APPLIED
PHYSICS
296

MAGNETISM
IN
SOLIDS

Outline of Applied Physics 296

H. Zeiger, Spring 1962

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I. 6, 7. A.Abragam - Nuclear Magnetism

II. Condon and Shortley
II. (and especially II. 4.) - Van Vleck
II. 5, 6. A. Abragam

III. Griffith - Theory of Transition Metal Ions
III (and especially III. 8) - Van Vleck
III 9, 10. - Abragam

IV. Wilson - Theory of Metals
IV. 8, 9. - Abragam

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APPLIED PHYSICS 296

SOLID STATE PHYSICS : MAGNETISM

INSTRUCTOR : ZEIGER — ROOM C 314 : MWF 11

LECTURE 1 : 2-7-62

I. The One-Electron Hamiltonian

Recall some of the results of electrodynamics:

$$\vec{F} = -e\vec{\mathcal{E}} - \frac{e}{c}\vec{v}\times\vec{B} = m\frac{d\vec{v}}{dt} \qquad \text{(Lorentz Force)}$$

$$\left.\begin{aligned} &\nabla\times\vec{\mathcal{E}} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \;;\; \nabla\times\vec{B} = \frac{4\pi}{c}\vec{J} + \frac{1}{c}\frac{\partial\vec{\mathcal{E}}}{\partial t} \\ &\nabla\cdot\vec{\mathcal{E}} = 4\pi\rho \;;\; \nabla\cdot\vec{B} = 0 \end{aligned}\right\} \text{(Maxwell's Equations)}$$

$$\left.\begin{aligned} &\vec{B} = \nabla\times\vec{A} \;;\; \nabla\times\left(\vec{\mathcal{E}} - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}\right) = 0 \\ &\vec{\mathcal{E}} - \frac{1}{c}\frac{\partial\vec{A}}{\partial t} = -\nabla V \end{aligned}\right\} \text{(Potential Relations)}$$

The potential relations are subject to gauge conditions:

$$\vec{A}' = \vec{A} + \nabla\lambda \;;\; V' = V - \frac{1}{c}\frac{\partial\lambda}{\partial t}$$

which yield identical Maxwell equations independent of λ. All of the above formalism can be derived from a Lagrangian or Hamiltonian formulation.

$$\frac{d}{dt}\frac{\partial\mathcal{L}(q_i,\dot{q}_i)}{\partial\dot{q}_i} - \frac{\partial\mathcal{L}(q_i,\dot{q}_i)}{\partial q_i} = 0$$

where $\mathcal{L} = \frac{mv^2}{2} + eV - \frac{e}{c}(\vec{v}\cdot\vec{A})$

Substitution in the Euler - Lagrange equation gives:

$$\frac{d}{dt}\left(m v_x - \frac{e}{c} A_x\right) - e\frac{\partial V}{\partial x} + \frac{e}{c}\left(\vec{v}\cdot\frac{\partial \vec{A}}{\partial x}\right) = 0$$

$$m\frac{dv_x}{dt} - \frac{e}{c}\left(\frac{\partial A_x}{\partial t} + (\vec{v}\cdot\nabla)A_x\right) - e\frac{\partial V}{\partial x} + \frac{e}{c}\left(\vec{v}\cdot\frac{\partial \vec{A}}{\partial x}\right) = 0$$

Note: $\left[(\vec{v}\cdot\nabla)\vec{A}\right]_x = \left[\nabla(\vec{v}\cdot\vec{A})\right]_x - \left[\vec{v}\times\underbrace{\nabla\times\vec{A}}_{\vec{B}}\right]_x$

Then:

$$m\frac{dv_x}{dt} - \frac{e}{c}\frac{\partial A_x}{\partial t} - \frac{e}{c}\left[\nabla(\vec{v}\cdot\vec{A})\right]_x + \frac{e}{c}(\vec{v}\times\vec{B})_x$$

$$- e\frac{\partial V}{\partial x} + \frac{e}{c}\left(\vec{v}\cdot\frac{\partial \vec{A}}{\partial x}\right) = 0$$

We then obtain the Lorentz Force: $m\frac{dv_x}{dt} = -eE_x - \frac{e}{c}(\vec{v}\times\vec{B})_x$

Note that we always take e to be positive.

