]$

$+ \left[\nabla^2 + \frac{2m}{\hbar^2}(E - V)\right] e^{ik\cdot r} \nabla_k u_k(r) = 0$

Integrate:

$$\hbar \int \psi_n^* \nabla \psi_n \, d\tau + \frac{2m}{\hbar^2} \nabla_k E(k) \int \psi_n^* \psi_n \, d\tau$$

$$+ \int \psi_n^* \nabla^2 \left[e^{ik\cdot r} \nabla_k u_n(r) \right] d\tau$$

$$+ \frac{2m}{\hbar^2} \int (E_n - V) \psi_n^* \left[e^{ik\cdot r} \nabla_k u_n(r) \right] d\tau = 0$$

Finally get:

$$\frac{2m}{\hbar^2} \nabla_k E(k) = \hbar \int \psi_n^* \nabla \psi_n \, d\tau$$

$$= \frac{\hbar}{2} \int d\tau \left(\psi_n^* \nabla \psi_n - \psi_n \nabla \psi_n^* \right)$$

or $$\langle v \rangle = \frac{1}{\hbar} \nabla_k E(k)$$

LECTURE 16 : 10-30-61

Bloch-Bohm Theorem:

The states of lowest free energy correspond to zero net current: (Bloch)

For every solution to the Schroedinger equation, there is another solution with a lower current and lower energy, except the lowest: (Bohm)

References: PR 75, 502 (1949)

$$\psi_k = e^{i k\cdot r} u_k(r)$$

$$\psi_{k+\delta k} = e^{i(k+\delta k)\cdot r} u_{k+\delta k}(r)$$

$$= e^{i\delta k\cdot r}\left[\psi_k + e^{ik\cdot r}\,\delta k\cdot\nabla_k u_k(r)\right]$$

Assume ψ_k diagonalizes H into E_0.

Find average potential:

$$\langle V\rangle = \int \psi^*_{k+\delta k}\, V\, \psi_{k+\delta k}\, d\tau$$

$$= V_0 + \int\left\{\left[e^{-i\delta k\cdot r - ik\cdot r}\,\delta k\cdot\nabla_k u_k^*(r)\right] V e^{i\delta k\cdot r}\,\psi_k\right\} d\tau$$

$$+ \text{cc.}$$

$$= V_0 + \delta k\cdot\int\left[\nabla_k\left(u_k^* u_k\right)\right] V(r)\, d\tau$$

$$\langle T\rangle = -\frac{\hbar^2}{2m}\int \psi^*_{k+\delta k}\,\nabla^2\,\psi_{k+\delta k}\, d\tau$$

$$= T_0 + \frac{\hbar^2}{m}\delta k\cdot k + \frac{\hbar^2}{2m}\delta k\cdot\nabla_k\int u_k^*(-\nabla^2)\,u_k\, d\tau$$

Then:

$$E = T+V = T_0 + V_0 + \frac{\hbar^2}{m}\delta k\cdot k + \delta k\cdot\nabla_k\int u_k^*\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)u_k\, d\tau$$

and:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right) u_k = \left[E_k - \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{m} k \cdot \frac{\nabla}{i}\right] u_k$$

Then:

$$E = T_0 + V_0 + \frac{\hbar^2}{m}\delta k \cdot k + \delta k \cdot \nabla_k \int u_k^* \left(E_k - \frac{\hbar^2 k^2}{2m} - \underbrace{\frac{\hbar^2}{m} k \frac{\nabla}{i}}_{0}\right) u_k \, d\tau$$

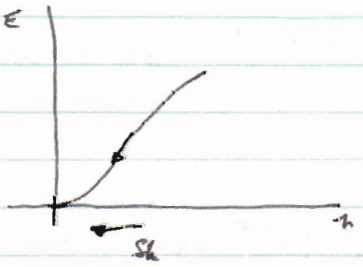
$$= T_0 + V_0 + \left[\delta k \cdot \nabla_k \cdot E_k\right)$$

$$= E_0 + \delta k \cdot \nabla_k E_k$$

Recall definition of velocity: $v = \frac{1}{\hbar}\nabla_k E_k$

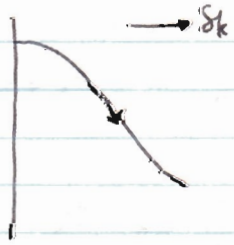
$$E = E_0 + \frac{\hbar}{e}\delta k \cdot \underbrace{(ve)}_{j}$$

Look near bottom of band: $E = E_0 + \frac{\hbar^2 k^2}{2m}$



To go to lower state δk in to left and hence decreases current in accordance with Bohm's statements.

$E_0 - \frac{\hbar^2 k^2}{2m}$



Current here increases in magnitude, but does not get more negative, but less.

This theorem has great application in the field of superconductivity.

Effective Masses:

Reference: PR 102, 605 (1956)

Acceleration:

Electric Field: $\psi_{nk} = e^{ik\cdot r} u_{nk}(r)$

where: $H_0 \psi_{nk} = E_0(k) \psi_{nk}$: $|nk\rangle$

Take: $H' = H_0 - eE\cdot r$

Take matrix elements:

$$\langle n'k'| H_0 - eE\cdot r | nk\rangle$$

$$= E_n(k)\,\delta_{nn'}\delta_{kk'} - eE\cdot\int e^{-ik'\cdot r} u^*_{n'k'}(r)\, r\, e^{ik\cdot r} u_{nk}(r)$$

Recall: $\nabla_k \psi_{nk} = ir\psi_{nk} + e^{ik\cdot r}\nabla_k u_{nk}(r)$

$\therefore r\psi_{nk} = -i\nabla_k \psi_{nk} + ie^{ik\cdot r}\nabla_k u_{nk}(r)$, giving

$$-eE\cdot\int\left\{\psi^*_{n'k'}(-i\nabla_k)\psi_{nk} + \psi^*_{n'k'} ie^{ik\cdot r}\nabla_k u_{nk}(r)\right\} d\tau$$

$$= -eE_i\int e^{i(k-k')\cdot r} u^*_{n'k'}\nabla_k u_{nk}\, d\tau$$

$$\Rightarrow \delta_{kk'}\Big[E_{n'}(k)\,\delta_{nn'} - eE\cdot r_{nn'}(k)\Big]$$

(interband term)

Now try to find representation that diagonalizes H', call it ϕ_{nk}. Adams guessed:

$$\phi_{nk} = \psi_{nk} - \sum'_{n''}\frac{\psi_{n''k}\, eE\cdot r_{n''n}}{E_n - E_{n''}}$$

This is first order in E field by perturbation.

LECTORE 17 : 11-1-61

Recall: $\phi_{nk} = (nk)$ diagonalizes $H_0 - eE\cdot r$;

$$\int \phi^*_{n'k} (H_0 - eE\cdot r)\, \phi_{nk}\, d\tau$$

$$= E_n(k)\,\delta_{nn'} - eE\cdot r_{n'n}(k)$$

$$+ (1-\delta_{nn'}) \left\{ \int \psi^*_{n'k} H_0 \left[\sum_{n''} \frac{\psi_{n''k}\, eE\cdot r_{n''n}}{E_n - E_{n''}} \right] d\tau \right.$$

$$\left. + \left[\sum_{n'''} \frac{\psi_{n'''k}\, eE\cdot r_{n'''n'}}{E_{n'} - E_{n'''}} \right] H_0\, \psi_{nk}\, d\tau \right\}$$

$$= E_n(k)\,\delta_{nn'} - eE\cdot r_{n'n}(k) + eE\, r_{n'n}\, \frac{E_n - E_{n'}}{E_{n'} - E_n}$$

Now:

$$H_0 \phi_{nk} = (E_n - eE\cdot r_{nn})\,\phi_{nk} + ieE\cdot\nabla_k \phi_{nk}$$

$$= i\hbar \frac{\partial \phi_{nk}}{\partial t}$$

$$\frac{\partial \phi}{\partial t} = \frac{1}{i\hbar}\left[\quad\right]\phi_{nk} + \frac{1}{i\hbar}\left(\frac{\partial k}{\partial t}\right)\left(\frac{\partial \phi}{\partial k}\right)$$

Then: $\quad \frac{\partial k}{\partial t} = \frac{eE}{\hbar}$

Now find $\langle v \rangle$:

$$\langle v \rangle = \frac{\langle p \rangle}{m} = \frac{1}{m} \int \phi^*_{nk}\, p\, \phi_{nk}\, d\tau$$

$$= \frac{1}{m} \int \psi^*_{nk}\, p\, \psi_{nk}\, d\tau - \sum_{n'} \frac{eE\cdot r_{nn'}}{E_{n'} - E_n} \int \psi^*_{n'k}\, p\, \psi_{nk}\, d\tau$$

$$- \sum_{n'} \frac{eE\cdot r_{n'n''}}{E_{n'} - E_{n''}} \int \psi^*_{nk}\, p\, \psi_{nk}\, d\tau = \frac{1}{m}\langle p \rangle$$

NB!! all this is only to first order in electric field.

k·p Approximation and Cellular Method:

$$\psi_k = e^{ik\cdot r}\, u_k(r)$$

$$\left[\nabla^2 + \frac{4m}{2\hbar^2}(E-V)\right]\psi_k = 0$$

$$\left(-k^2 + 2k\cdot\nabla + \nabla^2\right) u_k(r) + \frac{2m}{\hbar^2}(E-V)\, u_k(r) = 0$$

Assume a symmetry point at $k=0$, then:

$$\nabla^2 u_0(r) + \frac{2m}{\hbar^2}(E-V)\, u_0(r) = 0$$

We will apply this to s functions of an alkalli metall. Refer to Mott and Jones:

Now, in a direction normal to a WS cell:

$$\frac{\partial u(r)}{\partial r} = \frac{\partial\, u(r+nr)}{\partial r} \quad ; \quad u(r) = u(-r)$$

$$\frac{\partial u}{\partial r} = -\frac{\partial u(-r)}{\partial r}$$

hence it vanishes. This provided the BC for the Schroedinger equation, that is:

$$\frac{\partial u}{\partial r} = 0 \quad \text{at the normal to the WS cell.}$$

This process of forming a crystal, lowers the potential energy over the gas state.

Cohesive Energy = lower PE + higher electron KE due to Pauli principle, which counteracts the cohesive energy.

We now approximate the WS cell by a sphere with the same volume.

This gives: $r_s = a\left(\frac{3}{8\pi}\right)^{1/3}$ as radius of sphere.

For the Fermi energy:

$$\frac{3}{5} E_F = \frac{3\hbar^2}{10m}\left(3\pi^2 \frac{2}{a^3}\right)^{2/3}$$

$$= \frac{3\hbar^2}{10 m r_s^2}\left(\frac{9\pi}{4}\right)^{2/3}$$

$$\boxed{\frac{4}{3}\pi r_s^3 = \frac{a^3}{2}}$$

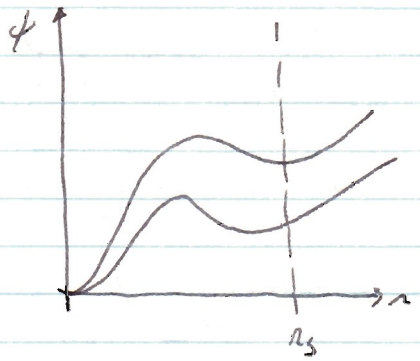
This method holds only if:

1) one electron at a time in an "S" sphere (exchange unimportant)

2) electron sees only N due to the ion core in its sphere.

This works only for monovalent metals.

What we want to find:



look for zero slope by varying energy.

LECTURE 18 : 11-3-61

We now consider the cellular method at some other point in the zone. ($k \cdot p$ perturbation)

$$\left\{ -\frac{\hbar^2 k^2}{2m} - i\frac{\hbar^2}{m} k \cdot \nabla - \frac{\hbar^2 \nabla^2}{2m} + V(r) - E_n \right\} u_k(r) = 0$$

Regard $-i\frac{\hbar^2}{m} k \cdot \nabla$ as a perturbation. Then:

$$u_{nk} = u_{no} + \sum_m a_m(k)\, u_{mo}$$

and: $E = E_{no} + E' \quad ; \quad H_o + H'$

$$(H_o + H') \left[u_{no} + \sum_m a_m(k)\, u_{mo} \right] = E_{no} \left[u_{no} + \sum_m a_m(k)\, u_{mo} \right]$$

and:

$$a_m(k) = \frac{H'_{mn}}{E_{no} - E_{mo}}$$

Then:

$$E_n(k) = E_n(0) + \frac{\hbar^2 k^2}{2m} + \sum_m{}' \frac{\left| \int u_{no}^* H' u_{no}\, d\tau \right|^2}{E_n^{(0)} - E_m(0)}$$

$$E_n(k) = E_n(0) + \frac{\hbar^2}{2m} \underline{k} \cdot \underline{\underline{\alpha}} \cdot \underline{k}$$

$$\underline{\underline{\alpha}} = \underline{\underline{1}} + \sum_m{}' \frac{2\hbar^2}{m(E_n - E_m)} \left[\int u_{no}^* \underline{\nabla} u_{no}\, d\tau \int u_{no}^* \underline{\nabla} u_{no}\, d\tau \right]$$

Now: $\underline{\nabla} = \frac{m}{\hbar^2} [H_o, \underline{r}]$ which leads to:

$$\underline{\underline{\alpha}} = \underline{\underline{1}} + 2 \int u_{no}^* \underline{r} \cdot \underline{\nabla} u_{no}\, d\tau$$

This is the effective mass term.

Now in the cellular approximation:

$$\nabla u_{no} = \frac{\underline{r}}{|\underline{r}|} \frac{\partial u_{no}}{\partial r}, \quad \text{then:}$$

$$\underline{\underline{\alpha}} = \underline{\underline{1}} + 2 \int \frac{\underline{r}\,\underline{r}}{|\underline{r}|} u^*_{no} \frac{\partial u_{no}}{\partial r} d\tau$$

Hence, for spherical symmetry, $\underline{\underline{\alpha}}$ is diagonal or the effective mass is isotropic. We then evaluate explicitly:

$$\alpha_{xx} = 1 + 2\int_0^{2\pi} d\varphi \int_{-1}^{1} \cos^2\theta \, d(\cos\theta) \int u^* \frac{\partial u}{\partial r} r^3 dr$$

$$= 1 + \frac{8\pi}{3} \int u^* \frac{\partial u}{\partial r} r^3 dr$$

Now integrate by parts:

$$\int u^* \frac{\partial u}{\partial r} r^3 dr = u^* u r^3 \Big|_0^{r_s}$$

$$- \int_0^{r_s} \frac{\partial u^*}{\partial r} u r^3 \qquad - 3 \int_0^{r_s} u^* u \, r^2 dr$$

$$= \frac{1}{2}\left[u^* u r_s^3 - \frac{3}{4\pi} \right] = \frac{1}{2} u^* u (r_s)^3 - \frac{3}{8\pi}$$

since:

$$\int u^* u \, r^2 dr = \frac{1}{4\pi}$$

Then:

$$\alpha = \frac{4\pi}{3} u^*(r_s)\, u(r_s)\, r_s^3$$

and: $$m^* = \frac{m}{\alpha}$$

Orthogonalized Plane Wave method:

Cellular method destroys orthogonality of valence states with core electron states. This method restores orthogonality.

We write the wave function expanded in plane waves:

$$u(x) = \sum_{2\pi g} A(g)\, e^{-2\pi i g \cdot r}$$

$G = 2\pi g$, then the Bloch function are:

$$\psi_k = \sum_G A(G)\, e^{i(k+G)\cdot r}$$

For the core states (s, only):

$$\Phi_{ks} = \sum_l e^{ik\cdot r_l}\, \phi_s(r - r_l)$$

Now define:

$$Y_n(k,r) = e^{i(k+G_n)\cdot r} - \sum_m u_{nm}\, \Phi_{k+G,m}$$

We want:

$$\int \Phi^*_{k's}\, Y_n(k,r)\, d\tau = 0$$

and will find:

$$u_{ns} = \int_{cell} e^{i(k+G_n)\cdot r}\, \phi^*_s(r)\, d\tau$$

LECTURE 19 : 11-6-61

OPW invented by Herring. Augmented plane wave invented by Slater (1932). What Slater did was take core function less than some prescribed radius and plane waves outside this radius and match ψ and grad ψ at this radius. Apparently, the augmented plane waves are better adapted to computer techniques.

Back to OPW: Recall:

$$\chi_n(k,r) = e^{i(k+G_n)\cdot r} - \sum_m \alpha_{nm}\, \phi_{k+G_n,m}$$

We want α_{nm}'s such that:

$$\int \phi^*_{k's'}\, \chi_n(k,r)\, d\tau = 0$$

or we want χ_n orthogonal to the core functions as a correction on the cellular method. We set; for s functions:

$$\int \sum_\ell e^{-i(k'\cdot R_\ell)}\, \phi_s^*(r-R_\ell)\, e^{i(k+G_n)\cdot r}\, d\tau$$

$$- \int \sum_\ell e^{-ik'\cdot R_\ell}\, \phi_s^*(r-R_\ell) \sum_{s'} \alpha_{ns'} \sum_{\ell'} e^{i(k+G_n)\cdot R_{\ell'}}$$

$$\phi_{s'}(r-R_{\ell'})\, d\tau$$

$$= \sum_\ell \int e^{-ik'\cdot R_\ell + ik\cdot r + iG_n\cdot r}\, \phi_s^*(r-R_\ell)\, d\tau$$

$$- \sum_{\ell s \ell'} \int e^{-ik'\cdot R_\ell + ik\cdot R_{\ell'} + iG_n\cdot R_{\ell'}}\, \alpha_{ns'}$$

$$\phi_s^*(r-R_\ell)\, \phi_{s'}(r-R_{\ell'})\, d\tau$$

Now since we assume core functions do not overlap, core function on different atoms are "orthogonal":

Then:

$$U_{ns} = \frac{\sum_l \int e^{-ik'\cdot r_l + ik\cdot r + iG_n\cdot r}\, \varphi_s^*(r-r_l)\, d\tau}{\sum_l e^{-ik'\cdot r_l + ik\cdot r_l + iG_n\cdot r_l}}$$

Now let $r = r_l + \rho$, ρ is cellular. Hence:

$$U_{ns} = \int_{cell} e^{i(k+G_n)\cdot\rho}\, \varphi_s^*(\rho)\, d\tau$$

But now the ψ_n's are not orthogonal to each other, but we hope that this will not be harmfull.

Now write entire crystal function as:

$$\psi_k(r) = \sum_n A(G_n)\, \psi_n(k,r)$$

where $\mathcal{H}\psi_k(r) = E_n \psi_k(r)$

In practice we restrict ourselves to only a few terms, usually along symmetry directions.

$$\sum_n A(G_n)\, \mathcal{H}\psi_n(k,r) = E \sum_n A(G_n)\, \psi_n(k,r)$$

Cutting off terms gives secular determinant.

$$\det \left| \int \psi_n^* (\mathcal{H} - E)\, \psi_n\, d\tau \right| = 0$$

This is the best method of calculating band structures to date.

Empty Lattice Method:

Assume $V = 0$, but still with lattice periodicity.

Take for wave functions:

$$\psi(k,r) = \sum_n e^{i(k+G_n)\cdot r}$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2$$

$$E_k = \frac{\hbar^2 (k+G_n)^2}{2m}$$

Consider a simple cubic as an example:

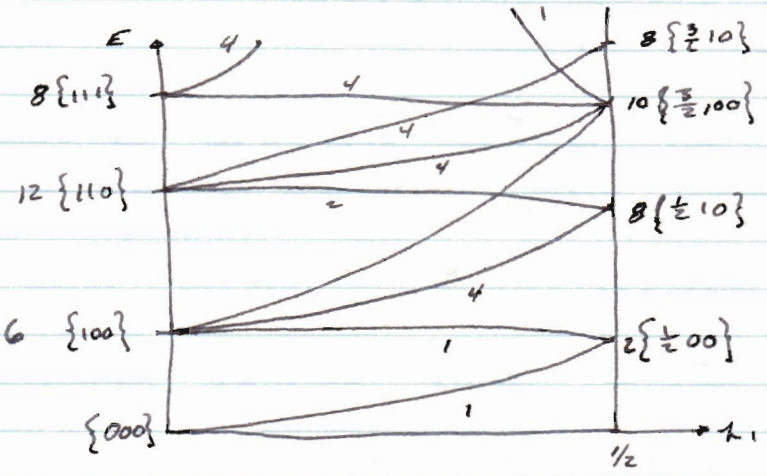
$$G_{nx} = \frac{2\pi}{a} n_1 \quad \text{, etc.}$$

$$k_x = \frac{2\pi}{a} k_1 \quad \text{, etc.}$$

Then:

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 \left[(n_1+k_1)^2 + (n_2+k_2)^2 + (n_3+k_3)^2 \right]$$

Plot E vs k_1 along 100 direction:



$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 \left[(n_1+k_1)^2 + n_2^2 + n_3^2 \right]$$

Reference: W. Schockley, Phys. Rev. 52, 866 (1937)

LECTURE 20 : 11-8-61

$k \cdot p$ Perturbations in Diamond Semiconductors.