To obtain the Hamiltonian, use:

$$\mathcal{H} = \sum_i p_i\dot{q}_i - \mathcal{L} = \mathcal{H}(p_i, q_i)$$

The Lagrange equations of motion give:

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \quad \text{leading to} \quad \vec{p} = m\vec{v} - \frac{e}{c}\vec{A}$$

Then:

$$\mathcal{H} = \left(m\vec{v} - \frac{e}{c}\vec{A}\right)\cdot\vec{v} - \frac{mv^2}{2} - eV + \frac{e}{c}(\vec{v}\times\vec{A})$$

In terms of $\vec{p}$:

$$\mathcal{H} = \frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2 - eV$$

To make the transition to Quantum Mechanics, we make the de Broglie substitution:

$$\vec{p} \rightarrow -i\hbar\nabla$$

The Pauli Electron

The addition of spin to the magnetic field problem leads to interaction terms of the type (for slowly varying magnetic fields):

$$-\vec{\mu}_s \cdot \vec{B}$$

with spin angular momentum $\vec{A} = \hbar \vec{S}$ with one electron eigenvalues of $\pm 1/2$. We also have the gyromagnetic equation: $\vec{\mu}_s = -\gamma_s \vec{A}$ where for a single orbiting electron $\gamma_s = \frac{e}{2mc}$. However, this is more correctly given by the expression:

$\vec{\mu}_s = -\gamma_s \vec{A} = -g_s \frac{e}{2mc} \vec{A}$ where from Thomas precession, $g_s = 2$ for a single electron. Or:

$$\vec{\mu}_s = -g_s \left(\frac{e\hbar}{2mc}\right)\vec{S} = -g_s \mu_0 \vec{S} = -2\mu_0 \vec{S}$$

where $\mu_0 \equiv \frac{e\hbar}{2mc}$

For classical spin-orbit (SO) coupling, we have:

$$\mathcal{H}_{SO} = -\vec{\mu}_s \cdot \vec{B}_{effective} = -\vec{\mu}_s \cdot \left(-\nabla V \times \frac{\vec{v}}{c}\right)$$

$$= \vec{\mu}_s \cdot \nabla V \times \frac{1}{mc}\left(\vec{p} + \frac{e}{c}\vec{A}\right)$$

$$\Rightarrow \vec{\mu}_s \cdot \nabla V \times \underbrace{\frac{1}{2mc}}_{\uparrow \text{Thomas}} \left(\vec{p} + \frac{e}{c}\vec{A}\right) + \frac{1}{4m^2c^2} e\hbar \nabla V \cdot \left(\vec{p} + \frac{e}{c}\vec{A}\right)$$

The first term is the spin orbit term and the second is the Darwin term which arises in the reduction of the Dirac equation. Finally, the complete Hamiltonian is:

$$\mathcal{H} = \frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2 - eV - \vec{\mu}_s \cdot \vec{B} + \mathcal{H}_{SO}$$

Case of the Uniform External Magnetic Field:

We will now use $\vec{B}$ and $\vec{H}$ interchangeably.

Choose for a gauge: $\vec{A} = \frac{1}{2}\vec{H}\times\vec{r}$. Then:

$$\vec{H} = \nabla\times\vec{A} = \frac{1}{2}\left[(\nabla\cdot\vec{r})\vec{H} - (\vec{H}\cdot\nabla)\vec{r}\right] = \vec{H}$$

Now, considering only the interaction terms which give the Zeeman and diamagnetic effects:

$$\mathcal{H}_{ZD} = \frac{e}{2mc}\underbrace{\{\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\}}_{\frac{e}{mc}\vec{A}\cdot\vec{p} \text{ because of choice of gauge}} - \vec{\mu}_s\cdot\vec{H} + \frac{e^2}{2mc^2}A^2$$

$$= \frac{e}{mc}\left(\frac{1}{2}\vec{H}\times\vec{r}\cdot\vec{p}\right) + \frac{e^2}{2mc^2}\left(\frac{1}{2}\vec{H}\times\vec{r}\right)^2 - \vec{\mu}_s\cdot\vec{H}$$

Now the definition of angular momentum is:

$$\vec{\mathcal{L}} = \vec{r}\times\vec{p} = \hbar\vec{L}$$

so that:

$$\left(\frac{e\hbar}{2mc}\right)\vec{H}\cdot\vec{L} = \mu_0\vec{L}\cdot\vec{H} = -\vec{\mu}_L\cdot\vec{H}$$

Then the Zeeman and diamagnetic terms become:

$$\mathcal{H}_Z = -(\vec{\mu}_L + \vec{\mu}_s)\cdot\vec{H} = \mu_0(\vec{L} + 2\vec{S})\cdot\vec{H}$$

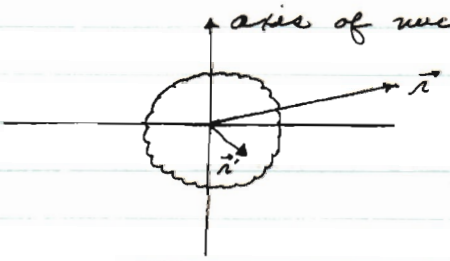
$$\mathcal{H}_D = \frac{e^2}{8mc^2}(x^2+y^2)H^2$$

In the latter we take the field in the z direction.