We will calculate E vs k for the valence band. At $k = 0$, the valence band wave functions look like:

$$xy\ f(r) = |3\rangle$$
$$yz\ f(r) = |1\rangle$$
$$xz\ f(r) = |2\rangle$$

All degenerate, corresponding to a single energy E_0. Taking:

$$\mathcal{H}' = \frac{\hbar}{m} k \cdot p$$

$$\psi_k^1 = |\nu\rangle + \frac{\hbar k}{m} \sum_{l\alpha_j} \frac{\langle l\alpha_j | p | \nu \rangle}{E_0 - E_{l\alpha}} |l\alpha_j\rangle$$

(band, level, states)

Now: $$\langle \nu | \mathcal{H}' | \nu' \rangle = \frac{\hbar^2}{m^2} \sum_{l\alpha_j} \frac{\langle \nu | k \cdot p | l\alpha_j \rangle \langle l\alpha_j | k \cdot p | \nu' \rangle}{E_0 - E_{l\alpha}}$$

Recall: $\nabla = \frac{m}{\hbar^2} [\mathcal{H}_0, r]$, Then:

$$\langle \nu | \mathcal{H}' | \nu' \rangle = \frac{\hbar^2}{m} k \cdot \langle \nu | r \nabla | \nu' \rangle \cdot k$$

Consider:

$$\langle 1 | r \nabla | 1 \rangle = \int yz\, f^*\, r \nabla\, yz\, f\, d\tau$$

must examine $r\nabla$ to determine when the m.e. vanishes:

$$\int yz\, f^*\, x \frac{\partial}{\partial x}\, yz\, f\, d\tau = \int \frac{y^2 z^2 x^2}{r} f^* f\, d\tau = L$$

Now consider:

$$\int yz\, f^* y \frac{d}{dy}\, yz f \, d\tau$$

$$= \int yz\, f^* \left(yzf + y^2 z \frac{y}{r} f' \right) d\tau$$

$$= \int \left[f^* y^2 z^2 f + f^* \frac{y^4 z^2}{r} f' \right] d\tau \qquad = M$$

This will generate the following secular matrix:

$$\begin{pmatrix} L k_x^2 + M(k_y^2 + k_z^2) - E & N k_x k_y & N k_x k_z \\ N k_x k_y & L k_y^2 + M(k_x^2 + k_z^2) - E & N k_y k_z \\ N k_x k_z & N k_y k_z & L k_z^2 + M(k_x^2 + k_y^2) - E \end{pmatrix} = 0$$

For diagonal. Now consider off diagonal terms

$$k \cdot \langle 1 | \wedge D | 2 \rangle \cdot k = k_x k_y \int yz f^* (\wedge D)\, zx\, f \, d\tau =$$

$$\Rightarrow k_x k_y \frac{\hbar^2}{m} \int yz f \left(x \frac{\partial}{\partial y} + y \frac{\partial}{\partial x} \right) zx\, f \, d\tau \qquad = N k_x k_y$$

This fills in above.

Now along 100 direction:

$$\begin{pmatrix} L k_x^2 - E & 0 & 0 \\ 0 & M k_x^2 - E & 0 \\ 0 & 0 & M k_x^2 - E \end{pmatrix} = 0$$

This shows that along 100, we split into 2 fold and 1 fold degenerate.

LECTURE 21 : 11-10-61

Cyclotron Resonance:

Consider center of coordinates on one of ellipsoids that appear in Ge and Si. Assume that for the conduction band we can write the energy as:

$$E = \hbar^2 \left(\frac{k_x^2 + k_y^2}{2 m_t} + \frac{k_z^2}{2 m_e} \right)$$

considering the ellipsoid on the k_z axis only. Also assume:

$$v = \frac{1}{\hbar} \nabla_k E(k) \quad ; \quad \frac{dk}{dt} = \frac{F}{\hbar} = \frac{eE}{\hbar} + \frac{e}{\hbar c} \vec{v} \times \vec{H}$$

Take $\vec{H} = H(\sin\theta, 0, \cos\theta)$

$$\vec{v} = \left(\frac{\hbar k_x}{m_t}, \frac{\hbar k_y}{m_t}, \frac{\hbar k_z}{m_e} \right)$$

Assume: $k \sim e^{i\omega t}$ and get:

$$i\omega k_x = \frac{e}{c} \frac{k_y}{m_t} H \cos\theta = \omega_t k_y \cos\theta$$

Define: $\omega_t = \frac{eH}{m_t c}$

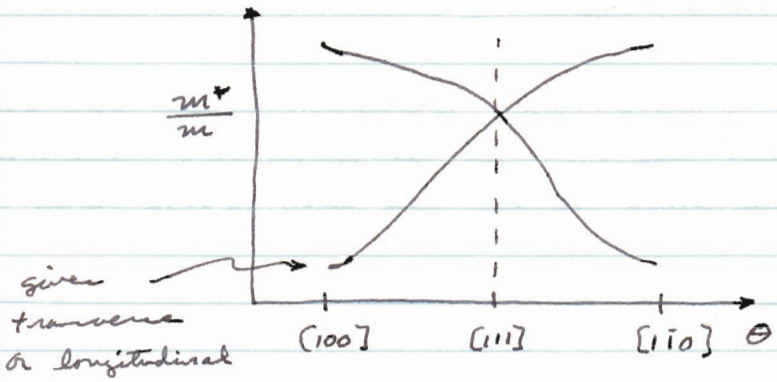
Furthermore:

$$i\omega k_x - \omega_t k_y \cos\theta = 0$$
$$i\omega k_y - \omega_e k_z \sin\theta + \omega_t k_x \cos\theta = 0$$
$$i\omega k_z + \omega_t k_y \sin\theta = 0$$

Get: $\omega^2 = \omega_t^2 \cos^2\theta + \omega_t \omega_e \sin^2\theta$

or: $\left(\frac{1}{m^*}\right)^2 = \frac{\cos^2\theta}{m_t^2} + \frac{\sin^2\theta}{m_e m_t}$

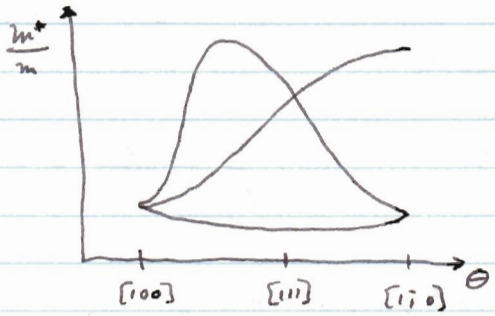
Keep ω constant and vary H and measure absorbtion. Eventually can form following plot.



Silicon

$m_\ell = .98\, m$

$m_t = .19\, m$



Germanium

$m_\ell = 1.58\, m$

$m_t = .082\, m$

We now go on to the consideration of the effective mass theorem.

For the unperturbed crystal:

$$H_0 \psi_{nk} = E_{nk} \psi_{nk}$$

We work in the $k\cdot p$ perturbation: $\psi_{no} = u_{no}(r)$ and:

$$|n k\rangle = \psi_{nk} = e^{ik\cdot r}\left[u_{no}(r) + \frac{\hbar}{m} k \cdot \sum_m \frac{p_{nm} u_{mo}}{E_n - E_m}\right]$$

We are now interested in $(nk|H_0|n'k')$, $(nk|u|n'k')$

References: L & K, PR 97, 869 (1955)
K & M, PR 96, 1488 (1954)

We set: $(nk|H_0|n'k')$

$$= E_n(0) + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} k k \sum_m \frac{p_{nm} p_{mn}}{E_n - E_m}$$

LECTURE 22: 11-13-61

Impurity Center Approximations:

We now compute $(nk|U|n'k')$:

We will use $\phi_{nk} = u_{no} e^{ik\cdot r}$
or the first order term of the k·p perturbation.

$$(nk|U(r)|n'k') = \int e^{i(k'-k)\cdot r} U(r) u^*_{no} u_{n'o} \, d\tau$$

Assume a fourier expansion of $U(r)$:

$$U(r) = \sum_k U(k) e^{ik\cdot r}$$

$$u^*_{no} u_{n'o} = \sum_m B_m^{nn'} e^{-iG_m\cdot r}$$

Then:

$$(nk|U(r)|n'k') = \sum_m B_m^{nn'} U(k-k'+G_m)$$

$$\sim B_0^{nn'} U(k-k')$$

since $U(k)$ is slowly varying, and only $m=0$ term contributes.

But $B_0^{nn'} = \delta_{nn'}$ since:

$$B_0^{nn'} = \int u^*_{no} u_{n'o} \underbrace{e^{iG_m\cdot r}}_{1} d\tau = \delta_{nn'}$$

Then:

$$(nk|H_0+U|n'k') = \delta_{nn'}\left[\left(E_{n0} + \frac{\hbar^2k^2}{2m} + \frac{\hbar^2}{m^2}\right.\right.$$

$$\left.\left.\cdot kk \sum' \frac{PP}{E_n - E_m}\right)\delta_{kk'} + U(k-k')\right]$$

Define system wave function:

$$\Phi(r) = \sum_{n'} \int dk' \, A_{n'}(k') \, \varphi_{n'k'}$$

where: $(H_0+U)\Phi = E\Phi$

$$\sum_{n'} \int dk' \, A_{n'}(k')(H_0+U)\varphi_{n'k'} = E \sum_{n'} \int dk' \, A_{n'}(k')\varphi_{n'k'}$$

Form matrix elements:

$$E_n(k) A_n(k) + \int dk' A_n(k) U(k-k') = E A_n(k)$$

Define Fourier transform:

$$F_n(r) = \int e^{ik\cdot r} A_n(k) \, dk$$

and transform equation; and replace k by $-i\nabla$. That is:

$$\int E_n(k) e^{ik\cdot r} A_n(k) \, dk = E_n(-i\nabla) \cdot F_n(r)$$

second term becomes:

$$\int dr' \, U(r') \underbrace{\int dk' \, e^{ik'\cdot r'} A_n(k')}_{F_n(r')} \int e^{ik(r-r')} dk$$

$$\sim \delta(r-r')$$

So we finally get:

$$E_n(-i\nabla) F_n(r) + U(r) F_n(r) = E F_n(r)$$

and the general system wave function becomes:

$$\Phi = \sum_{n'} F_{n'}(r)\, u_{n'0}(r) \sim F_n(r)\, u_{n0}(r)$$

We now consider phosphorous doped silicon: We take:

$$U = \frac{-e^2}{\kappa r}$$

Then:

$$\left[E_n(-i\nabla) - \frac{e^2}{\kappa r} \right] F_n(r) = E\, F_n(r)$$

However:

$$E_n(-i\nabla) = \frac{\hbar^2 (\nabla_x^2 + \nabla_y^2)}{2 m_t} + \frac{\hbar^2 \nabla_z^2}{2 m_l}$$

To begin treat as spherical:

$$\left(\frac{-\hbar^2 \nabla^2}{2 m^*} - \frac{e^2}{\kappa r} \right) F(r) = E\, F(r)$$

Then $E = -\frac{1}{2\kappa} \frac{e^2}{a_i n^2}$

where: $a_i = \frac{\hbar^2 \kappa}{m^* e^2} = 2 \cdot 10^{-7}$ cm

Energy comes out to be about .04 ev.

To solve complete problem, choose as wave function:

$$F = \left(\frac{a^2 b}{\pi} \right) e^{-\left\{ a^2 (x^2 + y^2) + b^2 z^2 \right\}}$$

We calculate : $E_A = -.029$ ev

Experimentally :

P	.044 ev
As	.049
Sb	.039
Li	.033

Reason so bad is because of s function.
Ought to be better than this for p function.
If use reduced mass concept:
set $m^* = .41\, m$, $E_A \sim .0382$ ev.

LECTURE 23 : 11-15-61

Acceptors in silicon:
Here we have degenerate valence band.

Construct ϕ_n with $H_0 \phi_n = E_0 \phi_n$

$$\sum_{j'} \left(E_0 \delta_{jj'} + \frac{\hbar^2 k^2}{2m} \delta_{jj'} + \frac{\hbar^2}{m^2} \hbar k \sum_m \frac{p_{jm} p_{mj'}}{E_0 - E_m} \right) A_{j'}(k)$$

$$+ \int U(k-k') A_j(k') \, dk' = E A_j(k)$$

Define a fourth rank tensor so that:

$$\sum_{j'} D^{\alpha\beta}_{jj'} k^\alpha k^\beta A_{j'}(k) + \cdots = E A$$

Replace k by $-i\nabla$ and get envelope equation:

$$\sum_{j'} \left[D^{\alpha\beta}_{jj'} (-i\nabla_\alpha)(-i\nabla_\beta) + U(r) \delta_{jj'} \right] F_{j'}(r) = E F_j(r)$$

The energy surfaces for silicon are:

(See valence band formula from previous lectures.)

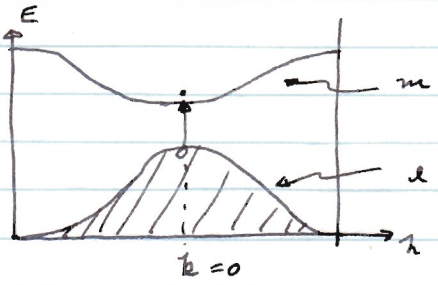
Set up secular equation as in cyclotron resonance.

$$\begin{pmatrix} L\nabla_x^2 + M(\nabla_y^2 + \nabla_z^2) + \frac{mU}{\hbar^2} & N\nabla_x\nabla_y & N\nabla_x\nabla_z \\ & & \\ & & \end{pmatrix} \begin{pmatrix} F_1 \\ F_2 \\ F_3 \end{pmatrix}$$

$$= E \begin{pmatrix} F_1 \\ F_2 \\ F_3 \end{pmatrix}$$

Theory of Excitons:

Assume:



The average potential before excitation is given in the Hamiltonian:

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + V(r_i) \quad ; \quad \psi = \prod_i \psi_{e,n}(r_i)$$

Now excite j^{th} electron:

$$\mathcal{H} = \sum_{i \neq j} \left[\frac{1}{2m} p_i^2 + V_e(r_i) \right] + \frac{1}{2m} p_j^2 + V_m(r_j)$$

$$= \sum_i' \left[\frac{1}{2m} p_i^2 + V_e(r_i) \right] - \underbrace{\frac{1}{2m} p_j^2 - V_e(r_j)}_{E_e(r_j)}$$

$$+ \underbrace{\frac{1}{2m} p_j^2 + V_m(r_j)}_{E_m(r_j)}$$

We that electron-hole pair is created. However, we have neglected correlation between hole and electron.

Thus we must add this Term to the Hamiltonian:

$$\frac{-e^2}{\kappa r_{eh}}$$

Now we assume: $\psi = F(r_e r_h)\, u_{c0}\, u_{h0}$, such that:

$$\left[E_m(-i\nabla_e) + E_e(-i\nabla_h) - \frac{e^2}{\kappa |r_e - r_h|} \right] F(r_e r_h) = E\, F(r_e r_h)$$

For simple bands:

$$\left[\frac{-\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2 \nabla_h^2}{2m_h} - \frac{e}{\kappa |r_e - r_h|} \right] F = EF$$

This is just the hydrogen equation and separates on center of mass coordinates:

$$R = \frac{m_e^* r_e + m_h^* r_h}{m_e^* + m_h^*}, \quad r = r_e - r_h$$

$$\mathcal{H} = \frac{-\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\kappa r}$$

$$M = m_e^* + m_h^*, \quad \mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$$

$$[\nabla_k, \mathcal{H}] = 0 \quad ; \quad F(R, r) = e^{iK \cdot R} F(r)$$

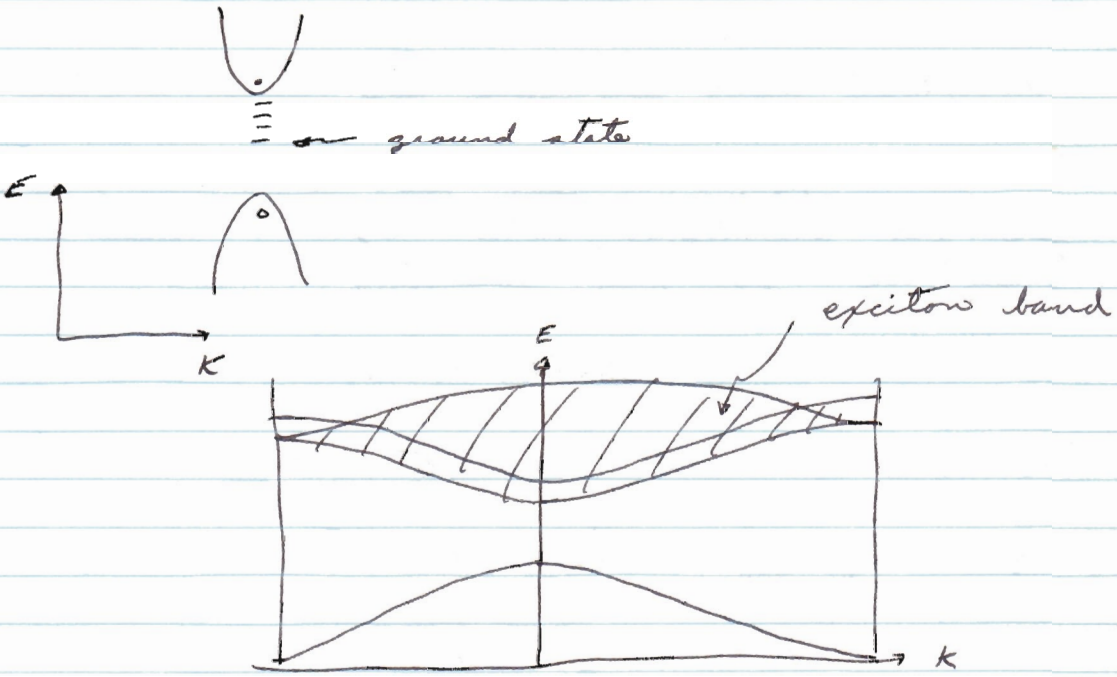
$$K = k_e + k_h$$

Then: $$\left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\kappa r} \right) F(r) = \left(E - \frac{\hbar^2 K^2}{2M} \right) F(r)$$

$$E_n = \frac{\hbar^2 K^2}{2M} - \frac{\mu e^4}{2\hbar^2 K^2 n^2} \quad \text{(exciton)}$$

We see that this is lower than crystal energy over without correlation:

We get as a result exciton bands



LECTURE 24: 11-17-61

Hartree - Fock Methods:

Hartree: Camb. Phil. Soc. 24, 89 (1928)
Condon and Shortley, 1955

Simplest wave function for many electron system:

$u_i(r_i)\,\chi_i(\sigma_i)$ for ith electron, then for all electron, the system wave function may be simply written:

$$\Psi = \prod_i u_i(r_i)\,\chi_i(\sigma_i)$$

We take for the Hamiltonian:

$$\mathcal{H} = \underbrace{\sum_i \frac{p_i^2}{2m}}_{T} + \underbrace{\left(\frac{-Ze^2}{r_i} + \sum_{i>j}\frac{e^2}{r_{ij}}\right)}_{V}$$

Hartree postulated an average potential such that we can write:

$$\left[-\frac{\hbar^2}{2m}\nabla_j^2 + V_j(r_j) + \underbrace{\sum_i{}' e^2 \int \frac{|u_i(r_i)|^2}{r_{ij}}\,d\tau_i}_{\text{average potential due to rest of electrons.}}\right] u_j(r_j)$$

$$= E_j\,u_j(r)$$

Now calculate the expectation value of $\mathcal{H}$:

$$\int \Psi^* \mathcal{H} \Psi\,d\tau = \sum_{i=1}^{n}\left[-\frac{\hbar^2}{2m}\int u_i^*\nabla_i^2 u_i\,d\tau_i + \int u_i^* V_i u_i\,d\tau\right] + \frac{1}{2}\sum_{ij}{}'\iint e^2 |u_i|^2 |u_j|^2\,d\tau_i\,d\tau_j$$

$$= \sum_{i=1}^{n} E_i - \frac{1}{2}\sum_{ij}{}' e^2 \iint \frac{|u_i|^2 |u_j|^2}{r_{ij}}\,d\tau_i\,d\tau_j$$

Further work was done in trying to derive these from many-electron principles by:

V. Fock, Z. Phys. 61, 126 (1932)
J.C. Slater, PR 32, 210 (1930)

Slater took for the wave function a determinant that satisfied completely the Pauli principle.

$$\psi = \sum_P (-1)^P P\left[\phi_1(1_1)\,\phi_2(1_2)\cdots\phi_n(1_n)\right]$$

$$\equiv \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1_1) & \phi_1(1_2) & \cdots & \phi_1(1_n) \\ \phi_2(1_1) & & & \vdots \\ \vdots & & & \\ \phi_n(1_1) & \cdots & & \phi_n(1_n) \end{vmatrix}$$

Now correlation is included in this wave function because equal columns of parallel spins vanish, but not for anti-parallel spins.