LECTURE 2 : 2-9-62

Nuclear Interaction Terms

We consider a classical localized model of the nucleus where we have some definite sphere-like shape:



$\vec{r}'$ is a "source point". The nuclear potentials are then:

$$V_N = \int \frac{\rho(\vec{r}')\, d\tau'}{|\vec{r} - \vec{r}'|} \quad ; \quad \vec{A}_N(\vec{r}) = \int \frac{\rho(\vec{r}')\, \vec{v}(\vec{r}')\, d\tau'}{|\vec{r} - \vec{r}'|}$$

Now we can expand the static scalar potential $V_N(\vec{r})$ into the usual coulomb, dipole and quadrapole terms:

$$V_N(\vec{r}) = \frac{1}{r} \int \rho(\vec{r}')\, d\tau' + \frac{\vec{r}}{r^3} \cdot \int \rho(\vec{r}')\, \vec{r}'\, d\tau'$$

$$+ \frac{1}{2} \sum_{k,l} \left[\frac{3 x^k x^l - r^2 \delta_{kl}}{r^5} \right] \int \rho(\vec{r}')\, x'_k\, x'_l\, d\tau'$$

The coulomb term leads to the usual phenomena. There is no known dipole interaction, but there is quadrapolar. For the far vector field, it follows from ordinary electrodynamic calculations:

$$\vec{A}_N(\vec{r}) = \vec{\mu}_N \times \frac{\vec{r}}{r^3}$$

where $\vec{\mu}_N = \frac{1}{2c} \int \rho(\vec{r}') \{ \vec{r}' \times \vec{v}'(\vec{r}') \}\, d\tau'$

This leads to the definition of the nuclear magnetic moment:

$$\frac{|\vec{\mu}_N|}{\mathcal{L}_N} = \frac{e}{2Mc}$$

Now classically we would expect:

$$\vec{\mu}_N = \frac{e\hbar}{2Mc}\vec{I} = \mu_{ON}\vec{I}$$

However, due to relativistic effects, we really have:

$$\vec{\mu}_N = g_I \mu_{ON} \vec{I}$$

g_I runs from less than one to about 4 or 5 and we will consider it an experimentally determined parameter.

The presence of a nuclear spin in a magnetic field should lead to a Zeeman effect given by:

$$\boxed{\mathcal{H}_{NZ} = -\vec{\mu}_N \cdot \vec{H}}$$

We should also have an electron-spin, nuclear-spin interaction of the form (far from the nucleus):

$$\mathcal{H} = -\vec{\mu}_S \cdot \nabla \times \vec{A}_N$$

This is true even though $\vec{A}_N$ may vary rapidly because the variation of $\vec{A}_N$ over the width of the orbit is still small. We call this interaction the Hyperfine interaction and since $\vec{A}_N = \vec{\mu}_N \times \vec{r}/r^3$:

$$(\mathcal{H}_{HFS})_{spin} = -\vec{\mu}_S \cdot \left[-\frac{\vec{\mu}_N}{r^3} + \frac{3(\vec{r}\cdot\vec{\mu}_N)\vec{r}}{r^5} \right]$$

Now to this we must add the orbital-nuclear interaction to complete the hyperfine structure term:

$$(\mathcal{H}_{HFS})_{orbital} = \frac{e}{mc}\left(\vec{p}\cdot\vec{A}_N + \vec{A}_N\cdot\vec{p}\right) = \frac{e}{mc}\vec{A}_N\cdot\vec{p}$$

$$= \frac{e}{mc}\left(\vec{\mu}_N \times \frac{\vec{r}}{r^3}\cdot\vec{p}\right) = 2\left(\frac{e}{2mc}\right)\vec{\mu}_N\cdot\frac{\vec{r}\times\vec{p}}{r^3}$$

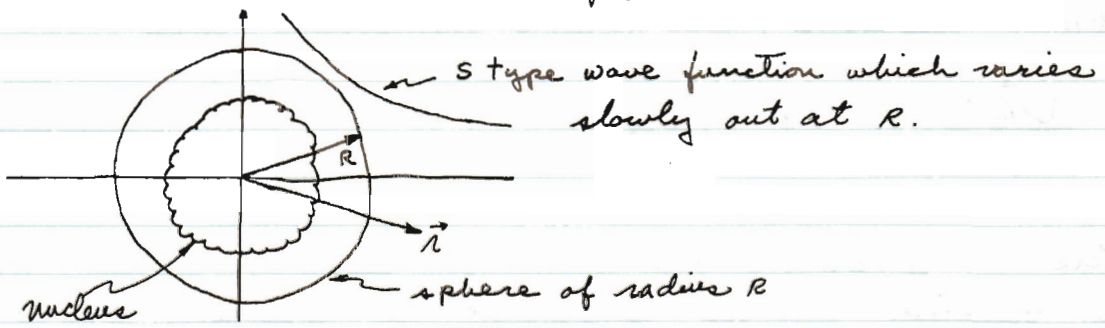
$$= -\frac{2\vec{\mu}_N\cdot\vec{\mu}_L}{r^3}$$