Let's play with some matrix elements of some operator. Assume:

$F = \sum_i f(1_i)$, not a function of spin coordinates.

Consider: $(A|F|B)$

$$|a) = \sqrt{\frac{1}{n!}} \sum_P (-1)^P P\left[a_1(1)\,a_2(2)\,a_3(3)\cdots\right] \leftarrow \psi_A$$

(spatial or electron)

$$|b) = \sqrt{\frac{1}{n!}} \sum_P (-1)^P P\left[b_1(1)\,b_2(2)\,b_3(3)\cdots\right] \leftarrow \psi_B$$

$$(a|F|b) = \frac{1}{n!} \sum_i \sum_P \sum_{P'} (-1)^{P+P'} \int\cdots\int$$

$$P\,\psi_A\; f(1)\; P'\,\psi_B\; d\tau_1\, d\tau_2 \cdots$$

Now the permutation operator acts on either spacial or orbital coordinates: We can write:

$$(a|F|b) = \underbrace{\int P a_1^*(1)\, P' b_1(1)\, d\tau_1}_{\text{vanishes unless } a_1(1) = b_1(1)} \cdots \int P a_n^*(n)\, f(n)\, P b_n(n)\, d\tau_n$$

and $P = P'$ because of orthonormality

If A, B differ by more than one set of quantum numbers, $(A|F|B) = 0$.

Now the state A is characterized by:

$A = a_1\ a_2 \cdots a_{n-1}\ a_n\ a_{n+1} \cdots$

$B' = a_1\ a_2 \cdots a_{n-1}\ b_n\ a_{n+1} \cdots$

where B' is B permuted into the A form and: $B' = \mp B$ depending on whether or not an odd or even number of permutations involved. The only integral left to consider is that over a_n, b_n:

$$(A|F|B) = \pm \frac{1}{n!}(n-1)! \sum_n \int a_n f(n)\, b_n\, d\tau_n$$

$$= \pm \int a(1)^* f(1)\, b(1)\, d\tau_1$$

Consider the diagonal matrix element:

$$(A|F|A) = \sum_{i=1}^{n} \int a_i^*(1)\, f(1)\, a_i(1)\, d\tau_1$$

Now consider the operator:

$$G = \sum_{i>j} g(i,j) \quad ; \quad g(i,j) = g(j,i)$$

Then:

$$(A|G|B) = \frac{(n-2)!}{n!} \sum_{\lambda > \gamma} (-1)^{P+P'} \iint P a_\lambda^\dagger \; P a_\gamma^\dagger \; g(\lambda,\gamma) \, P' b_\alpha \, P' b_\beta \, d\tau_\lambda d\tau_\gamma$$

Write out the a's again:

A: $a_1 a_2 a_3 \cdots a_{k-1} a_k a_{k+1} \cdots a_{\ell-1} a_\ell a_{\ell+1} \cdots$

B: $a_1 a_2 a_3 \cdots a_{\lambda-1} b_\alpha a_{\lambda+1} \cdots a_{\ell-1} b_\ell a_{\ell+1} \cdots$

Get for off-diagonal terms:

$$(A|G|B) = \frac{1}{n(n-1)} \sum_{\lambda > \gamma} \Big\{ \iint a_\lambda^\dagger(\lambda) \, a_\ell^\dagger(\gamma) \, g(\lambda\gamma) \, b_\alpha(\lambda) \, b_\ell(\gamma) \, d\tau_\lambda d\tau_\gamma$$

$$- \iint a_\ell^\dagger(\lambda) a_\ell^\dagger(\gamma) \, g(\lambda\gamma) \, b_\alpha(\lambda) \, b_\alpha(\gamma) \, d\tau_\lambda d\tau_\gamma$$

$$- \Big\{ + \iint a_\ell^\dagger(\lambda) \, a_k^\dagger(\gamma) \, g(\lambda\gamma) \, b_\alpha(\lambda) \, b_\ell(\gamma) \, d\tau_\lambda d\tau_\gamma$$

$$- \iint a_\ell^\dagger(\lambda) \, a_\lambda^\dagger(\gamma) \, g(\lambda\gamma) \, b_\ell(\lambda) b_\alpha(\gamma) \, d\tau_\lambda d\tau_\gamma \Big\} \Big]$$

$$= \pm \Big[\iint a_\lambda^\dagger(\lambda) \, a_\ell^\dagger(\gamma) \, g(\lambda\gamma) \, b_\alpha(\lambda) \, b_\ell(\gamma) \, d\tau_\lambda d\tau_\gamma$$

$$- \iint a_\lambda^\dagger(\lambda) \, a_\ell^\dagger(\gamma) \, g(\lambda\gamma) \, b_\ell(\lambda) \, b_\alpha(\gamma) \, d\tau_\lambda d\tau_\gamma \Big]$$

LECTURE 25: 11-20-61

$$\langle A|G|B\rangle = \langle A| \sum_{i<j} g_{ij} |B\rangle$$

$$= \pm \Big[\iint a_n^*(1)\, a_e^*(2)\, g(12)\, b_n(1)\, b_e(1)\, b_e(2)\, d\tau_1 d\tau_2$$

$$- \iint a_n^*(1)\, a_e^*(2)\, g(12)\, b_e(1)\, b_n(2)\, d\tau_1 d\tau_2 \Big]$$

the "-" sign since we switch electrons, we introduce the "-" sign. "±" sign are even or odd parity.

$$\langle A|G|B\rangle = \pm \sum_e \Big[\iint a_n^*(1)\, a_e^*(2)\, g(12)\, b_n(1)\, b_e(2)\, d\tau_1 d\tau_2$$

$$- \iint a_n^*(1)\, a_e^*(2)\, g(12)\, a_e(1)\, b_n(2)\, d\tau_1 d\tau_2$$

for only one wave function is different.

$$\langle A|G|A\rangle = \sum_{n>e=1}^{n} \Big[\underbrace{\iint a_n^*(1)\, a_e^*(2)\, g(12)\, a_n(1)\, a_e(2)\, d\tau_1 d\tau_2}_{\text{coulomb integral}}$$

$$\underbrace{- \iint a_n^*(1)\, a_e(2)\, g(12)\, a_e(1)\, a_n(2)\, d\tau_1 d\tau_2}_{\text{exchange integral}} \Big]$$

The exchange integral represents the interchange of electrons. We now require that the spin in a_e & a_n are the same, otherwise the exchange integral vanishes. For non-vanishing exchange integral <0, the $g_{ij} = \frac{e^2}{r_{ij}}$ correlation keeps the electrons with // spins apart by lowering the energy w.r.t. Hartree functions. For exchange integral >0, the electrons push closer or the energy is higher.

Recall: $\rho(r_1, r_2)$ is a probability:

$$\rho(r_1 r_2) = \int\int \psi^* \psi \, d\tau_3 \cdots d\tau_n = \frac{1}{n(n-1)} \left\{ \sum_{ij} \varphi_i^2(r_1)\varphi_j^2(r_2) - \sum_{ij}{}' \varphi_i^*(r_1)\varphi_j^*(r_2)\varphi_i(r_2)\varphi_j(r_1) \right\}$$

$\sum'$: ∥ spins

We will take wave functions for free electrons in box.

$$\psi_1 = \frac{1}{\sqrt{V}} e^{i k_1 \cdot r} \chi_1$$
$$\psi_2 = \frac{1}{\sqrt{V}} e^{i k_2 \cdot r} \chi_2$$

$$\psi_1(1) = \frac{1}{\sqrt{V}} e^{i k_1 \cdot r_1} \chi_1(1)$$
$$\psi_1(2) = \frac{1}{\sqrt{V}} e^{i k_1 \cdot r_2} \chi_1(2)$$

$$\psi = \frac{1}{\sqrt{2!}\,V} \begin{vmatrix} e^{i k_1 \cdot r_1}\chi_1(1) & e^{i k_1 \cdot r_2}\chi_1(2) \\ e^{i k_2 \cdot r_1}\chi_2(1) & e^{i k_2 \cdot r_2}\chi_2(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}\,V} \left[e^{i(k_1 \cdot r_1 + k_2 \cdot r_2)} \chi_1(1)\chi_2(2) - e^{i(k_1 \cdot r_2 + k_2 \cdot r_1)} \chi_1(2)\chi_2(1) \right]$$

$$\psi^*\psi = \frac{1}{2V^2} \left\{ \chi_1^\dagger(1)\chi_2^\dagger(2)\chi_1(1)\chi_2(2) - e^{i(k_1 - k_2)\cdot(r_1 - r_2)} \chi_1^\dagger(1)\chi_2^\dagger(2)\chi_1(2)\chi_2(1) \right.$$
$$- e^{i(k_1 - k_2)\cdot(r_1 - r_2)} \chi_1^\dagger(2)\chi_2^\dagger(1)\chi_1(1)\chi_2(2)$$
$$\left. + \chi_1^\dagger(2)\chi_1(2)\chi_2^\dagger(1)\chi_2(1) \right\}$$

For antiparallel spins, we have:

$$\psi^*\psi = \frac{1}{V^2}$$

For parallel spins:

$$\psi^*\psi = \frac{1}{V^2}\left[1 - \cos\left\{ (k_1 - k_2)\cdot(r_2 - r_1) \right\} \right]$$

If two electrons are in the same position, $\psi^*\psi = 0$

$$\left(\sum_n\right)^2 = \left(\frac{V}{8\pi^3} \int_0^{k_F} dk \right)^2 = \left(\frac{n}{2}\right)^2 = \frac{n^2}{4} \quad ; \; n = \text{number of electrons}$$

$$2\sum_k = \frac{2V}{8\pi^3}\int_0^{k_F} dk = \frac{N}{4\pi^3}\int_0^{k_F} 4\pi k^2\, dk = N$$

or: $k_F = (3\pi^2 \frac{N}{V})^{1/3}$

Reference: Seitz: pp 235 - 242

Finding the normalization factor:

$$I_1 = \frac{V^2}{64\pi^6}\iint \left[1 - \cos(k_2 - k_1)\cdot(r_2 - r_1)\right] dk_1\, dk_2$$

$$= \frac{V^2}{(2\pi)^6}\int \psi^* \psi\, dk_1\, dk_2$$

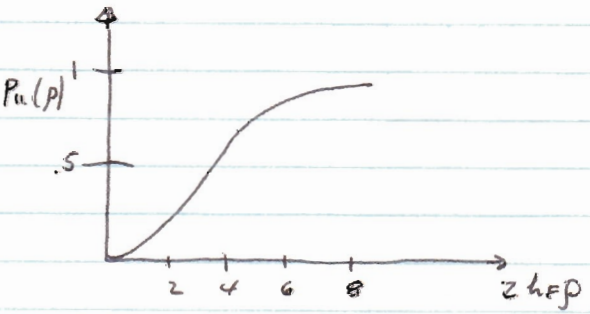
Let $r_2 - r_1 = \rho$; z-axis $\parallel \rho$, $q = \frac{k_2 - k_1}{2}$, $p = k_2 + k_1$

$$I_1 = \frac{V^2}{64\pi^6}\cdot\frac{4\pi k_F}{3}\cdot 2\int_0^{k_F} \sin^2(q\cdot\rho)\, dq$$

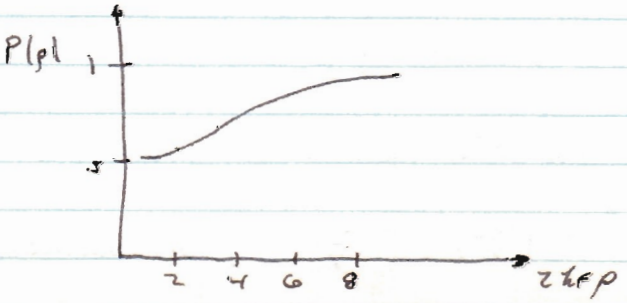
$$= \frac{V^2 k_F^6}{4\pi^4 9}\left[1 - \frac{3(\sin 2k_F\rho - 2k_F\rho\cos 2k_F\rho)}{(2k_F\rho)^3}\right]$$

Therefore, probability of parallel $= \frac{V^2}{(2\pi)^6}\int \psi^* \psi\, dk_1\, dk_2$

$$P_{\uparrow\uparrow}(\rho) = \underbrace{\left[1 - \frac{3(\sin 2k_F\rho - 2k_F\rho\cos 2k_F\rho)}{(2k_F\rho)^3}\right]}_{\text{correlation}}$$



The probability of finding two parallel electrons: $2k_F\rho = 4$



For spins $\uparrow\uparrow$, electrons push each other away. Assume electrons with equal probability between $\uparrow\uparrow$ and $\downarrow\uparrow$. This is given by the plot.

Now:

$$\mathcal{H} = \sum_i \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{i>j} \frac{e^2}{r_{ij}}$$

$$\int \psi^* \mathcal{H} \psi \, d\tau = \sum_i \phi_i^*(1) \left[-\frac{\hbar^2 \nabla_1^2}{2m} - \frac{Ze^2}{r_1} \right] \phi_i(1) \, d\tau_1$$

$$+ \sum_{i>j} \int\int \phi_i^*(1) \, \phi_j^*(2) \left(\frac{e^2}{r_{ij}} \right) \phi_i(1) \, \phi_j(2) \, d\tau_1 \, d\tau_2$$

$$- \sum_{\substack{i>j \\ \| }} \int\int \phi_i^*(1) \, \phi_j^*(2) \left(\frac{e^2}{r_{ij}} \right) \phi_j(1) \, \phi_i(2) \, d\tau_1 \, d\tau_2$$

Let the variation $\phi_i^* \rightarrow \phi_i^* + \delta\phi_i^*$, and minimize the result. We choose as the constraint, the normalization condition, and use the Lagrange multiplier E_i:

$$E_i \int \phi_i^*(1) \, \phi_i(1) \, d\tau_1 = 1$$

Reference: V. Fock, Z. Physik 61, 126 (1930)
J.C. Slater, PR 35, 210 (1930)

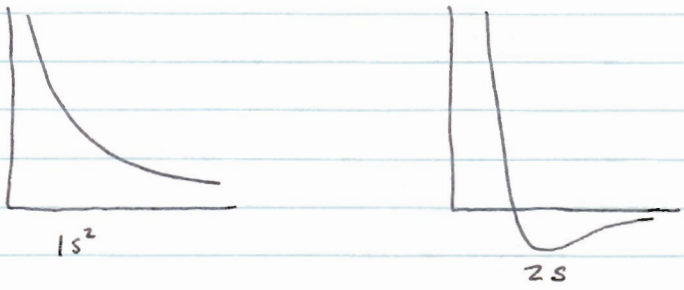
We then write Fock's equations:

$$\left(-\frac{\hbar^2 \nabla_1^2}{2m} - \frac{Ze^2}{r_1} \right) \phi_i(1) + \sum_{j \neq i} \left[\int \phi_j^*(2) \frac{e^2}{r_{ij}} \phi_j(2) \, d\tau_2 \right] \phi_i(1)$$

$$- \sum_{\substack{j \neq i \\ \| }} \left[\int \phi_j^*(2) \frac{e^2}{r_{ij}} \phi_i(2) \, d\tau_2 \right] \phi_j(1) = E_i \phi_i(1)$$

Note that it is not Schroedinger's equation. It is an integro-differential equation with coupling terms.

Example: Lithium, 3 electrons



LECTURE 26 : 11-22-61

References: J. C. Slater, PR 81, 385 (1951)
J. Bardeen, PR 49, 653 (1936)

Recall the Hartree - Fock equation:

$$\left(-\frac{\hbar^2\nabla_1^2}{2m} - \frac{Ze^2}{r_1}\right)\varphi_i(1) + \sum_{j\neq i}\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_j(2)\,d\tau_2\right]\varphi_i(1)$$

$$- \sum_{\substack{j\neq i\\ \uparrow\uparrow}}\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_i(2)\,d\tau_2\right]\varphi_j(1) = E_i\,\varphi_i(1)$$

The Hartree equation is:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1}\right)\varphi_i(1) + \left[\sum_j{}' e^2\int\frac{|\varphi_j(2)|^2}{r_{12}}\,d\tau_2\right]\varphi_i(1)$$
$$= E_i\,\varphi_i(1)$$

Note: the Hartree functions are not orthogonal, but the φ_j in the Hartree - Fock equations are orthogonal. We see the two equations are different by an exchange integral.

$$\sum_{j\neq i}\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_j(2)\,d\tau_2\right]\varphi_i(1) - \sum_{j\neq i}\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_i(2)\,d\tau_2\right]\varphi_j(1)$$

$$= \sum_j\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_j(2)\,d\tau_2\right]\varphi_i(1) - \sum_j\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_i(2)\,d\tau_2\right]\varphi_j(1)$$

Note if $i=j$ is also included, they are cancelled between the two summations. Multiply and divide by $\varphi_i^*(1)\,\varphi_i(1)$ to exchange energy:

$$\sum_j\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_j(2)\,d\tau_2\right]\varphi_i(1) - \left(\frac{\hbar^2}{2m}\nabla_1^2 + \frac{Ze^2}{r_1}\right)\varphi_i(1)$$

$$- \frac{\sum_j\left[\int \varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_i(2)\,d\tau_2\right]\varphi_j(1)\,\varphi_i^*(1)\,\varphi_i(1)}{\varphi_i^*(1)\,\varphi_i(1)}$$

$$= \sum_j \left[\int \varphi_j^*(2) \frac{e^2}{r_{ij}} \varphi_j(2)\, d\tau_2 \right] \varphi_i(1) - \left(\frac{\hbar^2}{2m} \nabla_1^2 + \frac{Ze^2}{r_1} \right) \varphi_i(1)$$

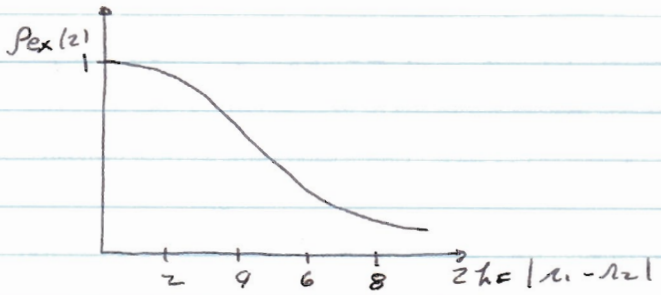
$$- \sum_{j \neq i} \left[\frac{\int \varphi_i^*(1)\, \varphi_j^*(2) \frac{e^2}{r_{ij}} \varphi_j(1) \varphi_i(2)\, d\tau_2}{\varphi_i^*(1)\, \varphi_i(1)} \right] \varphi_i(1) = E_i \varphi_i(1)$$

The Fock Hamiltonian is: $H_F = H_0 + U - A$, U being the coulomb integral and A the exchange integral. Also, $H_F \varphi_i = E_i \varphi_i$ with the φ_i orthogonal. The effective charge cancelled the electron self-energy. [The Dirac density matrix is $\rho(1,2) = \sum_j \varphi_j^*(1)\, \varphi_j(2)$]

The exchange charge density is defined as:

$$\rho_{ex}(2) = \sum_{j \| i} \frac{\varphi_i^*(1)\, \varphi_j^*(2)\, \varphi_j(1)\, \varphi_i(2)}{\varphi_i^*(1)\, \varphi_i(1)}$$

We plot $\rho_{ex}(2)$ for the case of φ_j and φ_i free electron wave functions.



If $r_1 = r_2$, then: $\rho_{ex}(1) = \sum_{j \| 1} |\varphi_j(1)|^2$

Assume charges are distributed uniformly in a sphere of radius R, then:

$$\int \rho_{ex}\, d\tau = \frac{4\pi}{3} \sum_{j \| i} |\varphi_j(1)|^2 R^3 = 1$$

This means if $\int \rho_{ex}(2)\, d\tau_2 = 1$, there is only one exchange hole. Replace it by a single electron. $\rho_{ex}(2)$ vs $2k_F |r_1 - r_2|$ by a rectangle, and we find the size of the exchange hole $\approx$ size of an atom.

The Hartree equation has no effective exchange hole, but restricts $\rho \pm \epsilon$ instead, which approximately includes the exchange hole effect. But the representation is bad as when the electron is near the atom, it feels only $\frac{1}{N}$ "+" charges, where N = number of atoms.

Consider a crystal (periodic lattice):

Hartree Method: Use one electron wave functions modified corresponding to $-\frac{e}{N}$ on each of the N atoms. The effect $\frac{1}{N}$ of an electron on each atom has a negligible effect on the potential field.

Hartree-Fock Method: The exchange charge is located near the position x_1 of the electron in question, moving around with it so that when this electron is on a given atom, the exchange charge is removed largely from that atom, leaving it in the form of a positive ion.