Then the complete hyperfine interaction term becomes:

$$\mathcal{H}_{HFS} = \frac{\vec{\mu}_S \cdot \vec{\mu}_N}{r^3} - \frac{3(\vec{r}\cdot\vec{\mu}_N)(\vec{\mu}_S\cdot\vec{r})}{r^5} - \frac{2\vec{\mu}_N\cdot\vec{\mu}_L}{r^3}$$

$$= \frac{\vec{\mu}_N}{r^3}\cdot(\vec{\mu}_S - 2\vec{\mu}_L) - \frac{3}{r^5}(\vec{r}\cdot\vec{\mu}_N)(\vec{r}\cdot\vec{\mu}_S)$$

What about near the nucleus? Here we cannot use the vector potential. However, the electron is only near the nucleus when it is in an s state. Although $L=0$, we still have spin. How can we write the interaction? Consider the so-called contact energy:



The contact energy is: $E_c = -\vec{\mu}_S \cdot \int \nabla \times \vec{A}_N(\vec{r})\,|\psi(\vec{r})|^2\,d\tau$

Since we say that ψ varies slowly in the region of interest, we take it outside the integral:

$$E_c = -|\psi(0)|^2\,\vec{\mu}_S \cdot \int_{VOL} \nabla\times\vec{A}_N\,d\tau$$

We can now change to a surface integral which allows us to take the surface where we please enabling the use of the far-field form of $\vec{A}_N$. This gives:

$$\int_{VOL}\nabla\times\vec{A}_N\,d\tau = \int_S d\vec{S}\times\vec{A}_N = \int_\Omega R^2\,d\Omega\;\hat{r}\times\vec{A}_N$$

$$= \int_\Omega d\Omega\;\hat{r}\times(\vec{\mu}_N\times\hat{r}) = \int_\Omega d\Omega\,(\vec{\mu}_N - \hat{r}\cdot\vec{\mu}_N\,\hat{r})$$

Then: $\int_{VOL} \nabla \times \vec{A}_N \, d\tau = \frac{8\pi}{3} \mu_N$

and:

$$\mathcal{E}_c = -\frac{8\pi}{3} |\psi(0)|^2 \vec{\mu}_s \cdot \vec{\mu}_N$$

To write in operator form, we construct:

$$\boxed{\mathcal{H}_c = -\frac{8\pi}{3} \vec{\mu}_N \cdot \vec{\mu}_s \, \delta(\vec{r})}$$

This $\mathcal{H}_c$ should be added to $\mathcal{H}_{HFS}$ and we assume in further work that it is included.

This form of $\mathcal{H}_c$ neglects the internal structure of the nucleus. This structure can be examined by measuring the $\vec{\mu}_N$ for different isotopes. For two different isotopes, we obtain something like:

$$\frac{|\vec{\mu}_{N1}|}{|\vec{\mu}_{N2}|} = \frac{\mathcal{E}_{c1}}{\mathcal{E}_{c2}} (1 + \Delta)$$

where Δ expresses the anomaly. Usually "current" models of the nucleus can be suggested to explain Δ.

Finally, in our hierarchy of one-electron interactions, we write the electrostatic quadrapole interaction:

$$\boxed{\mathcal{H}_Q = \frac{1}{2} \sum_{kl} \left[\frac{3 x_k x_l - r^2 \delta_{kl}}{r^5} \right] \int \rho(\vec{r}') \, x'_k \, x'_l \, d\tau'}$$

LECTURE 3: 2-12-62

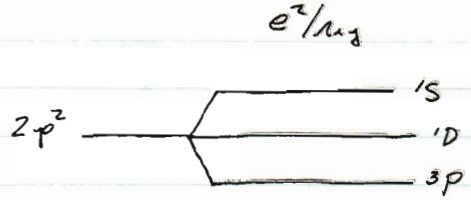
II. The Many Electron System

Neglecting magnetic effects for the moment, the many electron Hamiltonian is:

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i \frac{Ze^2}{r_i}$$

We will consider a hierarchy of interaction terms, starting with the coulomb interaction.

Consider the ground state of carbon $1s^2 2s^2 2p^2$ and ignore the filled shells $1s^2 2s^2$. The state p has the initially degenerate forms $m_\ell = 1, 0, -1$, but now the coulomb interaction destroys this degeneracy and we develop a term scheme as follows:



Actually, the justification for this scheme is the fact that L^2, L_z commute with the Hamiltonian, and also S^2 and M_S are constants of the motion. The Pauli principle suppresses some combinations of l, s, m_ℓ and m_s thus limiting the number of terms. We denote the many electron quantum numbers by capital letters, and those for single electrons by small letters.

Now, the ordering of the terms is governed by Hund's Rule:

> Hund's Rule: The term with highest multiplicity has the lowest energy.

Thus, in carbon ^3P is lowest because $2S+1=3$. Hund's Rule comes about because parallel spins tend to avoid each other on the Pauli principle and hence lower the energy.

Effects of Spin-Orbit Coupling

SO coupling is small or weak in light atoms but large in heavy atoms. We take:

$$\mathcal{H}_{SO} = \sum_i \frac{1}{2mc} \vec{\mu}_{Si} \cdot (\nabla V)_i \times \vec{p}_i$$

We neglect the Darwin term as this just shifts the whole configuration and gives no splitting effects. For a central field where we have $V(\vec{r}) = V(r)$:

$$(\nabla V)_i = -\frac{1}{r_i} \frac{\partial V(r_i)}{\partial r_i} \hat{r}_i$$

and hence:

$$\mathcal{H}_{SO} = \frac{2}{e} \mu_0^2 \sum_i \left(-\frac{1}{r_i} \frac{\partial V}{\partial r_i} \right) \vec{S}_i \cdot \vec{L}_i$$

The main contribution to $-\frac{1}{r_i} \frac{\partial V}{\partial r_i}$ comes from near the nucleus where the term is positive.

The Wigner-Eckhart Theorem

We will use this theorem, but will not prove it. See Rose, Angular Momentum, for proof.

We define a vector of type $\vec{T}$ with respect to the angular momentum vector $\vec{J}$ that obeys the commutation relations:

$$[J_x, T_y] = i T_z \text{, etc.}$$

$$[J_x, T_x] = 0 \text{, etc.}$$

Examples are $\vec{J} \to \vec{L}$ and $\vec{T} \to \vec{r}$:

$$[L_x, y] = \frac{1}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}, y \right] = i z$$

Also $\vec{p}$ is an example of type $\vec{T}$, and so are $\vec{r}_i$, $\vec{p}_i$, $\vec{L}_i$, $\vec{S}_i$.

Now, we can represent vectors in terms of symmetrized products of spherical harmonics. That is:

$\vec{r}\cdot\vec{r}$: $Y_2^2 \sim (x+iy)^2$ will form part of the result.

$\vec{r}\cdot\vec{p}$: $T_2^2 = \frac{1}{2}\left[(x+iy)(p_x+ip_y) + (p_x+ip_y)(x+iy)\right]$ will form part of the result.

Hence it appears that vector scalar products have representations in spherical harmonics (sometimes spherical tensor components).

Now the Wigner-Eckart (WE) theorem says that for any spherical tensor component:

$$\langle J'M_J' \mid T_L^M \mid J M_J \rangle = (J' \| T_L \| J) \quad C(J L J' \mid M_J M M_J')$$

where: $(J'\|T_L\|J)$ is a factor to be determined

$C(JLJ'|M_J M M_J')$ is a Clebsch-Gordan (CG) coefficient and contains all the M dependence.

Definition of CG Coefficients:

Suppose we have the product angular momentum state: $\psi(JM_J)\,\psi(LM_L)$. We can combine $\vec{J}$ and $\vec{L}$ to get the resultant angular momentum state if we multiply by the CG coefficients and sum over M_J, M_L:

$$\sum_{M_J M_L} \psi(JM_J)\,\psi(LM_L)\; C(JLJ' \mid M_J M_L M_J') = \psi(JLJ'M_J')$$

At all times we must have $M_J' = M_J + M_L$ because the CG coefficients vanish unless this is so and also we must have:

$$J' = J+L, \cdots, |J-L|$$

We will use the WE theorem mostly when $J=J'$ but $M_J \neq M_J'$ in which case:

$$\langle JM_J' \mid T_L^M \mid J M_J \rangle = (J \| T_L \| J) \quad C(JLJ \mid M_J M M_J')$$

Applying this to a spherical tensor component: J_L^M

$$\langle J M_J' | J_L^M | J M_J \rangle = (J \| J_L \| J)\, C(J L J | M_J M M_J')$$

Taking the ratio gives:

$$\boxed{\langle J M_J' | T_L^M | J M_J \rangle = K(JL) \langle J M_J' | J_L^M | J M_J \rangle}$$

Using the above relation, we can relate matrix elements of operators to matrix elements of J_L^M within a constant.