We now calculate the exchange energy in the plane wave approximation:

$$\psi_k = \frac{1}{\sqrt{V}} e^{i k_x \cdot r}$$

$$- \frac{e^2}{V^{3/2}} \sum_{k'} e^{i k' \cdot r_1} \int \frac{e^{-i(k'-k)\cdot r_2}}{r_{12}} d\tau_2$$

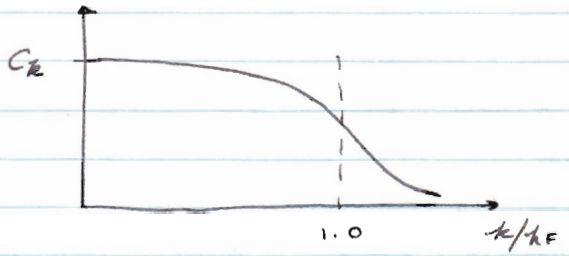
$$= -\frac{e^2}{V^{3/2}} e^{i k \cdot r_1} \sum_{k'} \int \frac{e^{i(k'-k)\cdot(r_1 - r_2)}}{r_{12}} d\tau_2$$

$$= - c_k \frac{e^{i k \cdot r_1}}{\sqrt{V}}$$

where:

$$c_k = e^2 k_F \left[2 + \frac{k_F^2 - k^2}{k_F k} \log \left| \frac{k + k_F}{k - k_F} \right| \right] = \frac{e^2}{V} \sum_{k'} \int \frac{e^{i(k'-k)\cdot(r_1 - r_2)}}{r_{12}} d\tau_2$$

c_k = Twice the exchange energy for an electron.



The total exchange energy is:

$$-\frac{1}{2}\int \psi^* C_k \psi \, d\tau = -\frac{e^2 V k_F^4}{4\pi^3} \quad ; \text{ now: } k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

as before. Thus:

$$\frac{-\frac{1}{2}\int \psi^* C_k \psi \, d\tau}{n} = -\frac{e^2 3^{4/3}}{4\pi^{1/3}} \left(\frac{n}{V}\right)^{1/3} = -\frac{.458\, e^2}{r_s}$$

$$\therefore \quad \frac{V}{n} = \frac{4\pi}{3} r_s^2$$

We take atomic units: Energy = 13.6 ev, Rydberg = $\frac{me^4}{2\hbar^2}$, distance = $a_0 \approx .5\text{Å} = \frac{\hbar^2}{me^2}$

Then:

$r_s = a_0 \rho_s$ and we have:

$$\frac{\text{Exchange Energy}}{\text{Electron Energy}} = -\frac{.458\, e^2}{\rho_s} \frac{2\hbar^2}{me^4} \frac{me^2}{\hbar^2} = -\frac{.916}{\rho_s}$$

The K.E. $= \frac{3}{5} E_F = \frac{3}{10} \frac{\hbar^2 k_F^2}{2m} = \frac{2.21}{\rho_s^2}$

The total energy in atomic units is:

$$E = \left[\frac{2.21}{\rho_s^2} - \frac{.916}{\rho_s}\right] \text{ Rydbergs}$$

If we include correlation energy E_c by expanding ρ_s^2:

$$E = \left[\frac{2.21}{\rho_s^2} - \frac{.916}{\rho_s} + E_c\right].$$

In the high density limit the KE is very large, and the coulomb energy becomes the perturbation term:

$$E = c \log \rho_s + D + \mathcal{O}(\rho_s)$$

LECTURE 27 : 11-24-61

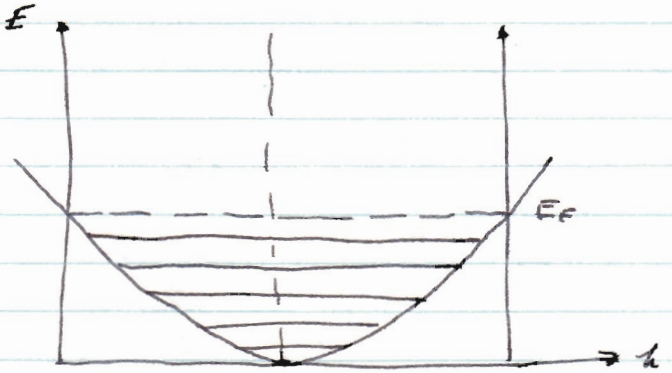
References : Mott and Jones, pp 86-88
Ziman, Ch IV
Pines, SSP I, 368
Bohm & Pines, PR 82, 625
85, 338
92, 609, 626

Recapitulation:

$$E = \frac{2.21}{r_s^2} - \frac{.916}{r_s}$$

while ignoring electrons with ↑ spins. A typical $r_s \sim 2 \to 5.5$; r_s goes as reciprocal density. However, we have not included correlations properly due to coulomb interaction. The first correct treatment was by Gell-Mann and Brueckner, PR 106, 164 (1957) in the high density limit, about twice that normal. This adds terms to E of $+.0622 \ln r_s - .096 + O(r_s)$. See also: Wigner, Trans. Faraday Soc. 1938 for the case of the low density limit $r_s \geq 20$. This is really the tight binding picture, because we assume low electron kinetic energy. Of course, not important for real metals.

The examples we have done are really the free electron gas at T=0:



Exchange from interaction between parallel spins. In dilute gas, all spins would be aligned by exchange. Then the new E_F would be larger because only one electron in each state or we have effectively doubled the number of states:

$$k_F'^3 = 2k_F^3 \quad \text{since } k_F \propto n \text{ or } N$$

Then:

KE increases by $2^{2/3}$

Exchange energy increases by $2^{1/3}$

Then:

$$E = \frac{3.5^2}{r_s^2} - \frac{1.156}{r_s'}$$

$$E - E' = \frac{1.31}{r_s^2} - \frac{.240}{r_s}$$

which is zero when $r_s = 5.47$. However, this result would predict ferromagnetism in Cs and alkali metals, but it isn't. Also find a result other than $C_V \propto T$. That is, if we include exchange,

$$E = \frac{\hbar^2 k^2}{2m} + e^2 k_F \left[2 + \frac{k_F^2 - k^2}{k_F k} \ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

we find $C_V = 0$, recall Wohlfarth paper. Get actually $T^{-1} \ln T$ from the Helmholtz free energy and the entropy.

Now the correlation should in principle subtract out almost the exchange contribution in order to give the expected result for C_V. We go to the limit of complete correlation, which denotes the plasma condition:

Calculate interaction between two centers

Write the classical equation of motion:

$$m^*\left(\frac{dv}{dt}+\frac{v}{\tau}\right) = F = \underbrace{e\left[E_{appl} - \mathcal{L} P\right]}_{e E_{eff}} + \frac{e}{c} v \times H$$

$$e E_{eff} = e\left[E_{appl} - \mathcal{L}\left(\chi E_{eff} + n e \underline{r}\right)\right.$$

$\underline{r}$ ↓ distance between centers of charge

$$E_{eff} = \frac{E_{appl} - \mathcal{L} n e \underline{r}}{1 + \mathcal{L}\chi} = E_L - \mathcal{L}_L n e \underline{r}$$

where $E_L = \dfrac{E_{appl}}{1+\mathcal{L}\chi}$; $\mathcal{L}_L = \dfrac{\mathcal{L}}{1+\mathcal{L}\chi}$

Then:

$$m^* \frac{d^2\underline{r}}{dt^2} + \frac{\mathcal{L}_L n e^2 \underline{r}}{m^*} = e E_L + \frac{e}{c}\frac{d\underline{r}}{dt} \times H$$

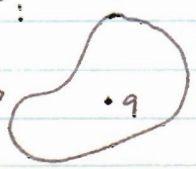
$$- \frac{m^*}{\tau}\frac{d\underline{r}}{dt}$$

We take the harmonic solution: $E_L \sim e^{i\omega t}$

$$\underline{r} = \frac{(e/m^*) E_L}{-\omega^2 - \omega_p^2 + i\frac{\omega}{\tau} + i\omega\omega_c} \quad ; \quad \omega_c = \frac{e H}{m^* c}$$

$$\omega_p^2 = \frac{\mathcal{L}_L N e^2}{m^*}$$

See: DKK, PR 100, 618 (1955) for treatment of ω_p in In Sb. Now go to the other limit which can screen out interruption of uniform density of charge. Treatment due to debye. Take a model of a uniform gas with an impurity charge q placed in it:



change in charge density $= q\,\delta(r) - e\,\delta p$

Now from Poisson's equation:

$$\nabla^2 \varphi = -4\pi \left[q\,\delta(r) - e\,\delta\rho \right]$$

where we assert: $\delta\rho = n_0 e^{e\varphi/kT} - n_0$; $n_0 = \frac{N}{V}$

and:

$$\delta\rho \simeq \frac{n_0 e \varphi}{kT}$$

Reference: AP231. Then:

$$\nabla^2 \varphi - \frac{4\pi e^2 n_0}{kT} \varphi = -4\pi q\,\delta(r)$$

What about the boundary condition? For small r we know:

$$\varphi \sim \frac{q}{r}$$

so take solution of the form: $\varphi = \frac{q}{r} e^{-r/\lambda_D}$

$$\frac{q}{\lambda_D^2 r} e^{-r/\lambda_D} - \frac{4\pi e^2 n_0}{kT} q e^{-r/\lambda_D} = -4\pi \delta(r)$$

Integrate over all space and get:

$$\lambda_D^2 = \frac{kT}{4\pi e^2 n_0}$$

At high T, KE interferes with screening.
At high n_0, so many electrons, the screening is enhanced, or electrons farther than λ_D are unaffected by q. This marks boundary of where classical argument above breaks down. This is important for correlation. λ_D refers to a kind of correlation distance.

LECTURE 28: 11-27-61

Recall: $\varphi = \frac{q}{r} e^{-r/d_D}$

$$d_D^2 = \frac{kT}{4\pi^2 e^2 n_0}$$

Some typical numbers: $n_0 = 10^{12}/cm^3$, $kT \sim 3$ ev
for plasma gas: $d_D \sim 10^{-3}$ cm $\quad T \sim 3\cdot 10^4$ °K

In semiconductor: $n_0 \sim 10^{16}/cm^3$, $T \sim 4$°K, $d_D \sim 100$ Å

In metals: $n_0 \sim 10^{22}/cm^3$, $T \sim 4$ °K, $d_D \sim 10^{-9}$ cm.

We now generate the plasma problem quantum-mechanically. Take for Hamiltonian:

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{i>j}{}' \frac{1}{|r_i - r_j|}$$

We want to transform to momentum space:
Consider $\frac{1}{r}$:

$$\frac{1}{V} \int \frac{1}{r} e^{-ik\cdot r}\, d\tau = \frac{4\pi}{2V} \int_0^\infty \int_{-1}^{1} e^{-ikr\cos\theta}\, d(\cos\theta)\, r\, dr$$

$$= \frac{2\pi}{V} \cdot \frac{2}{ik} \int_0^\infty \sin kr\, dr$$

Use convergence factor and get:

$$\frac{4\pi}{2V} \lim_{\alpha \to 0} \frac{k}{\alpha^2 + k^2} = \frac{4\pi}{k^2 V}$$

Then:

$$\frac{1}{r} = \sum_k{}' \frac{4\pi}{V} \frac{1}{k^2} e^{ik\cdot r}$$

$k = 0$ cancelled by balance in charge.

Then:

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{i \neq j} \sum_k{}' \frac{e^{i k \cdot (r_i - r_j)}}{k^2}$$

$$\underbrace{- 2\pi n_0 e^2 \sum_k{}' \frac{1}{k^2}}_{\text{Term comes from removing prime on } \sum_{i \neq j}'} \quad ; \quad n_0 = \frac{n}{V}$$

We now would like to formulate the problem in normal coordinates, because we suspect this from the oscillatory nature of plasma oscillations. We choose:

$$Q_k, P_k \quad ; \quad [P_k, Q_{k'}] = i\hbar \delta_{kk'}$$

Take: $n_0(r) = \sum_i \delta(r - r_i)$

Fourier transforming: $n_k = \frac{1}{\sqrt{V}} \int dr\, e^{-ik \cdot r} n_0(r)$

$$= \frac{1}{\sqrt{V}} \sum_i e^{-ik \cdot r_i}$$

Define the generating function (Goldstein):

$$S = -i \sum_{\substack{k \\ \leq k_c}} \left(\frac{4\pi e^2}{k^2} \right)^{1/2} Q_k n_k^*$$

We cut-off because of the screening action of the plasma. No sense to normal coordinates except outside the λ_D. k_c is related to λ_D.
Assume original wave function: ψ and new one:

$$\psi = e^{-iS/\hbar} \psi$$

$$p_k = e^{-iS/\hbar} p_k e^{iS/\hbar}$$

Or, to first order in S:

$$p_k = \left(1 - \frac{iS}{\hbar}\right) p_k \left(1 + \frac{iS}{\hbar}\right) = p_k + \frac{i}{\hbar} [p_k, S]$$

Then: $p_k' = p_k + \frac{i}{\hbar}\left[p_k, -i\sum_{k\le k_c}\left(\frac{4\pi e^2}{k^2}\right)^{1/2} Q_k u_k^*\right]$

$= p_k + \frac{1}{\hbar}\sum_{k\le k_c}\left(\frac{4\pi e^2}{k^2}\right)^{1/2} Q_k \left[p_k, u_k^*\right]$

$\left[p_k, u_{k'}^*\right] = \frac{\hbar}{i}\frac{1}{\sqrt{V}} i k e^{i k\cdot r_k}$

Then:

$$p_k' = p_k + \sum_{k<k_c}\left(\frac{4\pi e^2}{k^2}\right)^{1/2}\frac{1}{\sqrt{V}} Q_k\, k\, e^{i k\cdot r_k}$$

Note presence of only longitudinal mode.

Since we demand p_k Hermitean, then $Q_k^* = -Q_{-k}$ and $P_k^* = -P_{-k}$. Finally:

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2m}\sum_i\sum_{k<k_c}\left(\frac{4\pi e^2}{k^2}\right)^{1/2}\frac{1}{\sqrt{V}}\hbar Q_k$$

$$\left[p_k e^{i k\cdot r_k} + e^{i k\cdot r_k} p_k\right] + \frac{1}{2m}\sum_\nu \sum_{\substack{k<k_c\\ k'<k_c}} \frac{4\pi e^2}{k k'}$$

$$\frac{1}{V} Q_k\, k\, Q_{k'}\, k'\, e^{i(k+k')\cdot r}$$

Recall: $e^{i k\cdot r_k} p_k = \left[e^{i k\cdot r_k}, p_k\right] + p_k e^{i k\cdot r_k}$

In last term in H: $\sum_{\substack{k<k_c\\ k'<k_c}} \rightarrow \sum_{\substack{k<k_c\\ k'<k_c\\ k}}$

$$+ \underbrace{\frac{1}{2m}\sum_k \frac{4\pi e^2 n}{V} Q_k^* Q_k}$$

$$\frac{1}{2}\sum_k \omega_p^2 Q_k^* Q_k$$

We can now write the potential energy and kinetic energy separately:

$$KE = \sum_k \frac{p_k^2}{2m} + \frac{1}{2} \sum_{k<k_c} \omega_p^2 Q_k^* Q_k$$

$$+ \sum_j \sum_{k<k_c} \left(\frac{4\pi e^2}{k^2 V} \right)^{1/2} \left[\frac{k \cdot (p_k - \frac{\hbar k}{2})}{m} \right] Q_k \, e^{ik \cdot r_j}$$

$$+ \sum_j \sum_{\substack{k,k' < k_c \\ k \neq k'}} \frac{2\pi e^2}{mV} \frac{k \cdot k'}{k k'} Q_k Q_{k'} \, e^{i(k+k') \cdot r_j}$$

$$= H_e + H_p + \underbrace{H_{ep}}_{\text{this is negligible}} + \underbrace{v H_e^2 H_p^2}_{\text{this can be shown to vanish}}$$

We would like to add $\frac{1}{2} \sum_{k<k_c} P_k^+ P_k$.
We can do this if:
$P_k \Psi = 0$ since this effects diagonal terms. Or:

$$P_k \Psi = P_k e^{iS/\hbar} \Psi_n = 0$$

or: $$\left[e^{iS/\hbar} P_k e^{-iS/\hbar} \right] \Psi_n = 0$$

$$\left[e^{iS/\hbar} P_k e^{-iS/\hbar} \right] = P_k + \frac{i}{\hbar} [S, P_k]$$

$$= P_k + \frac{1}{\hbar} \left(\frac{4\pi e^2}{k^2} \right)^{1/2} n_k^+ [Q_k, P_k]$$

$$= P_k - i \left(\frac{4\pi e^2}{k^2} \right)^{1/2} n_k^+$$

so the condition is now:

$$\left[P_k - i \left(\frac{4\pi e^2}{k^2} \right)^{1/2} n_k^+ \right] \Psi_n = 0$$

LECTURE 29 : 11-29-61

Recall:

$$\left[p_k - i \left(\frac{4\pi e^2}{v k^2} \right)^{1/2} \pi_k^+ \right] \Psi = 0$$

Called subsidiary condition: Now:

$$\mathcal{H}_p = \frac{1}{2} \sum_{k<k_c} \left[P_k^+ P_k + \omega_p^2 Q_k^+ Q_k \right] \qquad \text{(plasma)}$$

$$\mathcal{H}_e = \sum_i \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{i \neq j \\ k \geq k_c}} \frac{e^{ik\cdot(r_i - r_j)}}{k^2}$$

$$- 2\pi n e^2 \sum_{k<k_c} \frac{1}{k^2} \qquad \text{(electron)}$$

$$\mathcal{H}_{ep} = \sum_{\substack{i \\ k<k_c}} \left(\frac{4\pi e^2}{V k^2} \right)^{1/2} \left[\frac{k}{m} \cdot \left(p_i - \frac{1}{2} \hbar k \right) \right] Q_k \, e^{ik\cdot r_i} \qquad \text{(electron-plasma)}$$

NB: The term $\sum_{k>k_c}$ has been left out in previous lecture. Will be considered later.

We consider that electron-plasma term is small, so treat independently. Plasma gives harmonic oscillator. Electron has short range term, $\mathcal{H}_{sr}$:

$$\mathcal{H}_{sr} = \frac{2\pi e^2}{V} \sum_{\substack{i \neq j \\ k>k_c}} \frac{e^{ik\cdot|r_i - r_j|}}{k^2}$$

$$= \sum_{i,j}{}' \frac{2\pi e^2}{V} \frac{V}{8\pi^3} 2\pi \int_{-1}^{1} \int_{k_c}^{\infty} \frac{e^{ik|r_i - r_j|\cos\theta}}{k^2}$$

$$= \sum_{i,j}{}' \frac{e^2}{\pi} \int_{k_c}^{\infty} \frac{\sin k|r_i - r_j|}{k|r_i - r_j|} \, dk$$

$$- \sum_{i,j} \frac{e^2}{\pi |r_i - r_j|} \int_{k_c|r_i - r_j|}^{\infty} \frac{\sin x}{x} \, dx$$

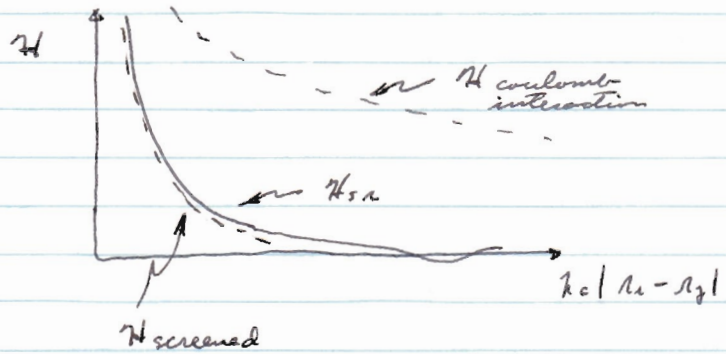
Note: $\int_{k_c|r_i-r_j|}^{\infty} = \int_0^{\infty} - \int_0^{k_c|r_i-r_j|}$

Then:

$$H_{sr} = \frac{1}{2} \sum_{ij} \frac{e^2}{|r_i-r_j|} \left\{ 1 - \frac{2}{\pi} S_i\left(k_c|r_i-r_j|\right) \right.$$

$$S_i(\alpha) = \int_0^{\alpha} \frac{\sin x}{x}\, dx$$

For given k_c:



This is because $\frac{1}{r_{ij}} e^{-k_c r_{ij}} = \frac{4\pi}{V} \sum_k \frac{e^{ik\cdot r_{ij}}}{k^2 + k_c^2}$

k_c prevents infinite answers. This is almost equivalent to cutting off the ordinary coulomb interaction Fourier transform. We have for the system energy:

$$E = \frac{3}{5} E_F + \sum_{k<k_c} \left(\frac{\hbar\omega_p}{2} - \frac{2\pi n_0 e^2}{k^2} \right) + \langle H_{sr} \rangle$$

Write n' for the number of plasmons:

$$E = \frac{3}{5} E_F + n' \frac{\hbar\omega_p}{2} - \frac{n e^2 k_c}{\pi} + \langle H_{sr} \rangle$$

We assume that we can minimize the energy with respect to k_c, although this is shaky, see Bohm and Pines.