Consider, for example, the scalar quantity with $M=L=0$ and with $J=J'$. The CG coefficient is:

$$C(J\,0\,J | M_J\,0\,M_J') = 1 \quad \text{with } M_J = M_J'$$

Then we must have:

$$\langle J M_J | T_0 | J M_J \rangle = (J \| T_0 \| J)$$

For a vector quantity, $L=1$ which corresponds to:
$Y_1' \sim (x+iy)$; $Y_1^0 \sim z$; $Y_1^{-1} \sim (x-iy)$

$$\langle J M_J' | \vec{T} | J M_J \rangle = K(J) \langle J M_J' | \vec{J} | J M_J \rangle$$

In the developments to follow, we will frequently write for the operator T the "effective" operator, diagonal in J, the quantity constant times J. We have already done this to a degree in considering nuclear spin:

$$\langle I M_I' | \vec{A}_N | I M_I \rangle = \langle I M_I' | \vec{\mu}_N | I M_I \rangle \times \frac{\vec{r}}{r^3}$$

$$= g_I \mu_N \langle I M_I' | \vec{I} | I M_I \rangle \times \frac{\vec{r}}{r^3}$$

where we consider $\langle I M_I' | \vec{I} | I M_I \rangle$ as supplying the definition of the effective operator $\vec{I}$. The same can be done for the nuclear Zeeman effect:

$$\langle I M_I' | -\vec{\mu}_N \cdot \vec{H} | I M_I \rangle = g_I \mu_N \langle I M_I' | \vec{I} | I M_I \rangle \cdot \vec{H}$$

For quadrapole interactions, we can use the WE theorem with $L = 2$.

We now apply the WE theorem to SO coupling and the case of Russell-Saunders (RS) and J-J coupling. We will assume that there is now no coupling between term levels so that interactions will be taken to be diagonal in L and S. In that case:

$$\langle LS\, M_S' M_L' | \mathcal{H}_{SO} | LS\, M_S M_L \rangle$$

$$= \langle LS\, M_S' M_L' | \sum_i \frac{2}{e} \mu_0^2 \left(-\frac{1}{r_i}\frac{\partial V}{\partial r_i}\right) \vec{L}_i \cdot \vec{S}_i | LS\, M_S M_L \rangle$$

We use the WE theorem in two parts so that $\vec{L}_i$ goes over into the effective operator $\vec{L}$ and $\vec{S}_i$ into $\vec{S}$, that is, we separate the spin and orbital problems:

$$\langle LS M_S' M_L' | \mathcal{H}_{SO} | LS M_S M_L \rangle$$

$$= \sum_i K_i(L)\, K_i(S) \left[\frac{2}{e}\mu_0^2\right] \langle LM_L' | \vec{L} | LM_L \rangle \cdot \langle SM_S' | \vec{S} | SM_S \rangle$$

$$= \lambda \langle L | \vec{L} | L \rangle \cdot \langle S | \vec{S} | S \rangle$$

Hence we can write: $\mathcal{H}_{SO\,eff} = \lambda \vec{L} \cdot \vec{S}$

providing we only work with one term at a time. λ can be calculated or, better yet, measured.

Now, what about splitting due to the SO coupling? Consider a state:

$$\psi(LS\,JM_J) \quad \text{(This is a degenerate term level)}$$

with $\vec{J} = \vec{L} + \vec{S}$ (RS coupling)

so that: $J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$

Then $\vec{L}\cdot\vec{S} = \dfrac{J^2 - L^2 - S^2}{2}$

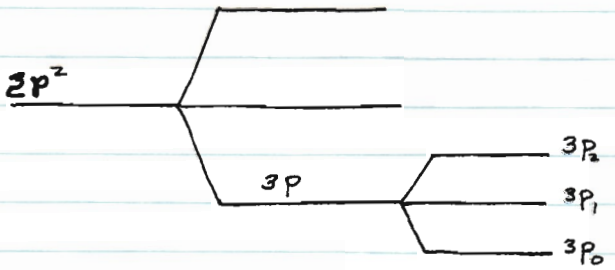
Hence:

$$\langle LS\,JM_J \mid \lambda \vec{L}\cdot\vec{S} \mid LS\,JM_J\rangle = \frac{\lambda}{2}\langle LS\,JM_J \mid (J^2 - L^2 - S^2) \mid LS\,JM_J\rangle$$

$$= \frac{\lambda}{2}\left(J\{J+1\} - L\{L+1\} - S\{S+1\}\right)$$

Since $J = L+S, \ldots, |L-S|$, the ^3P Hundá Rule ground state of carbon must split into three subterms.

The interaction splitting is then:



The SO splitting goes as λ.