Note: $\sum_{k<k_c} = \frac{V}{8\pi^3} \cdot 4\pi \int_0^{k_c} k^2 dk = nV$

$n' = \frac{k_c^3}{6\pi^2}$, Then, dividing by the number of electrons,

$$E = \frac{3}{5} n E_F + \frac{k_c^3}{6\pi^2}\left(\frac{\hbar\omega_p}{2}\right) - \frac{ne^2}{\pi} k_c + \langle H_{sr}\rangle$$

Assume that $\langle H_{sr}\rangle$ does not depend on k_c, actually does slightly:

$$k_c^2 = \frac{4\pi n e^2}{\hbar\omega_p} = \frac{k_F^2}{2.14} r_s^{1/2} \quad ; r_s \to 2 \sim 5.5$$

$k_c \sim .81\, k_F$, $1.05\, k_F$

In Na, $r_s \sim 4$, $k_c \sim k_F$

This means that the screening length is very tight. We find using k_c above, that, energy/electron

$$E = \frac{3}{5} E_F - \frac{2}{3}\frac{e^2 k_c}{\pi} + \frac{1}{n}\langle H_{sr}\rangle$$

This gives for the correlation energy:

$$E = \frac{2.21}{r_s^2} - \frac{.81}{r_s} + sr$$

↑ correlation

Note exchange is missing. This comes from S.R.

$$\langle H_{sr}\rangle_{\substack{\text{II} \\ \text{sperm}}} = \frac{-.3e^2 k_F n}{4\pi}\left\{1 - \frac{4}{3}\frac{k_c}{k_F} + \frac{k_c^2}{2k_F^2} - \frac{k_c^4}{48 k_F^4}\right\}$$

$$\frac{1}{n}\langle H_{sr}\rangle = \frac{-.916}{r_s}\left\{1 - \frac{4k_c}{3k_F} + \frac{k_c^2}{2k_F^2} - \frac{k_c^4}{48 k_F^4}\right\}$$

Finally:

$$E = \underbrace{\frac{2.21}{r_s^2}}_{KE} - \underbrace{\frac{0.916}{r_s}}_{HF\ exch} + \underbrace{\left[\frac{.866}{r_s^{3/2}}\beta^3 - \frac{1.22}{r_s}\beta\right]}_{Plasma} + \underbrace{\left[\frac{1.22}{r_s}\beta - \frac{.458}{r_s}\beta^2 + \frac{.019}{r_s}\beta^4\right]}_{\substack{Self-energy \\ H_{sr},\ correlation\ energy}}$$

We find: $\beta = .352\, r_s^{1/2}$, by minimizing energy.

$E_{correlation} = -.019 - .0003 r_s$ rydbergs

LECTURE 30 : 12-1-61

Errata: We added to Hamiltonian: $\sum_{k<k_c} \frac{P_k^* P_k}{2}$

However, to get rid of $\sum_{k<k_c} \frac{e^{i k\cdot r}}{k^2}$ term

must also add $\frac{1}{2} \sum_{k<k_c} \left(\frac{4\pi e^2}{k^2}\right)^{1/2} P_k n_k$

subject to $P_k \Psi = 0$.

$$\sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{k<k_c} \omega_p^2 Q_k^* Q_k + H_{ep} + \frac{2\pi e^2}{V} \sum_{i,j} \sum_{k'} \frac{e^{i k\cdot(r_i - r_j)}}{k^2}$$

$$- 2\pi n_0 e^2 \sum_k{}' \frac{1}{k^2}$$

Using $S = -i \sum_{k<k_c} \left(\frac{4\pi e^2}{k}\right)^{1/2} Q_k n_k^*$

$$H_{add} = \sum_{k<k_c} \frac{P_k^* P_k}{2} + \frac{1}{2} \sum_{k<k_c} \left(\frac{4\pi e^2}{k^2}\right)^{1/2} P_k n_k$$

We must now compute:

$$e^{-iS/\hbar} H_{add} e^{iS/\hbar} = H_{add} + \frac{1}{\hbar} [H_{add}, S]$$

H_{add} in added before transformation.

$$= H_{add} + \frac{1}{\hbar} \sum_{k k'} \left(\frac{4\pi e^2}{k'^2}\right)^{1/2} n_{k'}^* \left[P_{k'}^* P_{k'}, Q_{k'}\right]$$ ← cancels with above

$$+ \frac{1}{\hbar} \sum_{k k'} \frac{4\pi e^2}{k k'} n_k n_{k'}^* \left[P_k, Q_{k'}\right]$$

$$- \frac{1}{2} \sum_{k<k_c} \frac{4\pi e^2}{k^2} n_k n_k^*$$

Finally:

$$\mathcal{H}' = \sum_k \frac{\pi_k^2}{2m} + \frac{1}{2}\sum_{k<k_c} \omega_p^2 Q_k^* Q_k + \mathcal{H}_{ep}$$

$$+ \frac{2\pi e^2}{V} \sum_{kj} \sum_{k>k_c}{}' \frac{e^{ik\cdot(r_k - r_j)}}{k^2} - 2\pi n_0 e^2 \sum_k{}' \frac{1}{k^2}$$

$$+ \frac{1}{2}\sum_{k<k_c} P_k^* P_k$$

Transform $e^{-iS/\hbar} P_k \Psi = 0$

$$(e^{-iS/\hbar} P_k e^{iS/\hbar})\underbrace{(e^{-iS/\hbar}\Psi)}_{\Psi} = 0$$

or: $$\left[P_k + i\left(\frac{4\pi e^2}{k^2}\right)^{1/2} \pi_k^*\right]\Psi = 0$$

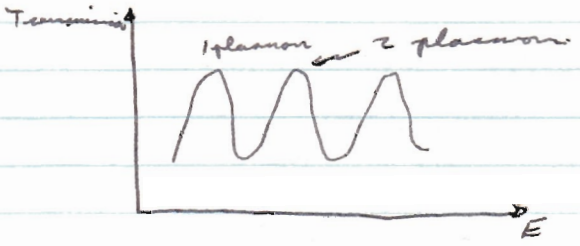
This is the new subsidiary condition.

Recall results of last lecture: $\beta = \frac{kc}{\omega_p}$, etc, for energy. The ratio of plasmons n' to n, number of electrons:

$$\frac{n'}{3n} = \frac{\beta^2}{6} = .0073\, r_s^{3/2} \approx 5\% \text{ for Na}$$

↑ longitudinal only.

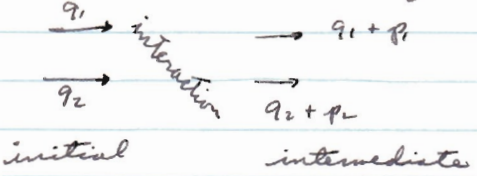
Can measure plasmon energies by shooting electron beams at thin foils.



Get second order effect from:

$$\mathcal{H}_{sr} = \frac{2\pi e^2}{V} \sum_{kj} \sum_{k>k_c} \frac{e^{ik\cdot(r_k - r_j)}}{k^2}$$

Consider two adjacent electrons:



} then back to initial

$$\Delta = = \frac{|\langle \text{initial} | \mathcal{H}_{SR} | \text{inter} \rangle|^2}{E_{init} - E_{int.}}$$

$$\frac{\hbar^2}{2m}\left(q_1^2 + q_2^2\right) - \frac{\hbar^2}{2m}\left[(q_1+p_1)^2 + (q_2+p_2)^2\right]$$

$$= -\frac{\hbar^2}{2m}\left[2q_1\cdot p_1 + 2q_2\cdot p_2 + p_1^2 + p_2^2\right]$$

Then:

$$\langle \mathcal{H}_{SR} \rangle = \int e^{-i(q_1+p_1)\cdot r_1} e^{ik\cdot r_1} e^{iq_1\cdot r_1}\, d\tau_1$$

$p_1 = k$
$p_2 = -k$
} we must have: $q_1 < k_F$, $q_1 + k > k_F$
$q_2 < k_F$, $q_2 - k > k_F$

We get basically:

$$\Delta E = \sum_{q_1 q_2} \sum_{k<k_c} \frac{1}{k^4} \frac{1}{k\cdot(q_1 - q_2) + k^2}$$

$$= -\left\{.0254 - .0626 \ln\beta + .000637\beta^2\right\} \text{ rydbergs}$$

This is added as second order term to correlation. Assume β is given in terms of r_s as before. Then:

$$E_c = -\left\{.1114 - .0313 \ln r_s + .0005 r_s\right\} \text{ rydbergs}$$

Gell-mann - Brueckner: High density limit.

$$E_c = -\left\{.096 - .0622 \ln r_s + \cdots\right\} \text{ rydbergs.}$$

Let's look at system wave function in new system:

$$H_e + H_p + H_{ep}$$

$$\psi = \psi_{plasma}\ \psi_0(r_1 \cdots r_N)$$

$$\psi_{plasma} = e^{-\left(\sum_{k<k_c} \rho_k^2 / 2\hbar\omega_p\right)}$$

Use the subsidiary condition:

$$\psi_{plasma} = e^{\left[-\frac{4\pi e^2}{v}\sum_{q}\sum_{k<k_c}\frac{e^{ik\cdot(r_i - r_j)}}{k^2}\right]/2\hbar\omega_p}$$

Hence:

$$\psi = e^{\left\{-\frac{1}{2}\sum_{ij} F(r_i - r_j)/\hbar\omega_p\right\}}\ \psi_0(r_1 \cdots r_N)$$

$$F(r_i - r_j) = \frac{2e^2}{|r_i - r_j|}\,\frac{\delta_i[k_c(r_i - r_j)]}{\pi}$$

$$= e^{-\frac{E_{coulomb}}{E_{plasma}}\frac{2}{\pi}Si(k_c|r_i - r_j|)}$$

At long range, $\psi_{plasma} = 1$, $\psi = \psi_0(r_1 \cdots r_N)$

LECTURE 31: 12-4-61

Recall:

$$\psi_{plasma} = \exp\left\{-\frac{1}{2}\sum_{ij}\frac{e^2}{|r_i - r_j|}\left(\frac{2}{\pi}\right)\frac{Si(k_c|r_i - r_j|)}{\hbar\omega_p}\right.$$

Large $(r_i - r_j)$ gives $\psi_{plasma} = 1$

Small $|r_i - r_j|$: $\psi_{plasma} = \exp\left\{-\frac{1}{\pi}\sum_{ij}\left(\frac{e^2 k_c}{\hbar\omega_p}\right)\right\}$

$$= \exp\left\{-.124\, p_3\right\}$$

This reduces ψ_0 amplitude for electrons close together.

This introduces more correlation than is contained in ψ_0 originally. Hence:

$r_s - r_s \gg \frac{1}{k_c}$; $\Psi = \psi_0$

$r_s - r_s \ll \frac{1}{k_c}$; $\Psi = e^{-.124 \rho_s} \psi_0$

What is k_c? We found by minimizing for $\rho_s \ll 1$, we have:

$$k_c = k_F (.3521 \rho_s^{1/2}$$

The screening length q is:

$q = \frac{1}{k_c} = 1.48 \rho_s^{1/2}$ which goes as atomic radius in a metal.

Compare with Debye length:

$$d_D = \left(\frac{1T}{4\pi e^2 n_0} \right)^{1/2} \sim .64 \rho^{1/2}$$

so Debye is even smaller than atomic radius. This is because in Debye, there is no correlation between electrons because this helps keep them apart and reduce screening.

Reference: Friedel, Adv. in Phys. 3, 446 (1954)

~~Specific Heats~~: Recall:

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

$$N = 2 \int_0^\infty f(E)\, N(E)\, dE$$

At $T=0$:

$$N = 2 \int_0^{E_F^\circ} N(E)\, dE$$

$$N(E)\,dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\,dE = C E^{1/2}\,dE$$

Find that:

$$\frac{d}{3} C (E_F^\circ)^{3/2} = \frac{N}{V}$$

$$N(E_F^\circ) = \frac{3}{4}\frac{(N/V)}{E_F^\circ} \quad . \quad \text{Recall:}$$

$$\int_0^\infty g(E)\, f(E)\, dE = \int_0^{E_F^\circ} g(E')\,dE' + \frac{\pi^2}{6}(kT)^2 \left(\frac{\partial g}{\partial E}\right)_{E_F^\circ} + \cdots$$

$$E_F^\circ = E_F\left[1 - \frac{\pi^2}{12}\frac{(kT)^2}{E_F^{\circ 2}}\right]$$

LECTURE 32 : 12-6-61

Recall:

$$\int_0^\infty f(E)\frac{d}{dE}F(E)\,dE = F(E_F) + \frac{\pi^2}{6}(kT)^2 F''(E_F)$$

To calculate energy; choose:

$$F(E) = \int_0^E N(E)\,E\,dE$$

$$U = 2\int_0^\infty N(E)\,E\,dE + \frac{\pi^2}{3}(kT)^2 \left.\frac{d(NE)}{dE}\right|_{E=E_F}$$

$$E_F = E_F^\circ - \frac{\pi^2}{6}(kT)^2 \left(\frac{d\log N}{dE}\right)_{E=E_F}$$

$$U = 2\int_0^{E_F^\circ} N(E)\,E\,dE - \frac{\pi^2}{8}(kT)^2 E_F \left(\frac{dN}{dE}\right)_{E=E_F}$$

$$+ \frac{\pi^2}{3}(kT)^2 \left(\frac{d(NE)}{dE}\right)_{E=E_F}$$

$$U = 2\int_0^{E_F^0} N(E)\,E\,dE + \frac{\pi^2}{3}(kT)^2\,N(E_F)$$

$$C = \frac{2\pi^2}{3}k^2\,T\,N(E_F)$$

which shows the proper behavior with temperature. For the non-interacting free electron gas:

$$N(E_F) = \frac{3}{4}\frac{(N/V)}{E_F}$$

$$C = \frac{\frac{1}{2}\pi^2 k\,T}{T_F}(N/V)$$

We now want to calculate C for the case where interactions are taken into account.

$$C = \frac{2\pi^2 k^2 T}{n_0}\,n_0(E_F)$$

$$n_0(E_F) = \left.\frac{dn_0}{dE}\right|_{E=E_F}$$

$$\frac{dn_0}{n_0} = \frac{d\left(\frac{4\pi}{3}k^3\right)}{\frac{4\pi}{3}k_F^3} = \frac{3k^2\,dk}{k_F^3}$$

Then:

$$\frac{n_0(E_F)}{n_0} = \frac{3k^2}{k_F^3}\left.\frac{dk}{dE}\right|_{E=E_F} = \frac{3}{k_F}\frac{1}{(dE/dk)_{E=E_F}}$$

$$C = \frac{2\pi^2 k^2 T}{k_F}\frac{1}{(dE/dk)_{k=k_F}}$$

Recall:

$$E(k) = \frac{\hbar^2k^2}{2m} - \frac{e^2k_F}{\pi}\left(2 + \frac{k_F^2-k^2}{k_F\,k}\ln\left|\frac{k_F+k}{k_F-k}\right|\right)$$

with exchange.

Higher order terms give $C \sim \frac{T}{\ln T}$, otherwise $C_v = 0$.

So we must include correlation in the hope that it will remove the divergence. Recall, in atomic units:

$$E(k) = \frac{3.68 k^2}{\rho_s^2 k_F^2} - \frac{.611}{\rho_s}\left\{1 - 2\beta + \frac{\beta^2 + \frac{3k^2}{k_F^2} - 1}{2k/k_F} + \frac{k_F^2 - k^2}{2 k k_F} \ln\left|\frac{k_F + k}{\beta k_F}\right|\right\}$$ in rydbergs, $\beta = \frac{k_c}{k_F}$

We see that the divergence is removed. We find:

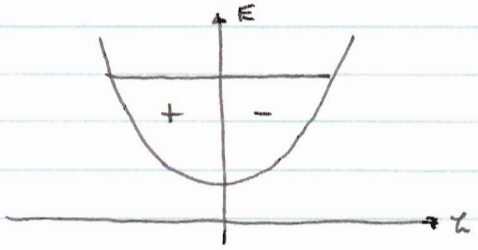
$$\frac{C_{BP}}{C_{free}} = \left[1 + \frac{\rho_s}{12.07}\left\{2 \ln \frac{2}{\beta} + \frac{\beta^2}{2} - 2\right\}\right]^{-1}$$

	Li	Na	K	Rb	Cs
$\frac{C_{BP}}{C_{free}}$	.84	.90	.93	.95	.96
		$\rho_s = 4$			$\rho_s = 5.5$

The higher the density, the closer the approach to the free value.

Magnetic susceptibilities

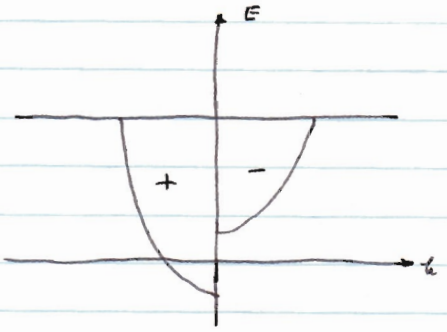
Single electron (Hartree-Fock) does not work well. Collective picture (Bohm-Pines) is true.



Exchange takes place between electrons of each group. Correlation takes place between groups.

In the H-F method; $\chi = \frac{M}{H}$ increased, in fact, increases to ∞.

We do for free electron, non-interacting gas, first:



situation when equilibrium sets in.

$$M = \mu_B \int_0^\infty f(E) \cdot N(E)\, dE - \mu_B \int_0^\infty \cdots$$

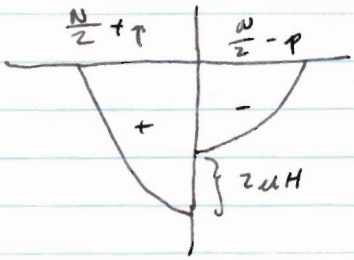
$$= \mu_B \int_0^\infty \left[N(E+\mu_B H) - N(E - H\mu_B) \right] f(E)\, dE$$

$$= 2\mu_B^2 H\, N(E_F^0)$$

$$\chi = 2\mu_B^2 N(E_F^0) = \frac{3}{2} \frac{N\mu_B^2}{k T_F}$$

LECTURE 33 : 12-9-61

Pauli Paramagnetism using exchange and correlation:



References: ~~Simpson and Kitty~~, PR 58, 633 (1940)
D. Pines SSP 5

$$\frac{1}{\chi} = \frac{1}{\chi_p}\left(1 - Q(P_s)\right)$$

$\chi = 2\mu_B^2 N(E_F)$ (last time)

Now:

$$E(p,H) = \sum_{i=1}^{\frac{1}{2}N-p} \left[E(i) + \mu_B H \right] + \sum_{i=1}^{\frac{1}{2}N+p} \left[E(i) - \mu_B H \right]$$

$M = 2p\mu_B N$; $\chi = \frac{\partial M}{\partial N}$

Recall: $E^{exch} = -.458\ e^2/r_s$; $\frac{4}{3}\pi r_s^3 = V/N$

Total $E_p^{exch} = -.458\ x''\ e^2/r_s \left(\frac{N}{2}\right)$; $\frac{N}{2} \to \frac{N}{2} + p$

Total $E_\downarrow^{exch} = -.458\ y^4\ e^2/r_s \left(\frac{N}{2}\right)$; $\frac{1}{r_s} \to \frac{1}{r_s} \frac{(N+2p)^{1/3}}{N^{1/3}}$

$y = \left(\frac{N-2p}{N}\right)^{1/3}$; $x = \left(\frac{N+2p}{N}\right)^{1/3}$; $\frac{1}{r} \to \frac{x}{r_s}$

We add the exchange onto $E(p,H)$.
For correlation energy:

$E_{corr} = -e^2 f(r_s)$

For $p \neq 0$:

$$-e^2 \left[\left(\tfrac{1}{2}N + p\right) f\left(\tfrac{r_s}{y}\right) + \left(\tfrac{1}{2}N - p\right) f\left(\tfrac{r_s}{x}\right) \right]$$

($\uparrow$ $\downarrow$ $\downarrow$ $\uparrow$)

Wigner has a functional form for $f(r_s)$:

$$f(r_s) = \frac{.288}{r_s + 5.1\,a_0}$$

The Bohm-Pines form is:

$$f(r_s) = f_{LR}(r_s) + f_{SR}(r_s)$$

$$f_{LR} = \frac{1}{2a_0}\left[.019 - .0003\ \beta_s \right]$$

$$f_{SR} = \frac{1}{2a_0}\left[.0905 - .0313 \ln \beta_s + .0008\ \beta_s \right]$$

The Wigner and Bohm - Pines forms are very close in the high density limit.

W: $\frac{.0565}{a_0}$; B-P: $\frac{.057}{a_0}$

Carrying out the minimization procedure on ρ.

$$\rho = \frac{\left(\frac{N}{V}\right) \mu_B H}{\alpha} \quad ; \quad \chi = \frac{2 (N/V) \mu_B^2}{\alpha}$$

	Li	Na	K	Rb	Cs
$\frac{4\bar{E}_F}{3}$	.326	.319	.221	.200	.191
α	.201	.240	.180	.176	.171
%	62	33	23	18	12

For experimental work: Schumacher, Lazarus, Schlicter, PR 95. Critical point in experimental work is subtraction of the Landau diamagnetic contributions.