In order to find the Hundá rule ground state after the SO splitting, we need to know the sign of λ. It can be shown that:

shell less than ½ full : $\lambda > 0$
shell more than ½ full : $\lambda < 0$

That is, in general:

$$\lambda = \pm \frac{\langle nl \mid \frac{Z}{e}\mu_0^2\left(-\frac{1}{r}\frac{\partial V}{\partial r}\right) \mid nl\rangle}{2S}$$

LECTURE 4: 2-14-62

We consider some one-electron operator summed over all electrons:

$$\sum_i f(\vec{p}_i, \vec{r}_i)$$

Take the matrix element of this operator with respect to a determinential wave function. We sketch the structure of a typical determinential wave function:

$D =$

$m_\ell \rightarrow$						
	×	×	×	×			$+1/2$
	×	×	×	×	×		$-1/2$

; The blank spaces represent unoccupied orbitals.

We define:

$\bar{D} =$

$m_\ell \rightarrow$						
					×	×	$+1/2$
						×	$-1/2$

What we want to show is:

$$\langle D | \sum_i f(\vec{r}_i, \vec{p}_i) | D \rangle = \sum_{\substack{\text{occupied} \\ \text{orbitals}}} \langle m_{\ell i}\, m_{si} | f(\vec{r}_i, \vec{p}_i) | m_{\ell i}\, m_{si} \rangle$$

$$= \sum_{\text{shell}} \langle m_{\ell i}\, m_{si} | f(\vec{r}_i, \vec{p}_i) | m_{\ell i}\, m_{si} \rangle - \sum_{\substack{\text{unoccupied} \\ \text{orbitals}}} \langle m_{\ell i}\, m_{si} | f(\vec{r}_i, \vec{p}_i) | m_{\ell i}\, m_{si} \rangle$$

For f not a spherical tensor component, $\sum_{\text{shell}}$ will not vanish. We must have the form f_L^M, not f_0, then $\sum_{\text{shell}} \to 0$. Hence:

$$\langle D | f_L^M | D \rangle = - \sum_{\substack{\text{unoccupied} \\ \text{orbitals}}} \langle m_{\ell i}\, m_{si} | f_L^M | m_{\ell i}\, m_{si} \rangle = - \langle \bar{D} | f_L^M | \bar{D} \rangle$$

We have shown that the matrix element of f_L^M with respect to the 3 hole determinant is equal to the negative of that for the 3 electron problem. Thus holes behave as electrons with the sign reversed. By choosing the phases of the wave orbital functions, we can get a one to one correspondence between electrons and holes.

Thus we have shown: $(g_L^M{}_{eff})_{electron} = -(g_L^M{}_{eff})_{hole}$

Check this with the SO coupling:

n electrons		n holes
$\lambda \vec{L}\cdot\vec{S}$	$\rightarrow$	$(-\lambda)\vec{L}\cdot\vec{S}$

This implies:

$\vec{L}$	$\rightarrow$	$-\vec{L}$
$\vec{S}$	$\rightarrow$	$-\vec{S}$
$\vec{e}$	$\rightarrow$	$-e$

Check:

$$(e e^2)(\vec{L})\cdot(\vec{S}) \rightarrow (-e e^2)(-\vec{L})\cdot(-\vec{S})$$

Hence λ changes sign but keeps its magnitude.

Now consider the effect of this on the Zeeman interaction:

electron		hole		
$\mu_0(\vec{L}+2\vec{S})\cdot\vec{H}$	$\rightarrow$	$-\mu_0(-\vec{L}-2\vec{S})\cdot\vec{H}$	$=$	$\mu_0(\vec{L}+2\vec{S})\cdot\vec{H}$

This is evident from the physics involved.

The spin orbit interaction does not change the fact that J^2 and J_z are constants of the motion. This means that H_{SO} can only couple states of the same J_z or J^2; that is, $^3P_0 \leftrightarrow {}^1S_0$ can couple. Ordinarily the coulomb configuration splitting is large enough that such interterm coupling is not important, but it may be in the heavy atoms.

Zeeman Effect:

We have:

$$H_z = -\sum_n (\vec{\mu}_{Sn} + \vec{\mu}_{Ln})\cdot\vec{H} = \mu_0 \sum_n (\vec{L}_n + 2\vec{S}_n)\cdot\vec{H}$$

$$= \mu_0(\vec{L}+2\vec{S})\cdot\vec{H}$$

If we consider this as a perturbation and use the WE theorem, we can deal with the following matrix elements:

$$\langle J M_J' \mid \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} \mid J M_J \rangle$$

$$= \mu_0 K(JL) \langle J M_J' \mid \vec{J} \mid J M_J \rangle \cdot \vec{H} + 2\mu_0 K(SJ) \langle J M_J' \mid \vec{J} \mid J M_J \rangle \cdot \vec{H}$$