We consider now a Hartree - Fock instead of a Bohm - Pines treatment where we neglect correlation:

$$E = E_K + E_{exch} - 2 \rho \mu_B H \frac{N}{V}$$

$$E_K = \frac{\hbar^2}{20 m \pi^2} (6\pi^2)^{5/3} \left[\left(\frac{N}{2} + \rho\right)^{5/3} + \left(\frac{N}{2} - \rho\right)^{5/3} \right]$$

$$E_{exch} = \frac{e^2}{8\pi^3} \left[(6\pi^2)^{4/3} \right] \left[\left(\frac{N}{2} + \rho\right)^{4/3} + \left(\frac{N}{2} - \rho\right)^{4/3} \right]$$

We say ρ is small, expand in power series, and minimize with respect to the first few terms of ρ.

$$E = \frac{\hbar^2}{10m\pi^2}(6\pi^2)^{5/3}\left(\frac{N}{2}\right)^{5/3}\left[1+\frac{20}{9}\frac{p^2}{N^2}\right]$$

$$-\frac{e^2}{8\pi^3}(6\pi^2)^{4/3}\left(\frac{N}{2}\right)^{4/3}\left[1+\frac{8}{9}\frac{p^2}{N^2}\right]-2\mu_B p_{11} N$$

$$\frac{1}{\chi} = \frac{1}{\chi_{pauli}}\left\{1-\frac{4me^2}{\hbar^2}\left(\frac{\pi}{3N}\right)^{1/3}\right\}$$

$$= \frac{1}{\chi_{pauli}}\left(1-4\pi\left(\frac{4\pi^2}{9}\right)^{1/3}\rho_s\right)$$

$$= \frac{1}{\chi_{pauli}}\left(1-20.6\,\rho_s\right)$$

But this is ridiculous; so correlation must be included. Actually would get ferromagnetic C_s if it were not for correlations.

LECTURE 34 : 12-11-61

References : Luttinger, Proc. Cam. Phil. Soc. 51, 707 (1955).
Slater, Mod. Th. of Solids, p. 470.

Electron - Phonon Interaction:

The basic assumption underlying independance of Phonon - electron field has been the adiabatic approximation (Born & Oppenheimer, Ann. Physik 4te F. (4) 84, 457 (1927)).

Position (lattice) : $(\overline{X}_1, \overline{X}_2, \cdots \overline{X}_N) = \overline{X}$
(electron) : $(\xi_1, \xi_2, \xi_3, \cdots \xi_N) = \xi$
Momentum (lattice) : $(\Pi_1, \Pi_2 \cdots \Pi_N) = \Pi$
(electron) : $(p_1, p_2 \cdots p_N) = p$

The total system Hamiltonian is:

$$\mathcal{H} = \sum_\ell \frac{1}{2M} \Pi_\ell^2 + U_n(\bar{X}) + \sum_\kappa \frac{1}{2m} p_\kappa^2 + \frac{1}{2} \sum_{\kappa \neq \gamma} \frac{e^2}{|\xi_\kappa - \xi_\gamma|}$$

$$+ U_{em}(\bar{X}, \xi)$$

The adiabatic approximation in splitting off an electronic Hamiltonian parameterized by $\bar{X}$:

$$\mathcal{H}_{e\bar{X}} \; \phi_{e\bar{X}}(\xi) = E_{\bar{X}} \; \phi_{e\bar{X}}(\xi)$$

We assume that $\Phi_{e\bar{X}}$ does not change state upon positional changes of the nuclei.

Write the total state function as:

$$\Psi(\bar{X}, \xi) = \psi_n(\bar{X}) \; \phi_{e\bar{X}}(\xi)$$

$$\mathcal{H} \; \Psi(\bar{X}, \xi) = \left\{ -\sum_\ell \frac{\partial^2}{\partial \bar{X}_\ell^2} + U_n(\bar{X}) + E_{\bar{X}} \right\} \Phi_{e\bar{X}}(\xi) \; \psi_n(\bar{X})$$

$$= \phi_{e\bar{X}}(\xi) \left\{ \sum_\ell \frac{\Pi_\ell^2}{2M} + U_n(\bar{X}) + E_{\bar{X}} \right\} \psi_n(\bar{X})$$

$$- \sum_\ell \frac{\hbar^2}{2M} \left\{ 2 \frac{\partial \psi_n(\bar{X})}{\partial \bar{X}_\ell} \frac{\partial \phi_{e\bar{X}}(\xi)}{\partial \bar{X}_\ell} + \psi_n(\bar{X}) \frac{\partial^2 \phi_{e\bar{X}}(\xi)}{\partial \bar{X}_\ell^2} \right\}$$

We must estimate the magnitude of the last term which is interaction. This goes as:

$\sim \frac{m}{M}$ (kinetic energy of electron)

Consider each term:

$$- \sum_\ell \frac{\hbar^2}{2m} \psi_n(\bar{X}) \frac{\partial^2 \phi_{e\bar{X}}(\xi)}{\partial \bar{X}_\ell^2}$$

Assume Bloch functions:

$$\phi_{e\bar{X}}(\xi) = e^{i k \cdot \xi_\ell} \; u_n(\bar{X}, \xi_\ell)$$

We further assume that $u_a(\bar{X}, \xi_e)$ is fairly localized:

$$u_a(\bar{X}, \xi_e) \approx u_a(\xi_e - \bar{X}_e)$$

Multiply by $\phi^*_{\bar{X}}(\xi_e)$ and integrate:

$$-\frac{\hbar^2}{2M}\psi_n(\bar{X}) \int u_a^*(\xi_e - \bar{X}_e) \underbrace{\frac{\partial^2}{\partial \bar{X}_e^2}}_{\frac{\partial^2}{\partial \xi_e^2}} u_a(\xi_e - \bar{X}_e)\, d\xi_e$$

$$= \frac{m}{M}\psi_n(\bar{X}) \int u_a^*(\xi_e - \bar{X}_e) - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial \xi_e^2} u_a(\xi_e - \bar{X}_e)\, d\xi_e$$

so we see that this term is down by $\frac{m}{M}$ over the electron kinetic energy. Also $u_a(\xi_e - \bar{X}_e)$ is sharply peaked, and the integral is almost independent of $\bar{X}_e$ so that this term just gives an additive constant to the phonon energy.

Now consider:

$$-\sum_e \frac{\hbar^2}{M}\frac{\partial \psi_n(\bar{X})}{\partial \bar{X}_e}\frac{\partial \phi_{e\bar{X}}(\xi)}{\partial \bar{X}_e}$$

$$= \left(\sum_e \frac{\bar{\Pi}_e}{M} \cdot i\hbar \nabla_e\right) \psi_n(\bar{X})\, \phi_{e\bar{X}}(\xi) = \mathcal{H}_{ep}$$

Then take the matrix element:

$$\int \phi^*_{e\bar{X}} \nabla_e \phi_{e\bar{X}}\, d\xi = \frac{1}{2}\nabla_e \int \phi^*_{e\bar{X}}(\xi)\, \phi_{e\bar{X}}(\xi)\, d\xi = 0$$

so the diagonal elements are zero but not the off diagonal when different $\bar{X}$'s are used.

Bloch's Treatment:

Interaction potential:

$$\delta V = \sum_{\underline{n}} \underline{u}_{\underline{n}} \cdot \frac{\partial V(\xi)}{\partial \underline{u}_{\underline{n}}}$$

Orbach claims that this is the Hep above.

Recall:

$$\underline{u}_n = \sum_{fs} Q_{fs}(t)\, e^{i f\cdot n}\, v(fs) + Q_{fs}^{+}(t)\, e^{-i f\cdot n}\, v^{*}(fs)$$

LECTURE 35 : 12-13-61

Adiabatic Approximation is good for alkalli metals and tight-binding cases. Calculate the destruction matrix element of δV:

$$(\delta V)^{fs}_{nn'} = \langle n_{fs}-1 \left| \int \psi_n^{*}(\xi)\, \delta V\, \psi_{n'}(\xi)\, d\xi \right| n_{fs} \rangle$$

$$= \sum_{u} \left(\frac{\hbar n_{fs}}{2NM\omega_{fs}} \right)^{1/2} e^{i f\cdot n} \int \psi_n^{*}(\xi) \left[v(fs)\cdot \nabla V \right] \psi_{n'}(\xi)\, d\xi$$

Change to cellular integral:

$$(\delta V)^{fs}_{nn'} = \left(\frac{\hbar n_{fs}}{2NM\omega_{fs}} \right)^{1/2} \sum_{n} e^{i(k'-k+f)\cdot n} \int \psi_n^{*} \left[v(fs)\cdot \nabla V \right] \psi_{n'}\, d\xi$$

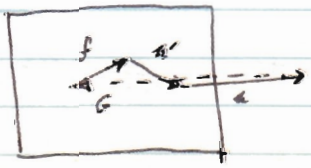
$$V^{fs}(nn') = (n_{fs})^{1/2} \left(\frac{\hbar}{2MN\omega_{fs}} \right)^{1/2} \delta_{G,\, k'-k+f}\; A_{fs}(k,k')$$

$$A_{fs}(k,k') = \int \psi_n^{*} \left(v(f,s)\cdot \nabla V \right] \psi_{n'}\, d\xi$$

$G \neq 0$: Umklapp Process
$G = 0$: Normal Process

Normal:

Umklapp:



Usually get this for high temps only. Most usual process.

1. Rigid Ion Approximation:

$$V(\xi) \rightarrow V(\xi + u_n)$$

static deformed

Hence: $\frac{\partial V}{\partial u_n} = -\nabla V$

This makes $\delta(k,k') \rightarrow -\delta(k,k')$

Compute:

$$\psi_n^*(\xi)\nabla \left\{ \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\xi) \right] \psi_{n'} = E_{n'}\psi_{n'} \right.$$

$$\psi_n^* \left[-\frac{\hbar^2}{2m} \nabla \nabla^2 \psi_{n'} + \nabla V(\xi)\, \psi_{n'} + V(\xi) \nabla \psi_{n'} \right]$$

$$= \psi_n^* E_{n'} \nabla \psi_{n'}$$

Solve for $\psi_n^* (\nabla V) \psi_{n'}$:

$$\psi_n^* (\nabla V) \psi_{n'} = \underbrace{\psi_n^* \left[\frac{\hbar^2 \nabla^2}{2m} + E_{n'} - V \right] \psi_{n'}}_{0,\ \text{since } E_{n'} = E_n}$$

$$+ \psi_n^* \frac{\hbar^2}{2m} \nabla^2 \left(e^{i k' \cdot \xi} \nabla u_{n'} \right)$$

$$\underbrace{- \psi_n^* \left[E_{n'} - V \right] e^{i k' \cdot \xi} \nabla u_{n'}}$$

$$\underbrace{- \psi_n^* \left[E_n - V \right] e^{i k' \cdot \xi} \nabla u_{n'}}_{-\frac{\hbar^2}{2m}\nabla^2 \psi_n^*}$$

$$\int \psi_n^* \nabla V \psi_n \, d\xi = \underbrace{\int \psi_n^* \frac{\hbar^2}{2m} \nabla^2 \left(e^{i k' \cdot \xi} \nabla u_{n'} \right) d\xi}$$

$$+ \int -\frac{\hbar^2}{2m} \left(\nabla^2 \psi_n^* \right) e^{i k' \cdot \xi} \nabla u_{n'} \, d\xi$$

Apply Green's Theorem and use the Wigner-Seitz approximation:

$$\int \phi_{k'}^{*} \nabla V \phi_{k} \, d\xi = \int \phi_{k'}^{*} e^{i k \cdot \xi} \frac{\hbar^2}{2m} \nabla^2 u \, dS$$

LECTURE 36: 12-15-61

In homework problem, use H_{eff} as derived in class as perturbation. See Pines, 1953; Pines IV, or III, or Ziman's book.

Recall: $\phi \leftrightarrow \psi$:

$$\int \phi_{k'}^{*} \nabla V \phi_{k} \, d\xi = \frac{\hbar^2}{2m} \int \left\{ \left(\phi_{k'}^{*} \nabla^2 \left[e^{i k \cdot \xi} \nabla u_{k} \right] \right) + \left(e^{i k \cdot \xi} \nabla u_{k} \right) \nabla^2 \phi^{*} \right\} d\xi$$

$$= \frac{\hbar^2}{2m} \int \left\{ \phi_{k'}^{*} \nabla \left[e^{i k \cdot \xi} \nabla u_{k} \right] + e^{i k \cdot \xi} \nabla u_{k} \nabla \phi_{k'}^{*} \right\} \cdot dS$$

Using WS approximation means we will localize potential to one cell. Now use WS sphere. Recall $\frac{\partial u}{\partial \xi} = 0$ at $\xi = \xi_s$. Then: assume u_k independent of k:

$$= \int \phi_{k'}^{*} e^{i k \cdot \xi} \frac{\hbar^2}{2m} \nabla^2 u_0 \, dS$$

Now use Schroedinger equation: $\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\xi) \right] u_0 = E(0) u_0$, $E(0)$ at bottom of band. Then:

$$= \left\{ V(\xi_s) - E(0) \right\} \int \phi_{k'}^{*} \phi_{k} \, dS$$

$$= \left\{ V(\xi_s) - E(0) \right\} \int \nabla \left(\phi_{k'}^{*} \phi_{k} \right) d\xi$$

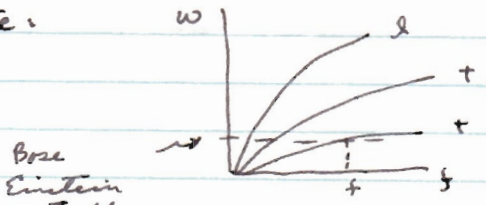
$$= i \left(k' - k \right) \left\{ V(\xi_s) - E(0) \right\} \int \phi_{k'}^{*} \phi_{k} \, d\xi$$

Then:

$$\mathcal{H}_{ss}(k,k') = i\, v(f_s)\cdot(k'-k)\left\{V(\xi_s) - E(0)\right\}\int_{cell} \phi_k^* \phi_{k'}\, d\xi$$

for the Rigid Ion Approximation. We see that in the absence of Umklapp, only longitudinal phonons interact with electrons. For presence of Umklapp, do have transverse interaction. For the absence of Umklapp in a general crystal symmetry have interaction with arbitrary f direction.

Note:



$$k'-k = f + G$$

Can see that transverse modes give large f so that Umklapp can occur and still keep $k'-k$ small. This is what happens in Na at low temperatures.

Assume dilation Δ: $\xi_s \to \xi_s\left(1+\frac{\Delta}{3}\right)$

For $\Delta = 0$: u_0

$\Delta = \Delta$: u_1

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + V - E_0\right\} u_0 = 0 \quad ; \quad \left.\frac{\partial u_0}{\partial \xi}\right|_{\xi_s} = 0$$

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + V - E_1\right\} u_1 = 0 \quad ; \quad \left.\frac{\partial u_1}{\partial \xi}\right|_{\xi_s(1+\frac{1}{3}\Delta)} = 0$$

Reference: Hunter & Nabarro, Proc. Roy. Soc. 220A, 542 (1953)

Multiply by u_1, u_0 respectively and subtract,

$$-\frac{\hbar^2}{2m}\left\{u_0\nabla^2 u_1 - u_1\nabla^2 u_0\right\} = u_0 u_1\, \delta E$$

Integrate over volume of original sphere:

$$\int_{\xi_s\ sphere} -\frac{\hbar^2}{2m}\left\{u_0\nabla^2 u_1 - u_1\nabla^2 u_0\right\} d\xi = \delta E \int u_0 u_1\, d\xi$$

Change to surface integral:

$$\int_S u_1 \nabla u_0 \, ds = 0$$

and on RHS take $u_1 \to u_0$ and get:

$$\delta E = -\frac{\hbar^2}{2m} \int_S u_0 \nabla u_1 \, ds$$

Now expand $u_1(\xi_s)$:

$$u_1(\xi_s) = u_1\left(\xi_s + \tfrac{1}{3}\Delta\xi_s\right) - \frac{1}{3}\Delta\xi_s \frac{\partial u_1}{\partial \xi}\bigg|_{\xi_s + \frac{1}{3}\Delta}$$

$$\nabla u_1(\xi_s) = \underbrace{\nabla u_0\left(\xi_s + \tfrac{1}{3}\Delta\xi_s\right)}_{0 \text{ from BC}} - \frac{1}{3}\xi_s \nabla^2 u_1 \, \Delta$$

Then:

$$\delta E = \frac{\hbar^2}{2m} \frac{\Delta}{3} \xi_s \int u_0(\xi) \nabla^2 u_1 \, ds$$

To first order, replace $\nabla^2 u_1$ by $\nabla^2 u_0$ because of one Δ already in front. Then:

$$\delta E = \frac{\Delta \xi_s}{3} \int u_0(\xi) \frac{\hbar^2}{2m} \nabla^2 u_0(\xi) = \frac{\Delta \xi_s}{3} \left\{ V(\xi_s) - E(0) \right\} \int u_0(\xi_s) u_0(\xi_s) \, ds$$

$$= \Delta \left\{ V(\xi_s) - E_0 \right\}$$

$$E = E_0 + \left\{ V(\xi_s) - E_0 \right\} \Delta + \frac{3}{5} E_F \Big|_{V = V(1+\Delta)}$$

We know: $E_F = \frac{\hbar^2 k_F^2}{2m}$; $k_F^3 = \frac{3\pi^2 N}{V(1+\Delta)}$

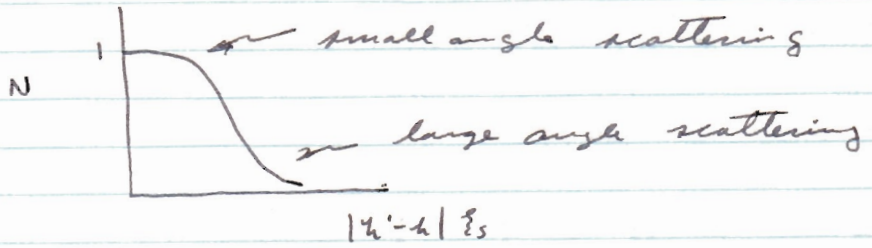
We now minimize with respect to Δ:

$$V(\xi_s) - E_0 = \frac{2}{5} E_F$$

which is of the order of 1eV. Can use this in $\xi_s(k)$

For free electrons, the normalization integral over the WS sphere is:

$$N = \int_0^{\xi_s} e^{-i(k-k')\cdot\xi} d\xi = 3\left\{ \frac{|k'-k|\xi_s \cos|k'-k| - \sin|k'-k|\xi_s}{(|k'-k|\xi_s)^3} \right\}$$



For Block functions, N almost impossible.

LECTURE 37: 12-18-61

Recall: $J_{fs}(kk') \sim v(f,s)(k'-k)\underbrace{(V(\xi_s)-E_0)}_{\frac{2}{3}E_F}\int_{cell}\phi^*_{k'}\phi_k\, d\xi$

$$\delta V = V(\xi - u_n) - V(\xi)$$

This is rigid ion approximation.

Deformable Ion Approximation

$$\delta V = V(\xi - u(\xi)) - V(\xi)$$

This potential depends upon the position of the electron in the cell because of $u(\xi)$ and not u_n hence ion is deformed. Then:

$$u_{fs}(\xi) \sim Q_{fs}(t)\, e^{if\cdot\xi}\, v(fs) + cc.$$

and: $\delta V \sim e^{if\cdot\xi}\, v(fs)\cdot\nabla V(\xi)$

The integral we examine now is then:

$$\mathcal{H}_{fs}(k'k) = -v(fs)\cdot\int \phi_{k'}^{*}\left(e^{\imath f\cdot\xi}\nabla V\right)\phi_{k}\, d\tau$$

Now, using previous methods:

$$e^{\imath f\cdot\xi}\phi_{k'}^{*}\nabla V\phi_{k} = e^{\imath f\cdot\xi}\phi_{k'}^{*}\frac{\hbar^2}{2m}\nabla^2\left(e^{\imath k\cdot\xi}\nabla u_k\right)$$

$$-\frac{\hbar^2}{2m}\nabla^2\left(e^{\imath f\cdot\xi}\phi_{k'}^{*}\right)e^{\imath k\cdot\xi}\nabla u_k$$

$$+\frac{\hbar^2}{2m}\left(-f^2\phi_{k'}^{*}+2\imath f\cdot\nabla\phi_{k'}^{*}\right)e^{\imath f\cdot\xi}\left(\nabla u_k\right)e^{\imath k\cdot\xi}$$

First two terms vanish by Ehrenfest theorem.
Then:

$$\mathcal{H}_{fs}(k'k) = \frac{\hbar^2}{2m}\left(-f^2+2f\cdot k\right)v(fs)\left[\int e^{\imath(k'-k+f)\cdot\xi}\, u_{k'}^{*}\nabla u_k\, d\xi\right]$$

$$-2\imath f\cdot\left[\int e^{\imath(k'-k+f)\cdot\xi}\frac{\hbar^2}{2m}\nabla u_{k'}^{*}\nabla u_k\, d\xi\right]\cdot v(fs)$$

Consider normal processes and WS wave functions, then first term $\to 0$. Make spherical approximation.

$$(v\cdot\nabla)(f\cdot\nabla) \to \frac{1}{3}v\cdot f$$

One finds, after these unjustified approximations,

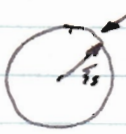
$$\mathcal{H}_{fs}^{def}(k,k') = \frac{2}{3}\imath\left(f\cdot v(fs)\right)\int u_0^{*}\left(V(\xi)-E_0\right)u_0\, d\xi$$

What is difference between two models?
Rigid ion is like empty lattice with one electron added. Deformable ion has potential depending on position of electron.

What we do not is to take empty lattice (rigid ion), then bring in sea of (+) electrons and then add phonon fluctuations.

Reference: J. Bardeen, PR 52, 688 (1937).

We already have rigid ion term. Now get second (electron sea).



$$V = -e\int_{\infty}^{\xi} E\cdot d\xi$$

$$V_{within} = -\int_{\infty}^{\xi_s}\frac{e^2}{\xi^2}d\xi - \int_{\xi_s}^{\xi}\left(\frac{e^2\xi^3}{\xi_s^3}\right)\frac{d\xi}{\xi^2} = \frac{3}{2}\frac{e^2}{\xi_s} - \frac{1}{2}\frac{e^2\xi^2}{\xi_s^3}$$

$$V_{outside} = \frac{e^2}{\xi}$$

Find: $d'_{fs}(kk') = \iota\, v(fs)\cdot(k-k')\,\frac{4\pi e^2(N/v)}{|k'-k|^2}\,3\left\{\frac{|k'-k|\xi_s\cos|k'-k|\xi_s - \sin|k'-k|\xi_s}{(|k'-k|\xi_s)^3}\right\}$

add to $d_{fs}(kk')$ of rigid ion.

LECTURE 38 : 12-20-61

Deformable ion is no good for metals but is good for semiconductors for long wavelength phonons.

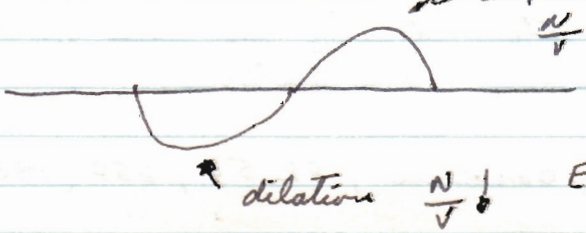
Bardeen Treatment:

Must add (subtract) shielding effects from rigid ion term. Find:

$$d^{ws}_{fs}(kk') = \iota\, v(fs)\cdot(\underline{G}-\underline{f})\cdot\left\{V(f) - E(0) + \frac{4\pi e^2 N/v}{|\underline{G}-\underline{f}|^2}\right\}$$

$$\cdot\,3\left\{\frac{|G-f|\xi_s\cos|G-f|\xi_s - \sin|G-f|\xi_s}{(|G-f|\xi_s)^3}\right\}$$

Suppose a phonon wave running thru crystal:



Now electrons will flow to equalize Fermi levels, and oscillations will occur.

Pines and Bardeen: PR 1955.

Conservation of momentum: $k' - k = G + f$

Interaction Potential: $\delta V = -\sum_n \underline{u}_n \cdot \nabla V$

$$= -\sum_n \sum_{fG} Q_{fs}(t)\, e^{i f \cdot n} \cdot \nabla V + HC$$

Expand $\delta V \phi_k$ in the reciprocal lattice:

$$\delta V \phi_k = \sum_n V_{n+} \phi_{k+f+G_n} + V_{n-} \phi_{k-f+G_n}$$

Hence:

$$V_{n+} = \int \phi^*_{k+f+G_n} \delta V \phi_k \, d\xi$$

$$\phi_k = e^{ik\cdot\xi} u_k(\xi)$$

$$\therefore V_{n+} = \int e^{-i(f+G_n)\cdot\xi} \left(v_{f,s} \cdot \nabla V\right) u_k u^*_{k+f+G_n} \, d\xi$$

Now expand deformed wave function:

$$\phi_k = \phi^0_k + \sum_n \left\{ b(k,n+)\, \phi_{k+f+G_n} + b(k,n-)\, \phi_{k-f+G_n} \right\}$$

what is charge density to first order? Use W's:

$$\rho = \sum_k \phi^*_k \phi_k = \rho_0 + \sum_{k,n} \left[e^{i(f+G_n)\cdot\xi} u_0^2 \left\{ b(k,n+) + b(k,n-)^* \right\} + e^{-i(f+G_n)\cdot\xi} u_0^2 \left\{ b(k,n+)^* + b(k,n-) \right\} \right]$$

We now use Poisson's equation to get a self-consistent potential:

$$\nabla^2 V_f = -4\pi e^2 (\rho - \rho_0)$$

Make free electron approximation, $M_0^2 \sim 1$
Use integral solution to Poisson's equation:

$$V_\rho = e^2 \int_V \frac{(\rho - \rho_0)}{\xi} d\xi$$

We have forms like:

$$\int \frac{e^{i(f+G_n)\cdot\xi}}{\xi} d\xi = \frac{4\pi}{|f+G_n|^2}$$

Finally:

$$V_\rho = \sum_n V_{\rho n} e^{i(f+G_n)\cdot\xi} + cc$$

$$V_{\rho n} = \frac{4\pi e^2}{|f+G_n|^2} \sum_k \left[b(k n+) + b(k n-)^* \right]$$

LECTURE 39 : 1-5-62

We now calculate the coefficients $b(k n+)$, $b(k n-)$ by time dependent perturbative theory

$$b(k n+) = \frac{\delta V_{k, k+f+G_n}}{E_k - E_{k+f+G_n}}$$

V_ρ is a self-consistent potential which both scatters the electrons and is created by the electrons. We have:

$$b(k n+) = \frac{V_{n+} + V_{\rho n}}{E_n - E_{k+f+G_n}}$$

$$b(k n-) = \frac{V_{n-} + V_{\rho n}^*}{E_k - E_{k-f-G_n}}$$

We can now substitute into V_{pn} and find:

$$V_{pn} = \frac{-V_{n+}}{1 + \frac{|f+G_n|^2}{8\pi e^2}\left\{\sum_k \frac{1}{E_k - E_{k+f+G_n}}\right\}^{-1}}$$

We then have for the scattering integral:

$$\Delta^{\text{self-cons.}}_{fs}(kk') = \frac{\Delta^{\text{orig}}_{fs}(kk')}{1 + \left\{\frac{8\pi e^2}{|f+G_n|^2}\sum_k \frac{1}{E_k - E_{n+f+G_n}}\right\}}$$

We modify the original scattering integral by a "dielectric constant."

Summary: Electron-Phonon Processes

1. Interaction is mainly with longitudinal phonons.
2. Energy factor ~ $\underbrace{\frac{2}{5}E_F}_{WS} + \underbrace{\frac{3}{5}E_F}_{KE} = E_F$
3. Matrix element for scattering (Δ) varies with scattering angle.
4. Δ is function only of $|k-k'|$
5. Δ is sometimes approximated by $v(fs)\cdot(k'-k)\cdot F(|k-k'|)$

LECTURE 40 : 1-7-62

Transport Phenomena

Reference : Luttinger and Kohn : PR109 , 1892 (1958).

We will consider Boltzmann equation and derive in semi-classical sense. Almost all experimental solid state physics is bound up with the Boltzmann equation.

Define density function:

$f(\vec{r}, \vec{k}, t)\, d\vec{r}\, d\vec{k}$ = Number of electrons in volume $d\vec{r}\, d\vec{k}$

In equilibrium : $f_0 = \dfrac{1/8\pi^3}{e^{(E_k - E_F)/kT} + 1}$

We write the logical expression:

$$\left(\frac{\partial f}{\partial t}\right) = \left(\frac{\partial f}{\partial t}\right)_{drift} + \left(\frac{\partial f}{\partial t}\right)_{collision}$$

non interacting term in external fields

interactions with phonons and other electrons

$$\left(\frac{\partial f}{\partial t}\right)_{drift} + \operatorname{div}(f \vec{u}) = 0 \qquad \text{(conservation of density)}$$

$$\vec{u} = (\dot{r}_1\ \dot{r}_2\ \dot{r}_3\ \dot{k}_1\ \dot{k}_2\ \dot{k}_3)$$

Now: $\operatorname{div} f\vec{u} = f \operatorname{div} \vec{u} + \vec{u} \cdot \operatorname{grad} f$

Want to show $f \operatorname{div} \vec{u} = 0$.

Write: $\operatorname{div} \vec{u} = \operatorname{div}_r (\dot{r}_1\ \dot{r}_2\ \dot{r}_3) + \operatorname{div}_k (\dot{k}_1\ \dot{k}_2\ \dot{k}_3)$

Recall: $\dot{\xi} = \frac{1}{\hbar}\frac{\partial E}{\partial k}$; $\vec{p} \to \hbar k$; $\therefore \dot{\xi} = \frac{\partial E}{\partial p}$; $\dot{p} = -\frac{\partial E}{\partial \xi}$

Or we can write: $\dot{\xi} = \frac{\partial E}{\partial p} = \nabla_p \mathcal{H}$; $\dot{p} = -\nabla_\xi \mathcal{H}$

Then:

$$\text{div}\,\vec{u} = \nabla_\xi \cdot \left(\frac{1}{\hbar}\frac{\partial \mathcal{H}}{\partial k}\right) + \nabla_k\left(-\frac{1}{\hbar}\frac{\partial \mathcal{H}}{\partial \xi}\right) = 0$$

Then:

$$\left(\frac{\partial f}{\partial t}\right)_{drift} = -\vec{u}\cdot \text{grad}\, f = -\dot{\xi}\,\nabla_\xi f - \dot{k}\cdot\nabla_k f$$

and we finally have the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \dot{\xi}\,\text{grad}_\xi f + \dot{k}\,\text{grad}_k f = \left(\frac{\partial f}{\partial t}\right)_{collision}$$

We take as the form of $\left(\frac{\partial f}{\partial t}\right)_{collision}$ the logical equilibrizing expression:

$$\left(\frac{\partial f}{\partial t}\right)_{collision} = \frac{-(f-f_0)}{\tau}$$

This gives: $(f-f_0)_t = (f-f_0)\,e^{-t/\tau}$

τ is a characteristic lifetime of "free" particle. We will assume τ dependent on $|\vec{k}|$ and not its direction.

We assume no thermal gradients present, $\text{grad}_\xi f = 0$ no time dependence, $\frac{\partial f}{\partial t} = 0$. We apply a constant electric field F:

$$\dot{k} = \frac{eF}{\hbar} \quad ; \quad -\frac{f-f_0}{\tau} = \frac{eF}{\hbar}\cdot\nabla_k f$$

We assume that F is small enough so that $f - f_0$ is small and find:

$$-\frac{(f-f_0)}{\tau} = \frac{eF}{\hbar}\cdot\nabla_k f_0$$

Write: $\nabla_k f_0 = \left(\frac{\partial E}{\partial k}\right) \frac{\partial f_0}{\partial E}$

$\|$

$\hbar v$

and:

$$f - f_0 = -\tau e v \cdot F \left(\frac{\partial f_0}{\partial E}\right)$$

We want to find the current j:

$$j = \int \frac{e v}{8\pi^3} 2 f(k)\, dk$$

$$= \frac{2e}{\hbar 8\pi^3} \int \left(\frac{\partial E}{\partial k}\right) f(k)\, dk$$

$$= \frac{e}{4\pi^3 \hbar} \underbrace{\int |\nabla_k E|\, f_0\, dk}_{0} - \frac{e^2}{4\pi^3 \hbar^2} \int \left[\nabla_k |E|\right]\left[\nabla_k (E) \cdot F\right] \tau \frac{\partial f_0}{\partial E}\, dk$$

$$\therefore j = -\frac{e^2}{4\pi^3 \hbar^2} \int \underbrace{\nabla_k (E)\left(\nabla_k (E) \cdot F\right)}_{\frac{1}{3} |\nabla_k (E)|^2 F \text{ under spherical symmetry.}} \tau \frac{\partial f_0}{\partial E}\, dk$$

Now at low temperatures: $\frac{\partial f_0}{\partial E} dk = -\delta(E - E_F) \frac{dE}{\nabla_k (E)}$

Finally:

$$\sigma = \frac{e^2}{3\pi^2 \hbar} \left|\nabla_k (E)\right|_{E=E_F} \tau(k_F)\, k_F^2$$

Use $E = \frac{\hbar^2 k^2}{2 m^*}$ and get; with $k_F^3 = 3\pi^2 \frac{N}{V}$:

$$\sigma = \frac{e^2 \cdot (N/V)\, \tau(k_F)}{m^*}$$

LECTURE 41 : 1-10-62

Recall : $\sigma = \dfrac{e^2 (N/V)\, \tau(k_F)}{m^*}$

M.B. statistics : τ ≠ fn. of velocity
F.D. statistics : τ at Fermi surface, τ ≠ fn. of $|k|$, not direction.

We will compute τ for electron - phonon interaction.
Recall:

EP interaction = $v(fs) \cdot (k' - k)\, F(|k - k'|)$

with $k + f = k' \pm G$ (destruction of phonon)

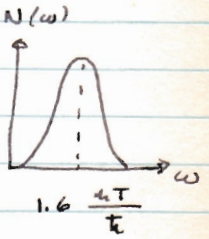
Recall for destruction : $I = n_{sf}^{1/2} \left(\dfrac{\hbar}{2MN\omega_{fs}}\right)^{1/2} \delta_{fs}(k, k')$

For creation :

$k = k' + f \pm G$: $I = (n_{fs} + 1)^{1/2} \left(\dfrac{\hbar}{2MN\omega_{fs}}\right)^{1/2} \delta_{fs}(k, k')$

Want to find $\left(\dfrac{\partial f}{\partial t}\right)_{\text{collisions}}$ from state k.

Assume Debye limit phonons : $f = \dfrac{\omega}{v} = \dfrac{kT}{\hbar v}$



Replace v by the Debye temperature :

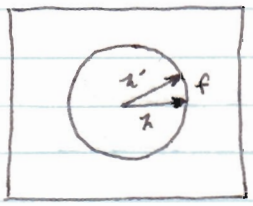
$$\int_0^{k_D} \frac{V}{8\pi^3} (4\pi k^2 dk) = N$$

$$v = \frac{k\,\Theta_D}{\hbar} \left(\frac{V}{6\pi^2 N}\right)^{1/3}$$

What is $\dfrac{f}{k_F}$? ; $k_F = \left(\dfrac{3\pi^2 N}{V}\right)^{1/3}$

$$\frac{f}{k_F} = \frac{T}{\Theta_D} \frac{1}{2^{1/3}}$$

f can be of the magnitude of k_F at $T = \Theta_0$ but can be neglected at low temperatures



Hence at low temperature have low-angle scattering and $\alpha_{fs}(k,k') = 1$. Consider Umklapp later.

Proceeding:

$$\left(\frac{\partial f}{\partial t}\right)_{collision} = 2\int dk' \frac{V}{8\pi^3} W$$

W = transition probability per unit time for an electron to be scattered from k to k'.

$$W^{k\to k'}_{destruction} = \frac{2\pi}{\hbar} \overset{n_{fs}}{\overbrace{I^2}} \delta(E_k + \hbar\omega - E_{k'}) \cdot f_k (1-f_{k'})$$

(f_k: initial filled; $(1-f_{k'})$: final empty)

Must subtract process going in opposite directions:

$$W^{k'\to k}_{\cancel{destruction}\ creation} = \frac{2\pi}{\hbar} \overset{n_{fs}+1}{\overbrace{I^2}} \delta(E_k + \hbar\omega - E_{k'}) f_{k'}(1-f_k)$$

$$\left(\frac{df}{dt}\right)_{collision} = \frac{2V}{8\pi^3}\int dk' \frac{2\pi}{\hbar} \frac{\hbar}{2MN\omega_{fs}} |\alpha_{fs}(k,k')|^2 \delta(E_k + \hbar\omega - E_{k'})$$

$$\cdot n_{fs}\left\{\left[f_k(1-f_{k'})\right] - e^{\hbar\omega_{fs}/kT}\left[f_{k'}(1-f_k)\right]\right\}$$

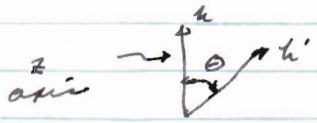
$$d = v(fs)\cdot(k'-k)\, F(|k'-k|)$$

Define: $K = k'-k$, $d = v\cdot K\, F(K) = v\cdot f\, F(K)$

Assume crystal elastically isotropic, hence only consider longitudinal phonons. Then:

$$\omega = K\, F(K)$$

Choose coordinate system along $\vec{k}$:



$$f = k' - k \quad ; \quad f^2 = k'^2 + k^2 - 2k'k\cos\theta$$

At low temperatures $k'^2 \approx k^2$, then:

$$f^2 = 2k^2(1-\cos\theta) = K^2$$

Transform δ function:

$$\text{If } f(x) = 0,\ x = x_0 \quad ; \quad \delta(f(x)) = \frac{\delta(x-x_0)}{|f'(x_0)|}$$

$$\delta(E_n - E_{n'}) = \frac{\delta(k-k')}{\frac{\partial E}{\partial k}\Big|_{k=k'}} = \frac{m^*}{\hbar k}\,\delta(k-k')$$

LECTURE 42 : 1-12-62

$e^{\hbar\omega/kT}$ corrects for conservation of energy. If we use $f = f_0$ in the above equations find that $\frac{\partial f}{\partial t}$ vanishes as it should. For non-vanishing can assign an electron temperature or expand f.

Usually we neglect $e^{\hbar\omega/kT}$ or we have elastic scattering or high temperatures. We then want to evaluate:

$$f_k(1-f_{k'}) - f_{k'}(1-f_k)$$

subject to $k + f = k'$.

$$f_k - f_{k'} = \left(\frac{\partial f}{\partial k}\right)(k - k')$$

Now: $(k^2 + f^2 + 2k\cdot f)^{1/2} = k' \quad ; \quad k \gg f$

$$k\left(1 + \frac{k\cdot f}{k^2}\right) = k'$$

$$k' - k = \frac{k\cdot f}{k^2} = \frac{k\cdot(k'-k)}{k} = k(\cos\theta - 1)$$

Then:

$$f_k - f_{k'} = \left(\frac{\partial f}{\partial k}\right) k(1-\cos\theta)$$

Assume we can write: $f = f_0 - \Phi\frac{\partial f_0}{\partial E}$

Normally Φ is left undetermined and must satisfy a variational principle to give minimal resistance. Then:

$$f_k - f_{k'} = -\left[\Phi(k) - \Phi(k')\right]\frac{\partial f_0}{\partial E}$$

We postulate that $\Phi(k)$ takes the form in the electric field:

$$\Phi(k) = c(E_k) \frac{\vec{F} \cdot \vec{k}}{F}$$

Then:

$$f_k - f_{k'} = -c(E_k)\left[k - k\cos\theta\right]\frac{\partial f_0}{\partial E}$$

$$-c(E_k)\frac{\partial f_0}{\partial E} = \frac{\partial f}{\partial k}$$

We return to problem containing $e^{\hbar\omega/kT}$

using $f = f_0 - \Phi\frac{\partial f_0}{\partial E}$; $\frac{\partial f_0}{\partial E} = -\frac{1}{kT} f_0(1-f_0)$

$$\therefore f = f_0 + \frac{\Phi}{kT} f_0(1-f_0)$$

$$\left[f_k(1-f_{k'}) - f_{k'}(1-f_k)\, e^{\hbar\omega/kT} \right]$$

$$= f_0(k)\cancel{\left[1-f_0(k')\right]} + \Phi(k)\left.\frac{\partial f_0}{\partial E}\right|_k \left[f_0(k') - 1\right]$$

$$+ f_0(k)\,\Phi(k')\left.\frac{\partial f_0}{\partial E}\right|_{k'} \cancel{- f_0(k')\left[1-f_0(k)\right]} e^{\hbar\omega/kT}$$

$$+ \Phi(k')\left.\frac{\partial f_0}{\partial E}\right|_{k'}\left[f_0(k) - 1\right] e^{\hbar\omega/kT} + f_0(k')\,\Phi(k)\left.\frac{\partial f_0}{\partial E}\right|_k e^{\hbar\omega/kT}$$

neglecting terms in Φ^2. We substitute $\frac{\partial f_0}{\partial E}$ and regroup: (also substitute eq. expression for $e^{\hbar\omega/kT}$)

$$= \left[\Phi(k) - \Phi(k')\right]\frac{f_0(k)\left[1-f_0(k')\right]}{kT}$$

$$= -\left[\Phi(k) - \Phi(k')\right]\frac{\partial f_0}{\partial E}$$

$$= -\left[C(E_{k'}) - \frac{C(E_{k'})}{\cos\theta}\right] k \frac{\partial f_0}{\partial E}$$

$$= -k \frac{\partial f_0}{\partial E} C(E_k)(1-\cos\theta)$$

Finally:

$$\frac{\partial f}{\partial t} = -k\left(\frac{\partial f_0}{\partial E}\right) C(E_k) \frac{1}{4\pi^2\rho} \frac{m^*}{\hbar^2} \int \frac{1}{e^{\hbar\omega/kT}-1}$$

$$\cdot \frac{1}{v_f} 2k^2(1-\cos\theta)\left[F(k,\theta)\right]^2 (1-\cos\theta)$$

$$\cdot \frac{1}{k} k^2 \, d\varphi \, d(\cos\theta)$$

using $f = v \cdot K F(K)$

Use: $f^2 = 2k^2(1-\cos\theta)$

$$\frac{\partial f}{\partial t} = \frac{-2\pi C(E_k) m^*}{4\pi^2\rho\hbar^2} \frac{\sqrt{2}}{v} k^3 \frac{\partial f_0}{\partial E}$$

$$\cdot \int \frac{[F(k\theta)]^2 (1-\cos\theta)^{3/2} \, d(\cos\theta)}{e^{\hbar\omega/kT}-1}$$

Use:
$1-\cos\theta \quad \frac{f^2}{2k^2}$
$d(\cos\theta) = -\frac{f\,df}{k^2}$

$$\frac{\partial f}{\partial t} = \frac{+ m^* C(E_k) \frac{\partial f_0}{\partial E}}{4\pi\rho\hbar^2 v^6 k^2} \int_0^{\omega_D} \frac{\omega^4 \, d\omega \left[F(k\omega)\right]^2}{(e^{\hbar\omega/kT}-1)}$$

LECTURE 43: 1-15-62

Because $f_{k'}(1-f_{k'}) \sim f_k(1-f_k)$ only holds for high temperatures, there is really no quantity like a relaxation time at low temperatures.

Recall:

$$\left(\frac{\partial f}{\partial t}\right)_{coll.} = + \frac{m^* C(E_k)}{4\pi \rho \hbar^2 v^6 k^2} \frac{\partial f_0}{\partial E} \int_0^{\omega_D} \frac{\omega^4 \, d\omega \, [F(k,\omega)]^2}{e^{\hbar\omega/kT} - 1} = - \frac{f - f_0}{\tau}$$

$$f = f_0 - \phi \frac{\partial f_0}{\partial E} = f_0 - \lambda C(E_k) \frac{\partial f_0}{\partial E}, \quad k \| F$$

Then: $$\left(\frac{\partial f}{\partial t}\right)_{coll.} = \frac{\lambda C(E_k)}{\tau} \frac{\partial f_0}{\partial E}$$

and:

$$\boxed{\frac{1}{\tau(k_F)} = \frac{m^*}{4\pi \rho \hbar^2 v^6 k_F^3} \int_0^{\omega_D} \frac{\omega^4 \, d\omega \, [F(k,\omega)]^2}{e^{\hbar\omega/kT} - 1}}$$

Change variables: $\frac{\hbar\omega}{kT} = x$, then integral becomes

$$I = \left(\frac{kT}{\hbar}\right)^5 \int_0^{\theta_D/T} \frac{x^4 \, dx \, [F(k,x)]^2}{e^x - 1}$$

We see that for:

$T < \theta_D$; $\frac{1}{\tau} \propto T^5$

$T > \theta_D$; $\frac{1}{\tau} \propto T$

Conductivity: $$\sigma = \frac{e^2 N/V \, \tau(k_F)}{m^*}$$

$T < \theta_D$; $\sigma \propto T^{-5}$

$T > \theta_D$; $\sigma \propto T^{-1}$

If we put in numbers and no scattering:

$$\tau = 10^{-1}\, T^{-5} \text{ sec} \quad \text{for } T < \Theta_D$$

For $T = 10^\circ K$, $\tau = 10^{-6}$ sec (quite long, scattering not due to phonons but impurity centers)

$T = 100^\circ K$; $\tau = 10^{-11}$ sec

Typical τ's from σ: 10^{-13} sec.

Thermal Conductivity

Recall Boltzmann equation:

$$\dot{\xi}\, \text{grad}_\xi f + \frac{eF}{\hbar}\, \text{grad}_k f = -\frac{f - f_0}{\tau}$$

$$\frac{\partial}{\partial \xi} = \frac{\partial T}{\partial x}\frac{\partial}{\partial T} \quad ; \quad \dot{\xi} = \frac{1}{\hbar}\frac{\partial E}{\partial k_x}$$

Then:

$$\frac{1}{\hbar}\frac{\partial E}{\partial k_x}\frac{\partial T}{\partial x}\frac{\partial f}{\partial T} + \frac{eF}{\hbar}\frac{\partial f}{\partial k_x} = -\frac{f - f_0}{\tau}$$

$$f = f_0 - \frac{eF\tau}{\hbar} - \frac{\tau}{\hbar}\frac{\partial T}{\partial x}\frac{\partial f_0}{\partial T}\frac{\partial E}{\partial k_x}$$

making same approximation as in electrical case.

$$j = \frac{2V}{8\pi^3}\, e \int v f\, dk$$

$$Q = \frac{2V}{8\pi^3} \int E(k)\, v f\, dk$$

Change variables:

$$\frac{\partial f_0}{\partial k_x} = \frac{\partial f_0}{\partial E}\left(\frac{\partial E}{\partial k_x}\right)$$

$$\frac{\partial f_0}{\partial T} = -\frac{\partial f_0}{\partial E}\left[\frac{\partial E_F}{\partial T} + \frac{E-E_F}{T}\right]$$

Then:

$$f = f_0 - \frac{\tau(k)}{\hbar}\frac{\partial E}{\partial k_x}\frac{\partial f_0}{\partial E}\left[eF - \left(\frac{\partial E_F}{\partial T} + \frac{E-E_F}{T}\right)\frac{\partial T}{\partial x}\right]$$

$$j = \frac{eV}{4\pi^3\hbar}\int \frac{\partial E}{\partial k_x}\left[-\frac{\tau(k)}{\hbar}\frac{\partial E}{\partial k_x}\frac{\partial f_0}{\partial E}\left[\quad\right]\right]$$

Finally:

$$j = e\left[eF + \left(\frac{E_F}{T} - \frac{\partial E_F}{\partial T}\right)\frac{\partial T}{\partial x}\right]K_0 - \frac{e}{T}\frac{\partial T}{\partial x}K_1$$

$$Q = \left[eF + \left(\frac{E_F}{T} - \frac{\partial E_F}{\partial T}\right)\frac{\partial T}{\partial x}\right]K_1 - \frac{1}{T}\frac{\partial T}{\partial x}K_2$$

where:

$$K_n = -\frac{1}{4\pi^3\hbar^2}\int [E(k)]^n \left(\frac{\partial E}{\partial k_x}\right)^2 \tau(k)\frac{\partial f_0}{\partial E}\,dk$$

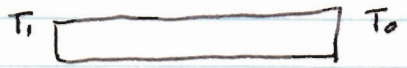
Because of $\frac{\partial f_0}{\partial E}$ we can approximate K_n. If we write:

$$\phi(E) = \frac{\tau(E)}{4\pi^3\hbar^2}\int\int\left(\frac{\partial E}{\partial k_x}\right)^2 \frac{\hbar^2\, d(\cos\theta)\, d\varphi}{|\text{grad}_k E|}$$

$$K_n = -\int \phi(E)\, E^n \frac{\partial f_0}{\partial E}\,dE$$

$$= E_F^n\,\phi(E_F) + \frac{\pi^2}{6}(kT)^2\,\frac{\partial^2\left\{E_F^n\,\phi(E_F)\right\}}{\partial E_F^2}$$

LECTURE 44: 1-16-62



To prevent electrical current flow, put $\chi = 0$ or that an electric must be set up by the heat flow.

$$F = \frac{1}{e}\frac{\partial T}{\partial x}\left[\frac{K_1}{TK_0} - \left(\frac{E_F}{T} - \frac{\partial E_F}{\partial T}\right)\right] = \frac{1}{e}\frac{\partial T}{\partial x}\frac{\partial E_F}{\partial T}$$

F gives rise to the thermoelectric power. Using this F, we find for the heat current:

$$Q = \left[\frac{\partial T}{\partial x}\left(\frac{K_1}{TK_0} + \frac{\partial E_F}{\partial T} - \frac{E_F}{T}\right) + \left(\frac{E_F}{T} - \frac{\partial E_F}{\partial T}\right)\frac{\partial T}{\partial x}\right]K_1 - \frac{1}{T}\frac{\partial T}{\partial x}K_2$$

$$= \frac{\partial T}{\partial x}\frac{1}{T}\left[\frac{K_1^2}{K_0} - K_2\right]$$

$$K_n = E_F^n \phi + \frac{\pi^2}{\phi}(kT^2)\frac{\partial^2(E_F^n \phi)}{\partial E_F^2}$$

$$\frac{1}{K_0} \sim \frac{1}{\phi + \frac{\pi^2}{6}k^2T^2\phi''} \sim \frac{1}{\phi}\left(1 - \frac{\pi^2}{6}k^2T^2\frac{\phi''}{\phi}\right)$$

Then:

$$Q = \frac{\partial T}{\partial x}\frac{1}{T}\left[-\frac{\pi^2}{3}k^2T^2\phi(E_F)\right]$$

Now:

$$\eta = \frac{-Q}{\partial T/\partial x} = \frac{\pi^2}{3}k^2T\,\phi(E_F)$$

for the thermal conductivity. Kittel shows that η is much more due to electrons than phonons.

Define electrical conductivity as situation where thermal gradients vanish. Then:

$$\sigma = \frac{1}{F} = e^2 K_0 = e^2 \phi(E_F)$$

Wiedemann - Franz Law: $\frac{\kappa}{\sigma} = \text{constant} \times T$

or: $$\frac{K}{\sigma} = \frac{\pi^2}{3e^2} k^2 T$$

so to first order we verify the WF law. Note that constant is independent of temperature.

The Lorentz Number is:

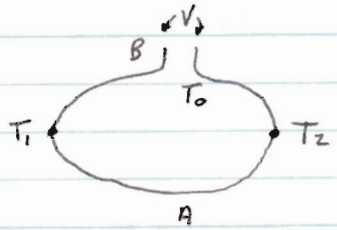
$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \frac{k^2}{e^2} = 2.45 \times 10^{-8} \frac{\text{volts}^2}{\text{deg}^2}$$

which holds to a remarkable degree.

Going back:

$$F = S(T) \frac{\partial T}{\partial x}$$

where $S(T)$ = absolute thermoelectric power. Actually can only measure $S(T)$ with respect to some other material.



$$V = -\int F \cdot dx = -\int S \frac{\partial T}{\partial x} dx$$

$$= \int_{T_0}^{T_1} S_B \, dT + \int_{T_1}^{T_2} S_A \, dT + \int_{T_2}^{T_0} S_B \, dT$$

$$= \int_{T_1}^{T_2} (S_A - S_B) \, dT$$

Define: Absolute Thermoelectric Force

$$= \int_0^T S(T)\, dT$$

Finally one finds:

$$S(T) = \frac{1}{e}\left[\frac{\partial E_F}{\partial T} + \frac{\pi^2}{3} k^2 T \frac{\phi'}{\phi}\right] = \int_{T_1}^{T_2} (S_A - S_B)\, dT$$

Recall:

$$E_F = E_F^\circ + \frac{\pi^2}{6} k^2 T^2$$

so $S(T) \sim T$

Of course, this is known as the Seebeck effect.

Peltier Effect: inverse of Seebeck effect, we have thermal current concurrent with electrical current.

$$Q = eFK_1 \quad ; \quad J = e^2 F K_0 \quad ; \quad Q = \frac{K_1}{eK_0} J$$

$$\Pi = \frac{Q}{J} = \frac{K_1}{eK_0} = T S(T) + \frac{1}{e}\left(\frac{E_F}{T} - \frac{\partial E_F}{\partial T}\right)$$

Π = Peltier coefficient.

Onsager Relations

Write general current equations:

$$J_i = \sum_j L_{ij} X_j$$

L_{ij} ↓ transport coefficient

Suspect this from coupling of electrical and thermal currents. Since don't know form of X_j, get from entropy:

(rate of generation) $\dot{S} = \sum_i X_i J_i$

Onsager's relations are that the L's are symmetric:

$$L_{xy} = L_{yx}$$

Here we would have:

$$J = L_{FF} F + L_{FT} \frac{\partial T}{\partial x}$$

$$Q = L_{TF} F + L_{TT} \frac{\partial T}{\partial x}$$

However, $L_{FT} \neq L_{TF}$ since entropy generation rate is not satisfied

$$\dot{S} = \frac{J \cdot F}{T} \quad \text{so } \frac{F}{T} \text{ is the proper force to use}$$

For $\frac{\partial T}{\partial x}$, use conservation law:

$$\frac{\partial S}{\partial t} + \nabla \cdot \underbrace{\vec{v} S}_{Q/T} = 0$$

$$\therefore \frac{\partial S}{\partial T} = \frac{1}{T^2} \nabla T \, Q$$

Hence we have:

$$J = (T L_{FF}) \frac{F}{T} + (T^2 L_{FT}) \left(\frac{\partial T}{\partial x} \left(-\frac{1}{T^2} \right) \right)$$

$$Q = (T L_{TF}) \frac{F}{T} + (T^2 L_{TT}) \left(\frac{\partial T}{\partial x} \left(\frac{1}{T^2} \right) \right)$$

Then the Onsager relation is:

$$T L_{FT} = L_{TF}$$

The thermoelectric power is: $S(T) = \dfrac{-L_{FT}}{L_{FF}}$

The Peltier coefficient is: $\Pi = \dfrac{L_{TF}}{L_{FF}}$

Then: $\boxed{S(T) = \dfrac{\Pi}{T}}$

Homework Problems for AP295: Due: Monday, October 2, 1961

1) Find the group velocity for the diatomic string for both modes.

Assume:

1) $M = 2m$

2) $M = 10m$

and plot v_g against k. Approximate v_g for small k.

2) Discuss the behaviour of a diatomic periodic linear chain for frequencies in the forbidden gap.

3) Read: Chapter 6, Kittel.

Homework Problems for AP 295: Problem Set 2

Due: Monday, October 9, 1961

1) Chapter IV of Kittel, Introduction to Solid State Physics

Problems: 4.3; 4.4; 4.5; 4.6; 4.7

2) Chapter VI of Kittel, ibid.

Problems: 6.1; 6.2; 6.5; 6.6

3) Prove, using the general treatment presented in class, that for small $|\underline{f}|$, there always exists three modes for which $\omega(\underline{f},s)$ is linear in $|\underline{f}|$. Thus, define the group velocity for small $|\underline{f}|$ in terms of the A's for these modes.

Homework Problems for AP 295 Due: Monday, October 16, 1961

Problem Set 3

1) Chapter I of Kittel, Introduction to Solid State Physics.

Problems: 1.1(a), (b); 1.2(b); 1.4+; 1.5; 1.7; 1.10; 1.12

2) Chapter XI of Kittel, ibid.

Problems 11.5; 11.6

+This is not an easy problem. Do a careful job.

RO

Homework Problems for AP 295

Problem Set 4 Due: Monday, October 23, 1961

1. Chapter X of Kittel, Introduction to Solid State Physics

   Problems: 10.1; 10.2; 10.4; 10.5; 10.7 (all); 10.9

2. Chapter XI of Kittel, ibid

   Problems: 11.2; 11.3; 11.7(a), (b); 11.8 (all)

3. Chapter XII of Kittel, ibid

   Problems 12.2; 12.3

Homework Problems for AP 295

The previous assignment (Problem Set 4) is to be changed in the following way:

1. Chapter X of Kittel, Introduction to Solid State Physics
   Problems: 10.1; 10.2; 10.4; 10.5; 10.7 (all); 10.9

   We shall refer to the above as Problem Set 4.
   It remains due on Monday, October 23, 1961.

Problem Set 5, due on Monday, October 30, 1961, shall consist of:

1. Chapter XI of Kittel, ibid.
   Problems: 11.2; 11.3; 11.7 (all); 11.8 (all).

2. Chapter XII of Kittel, ibid.
   Problem: 12.2

The special Problem Set 1 will now be due Monday, November 6, 1961.

Homework Problems for AP 295

Problem Set 7

Due: Monday, November 20, 1961

1. Chapter XIII of Kittel, "Introduction to Solid State Physics"

   Problems 13.1; 13.2; 13.3; 13.4; 13.5

Homework Problems for AP 295

Special Problem Set I — Due: Monday, October 30, 1961

1. Work out the relationship between the $A_{\underline{n}\,\underline{n}'}^{\alpha\,\beta}$ and the elastic constants (as defined by Kittel) C_{ij}. Apply the theory to a simple cubic lattice, working up to and inclusive of interactions between second nearest neighbors. For help, see Pierls in the suggested reading for phonons. Be sure to include non central forces.

2. Prove that

$$\sum_{\underline{f}\,s} M\omega(\underline{f}\,s)^2 = N\sum_{\alpha} A^{\alpha\alpha}(0) \equiv N\,\mathrm{Tr}\,A(0)$$

and hence that

$$C_v = 3Nk = \frac{k N \hbar^2}{12\,M(kT)^2}\,[\mathrm{Tr}\,A(0)]$$

at high temperatures. Make use of the orthogonality relations for the v's, and of the summation tricks we developed in class. Interpret the result in physical terms. What does $A^{\alpha\alpha}(0)$ mean?

3. Derive the free energy F of the phonon system as we did in class. Show that the classical limit is

$$F = U_o + kT\sum_{\underline{f}\,s} \log(\hbar\omega(\underline{f}\,s)/kT)$$

4. Read the letter by J. G. Daunt and J. L. Olsen in the Physical Review Letters, Volume 6, No. 6, page 267, March 15, 1961. Prove equations (1) and (2), and derive (4). What do you think of their arguments regarding modulation of the zero point energy? Relate your remarks to the derivation of the entropy S given in class which showed that the zero point contribution cancelled when one computed S. Finally, read the letter by Richard Ferrell in Phys. Rev. Lett. 6, 541 (1961) for your edification, and as a check on your reasoning.

Homework Problems for AP 295

Special Problem Set II — Due: Monday, Nov 27, 61

1) Show with a full discussion that the space group of the diamond structure is $F4_1/d\,\bar{3}\,2/m$. Find the space group of the cubic Z n S (zinc blende) structure.

2) Prove that a wave packet formed from Block functions has an initial acceleration in an electric field given by the free electron mass. E. N. Adams

3) Draw the energy surfaces along the (100), (110), and (111) directions in an empty face centered cubic lattice. Characterize the wave functions at symmetry points and assign degeneracies.

4) Show that waves which have been orthogonalized with respect to core functions (OPW) are not in general mutually orthogonal. Express the lack of orthogonality in terms of the μ_{nm}'s.

Special Problem Set III

Applied Physics 295

Due: January 3, 1962

1. Prove Koopman's Theorem: the energy parameter in the Hartree - Fock equation, E_j, is the negative of the energy required to remove the electron in the state ϕ_j from the solid when the space part of the ϕ are Bloch type functions.

2. Use the modified $\underline{k} \cdot \underline{p}$ approximation (i.e. $\underline{p} = \underline{p} - \frac{e}{c}\underline{A}$) to generate the effective mass equation in the presence of an external magnetic field. Choose the gauge $A_x = -Hy$, $A_y = A_z = 0$. See Luttinger & Kohn, P.R. 97, 869 (1955). Be explicit concerning the order to which you are carrying your calculation.

3. Prove the "f" sum rule:

$$\frac{1}{m} \sum_{n' \neq n} \frac{p^{\alpha}_{n\,n'}\, p^{\beta}_{n'\,n}}{E_n - E_{n'}} = \delta_{\alpha\beta} - \frac{m}{\hbar^2} \frac{\partial^2 E_n}{\partial k^{\alpha} \partial k^{\beta}}$$

where the superscripts α and β refer to the components of $\underline{k}$.

4. Compute the correction to the energy levels of H_e and H_p (the modified electron and plasma terms in the Bohm - Pines Hamiltonian) of H_{ep}, the electron - plasma interaction. Give the conditions under which it can be neglected.

Term Paper Assignment

Due: January 19, 1962

Read Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936). Rederive their important results, being sure to explain the consequences. Give a discussion of the effects of time reversal symmetry upon the degeneracy of energy bands in crystals.

References:

1. Quantum Chemistry, by Eyring, Walter and Kimball
2. Group Theory in Quantum Mechanics, by V. Heine
3. Group Theory, by E. P. Wigner
4. Quantum Mechanics, non-relativistic, Landau and Lifshitz
5. R. J. Elliott, Phys. Rev. 96, 280 (1954)