Thus we have the equivalent operator: constant times $\vec{J} \cdot \vec{H}$

If we operate on both sides of the equation above with $\vec{J}$, we immediately obtain:

$$K(LJ) = \frac{\langle J L S M_J \mid \vec{J} \cdot \vec{L} \mid J L S M_J \rangle}{J(J+1)}$$

$$K(SJ) = \frac{\langle J L S M_J \mid \vec{J} \cdot \vec{S} \mid J L S M_J \rangle}{J(J+1)}$$

We have used the following form of the WE theorem:

$$\langle J M_J' \mid \vec{T} \mid J M_J \rangle = \frac{\langle J M_J \mid \vec{T} \cdot \vec{J} \mid J M_J \rangle}{J(J+1)} \langle J M_J' \mid \vec{J} \mid J M_J \rangle$$

Now, since $\vec{J} = \vec{L} + \vec{S}$; $(\vec{J} - \vec{L})^2 = S^2$, $J^2 + L^2 - 2\vec{J} \cdot \vec{L} = S^2$

Then: $\vec{J} \cdot \vec{L} = \frac{1}{2}(J^2 + L^2 - S^2)$

and similarly: $\vec{J} \cdot \vec{S} = \frac{1}{2}(J^2 + S^2 - L^2)$

Then: $\langle J M_J' \mid \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} \mid J M_J \rangle = g(LSJ) \mu_0 \langle J M_J' \mid \vec{J} \mid J M_J \rangle \cdot \vec{H}$

$g(LSJ)$ is the <u>Landé g factor</u> and can be seen to be:

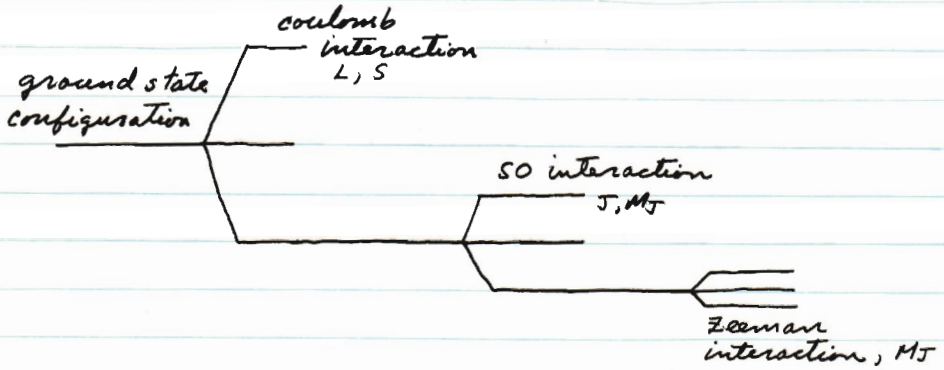
$$g(LSJ) = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + \frac{2\{J(J+1) + S(S+1) - L(L+1)\}}{2J(J+1)}$$

The effective Zeeman Hamiltonian is then:

$\mathcal{H}_Z = g(LSJ) \mu_0 \vec{J} \cdot \vec{H}$ with eigenvalues $E_Z = g(LSJ) \mu_0 M_J H$

LECTURE 5 : 2-16-62

We have now arrived at the following point in the hierarchy of interactions in the many electron atom:



Magnetic Susceptibilities in a Gas of Free Atoms

The crux of these calculations is the free energy: For a non-interacting gas of atoms obeying Boltzmann statistics:

$$F = -NkT \ln \sum_i e^{-E_i/kT}$$

For electrons in solids obeying Fermi statistics:

$$F = N\zeta - kT \sum_i \ln \left\{ 1 + e^{-(E_i - \zeta)/kT} \right\}$$

We will work with the Boltzmann case for now and assume all the usual statistical mechanics relations to hold, viz:

$$M = -\frac{\partial F}{\partial H} \; ; \quad \chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 F}{\partial H^2}$$

Then:

$$M = -\frac{\partial F}{\partial H} = N \frac{\sum_i \left(-\frac{\partial E_i}{\partial H}\right) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

We first work the diamagnetic problem where ε_i is a single value, just the energy of the closed shell.

$$F = -NkT\left(-\frac{\varepsilon_i}{kT}\right) = N\varepsilon_{\substack{\text{closed}\\\text{shell}}} = N\varepsilon_{dia}$$

where from previous developments:

$$\varepsilon_{dia} = \langle D | \sum_i \frac{e^2}{8m^2c^2}(x_i^2 + y_i^2) H^2 | D \rangle$$

$$= \sum_{m_{li} m_{si}} \langle m_{li} m_{si} | \frac{e^2}{8m^2c^2}(x_i^2 + y_i^2) H^2 | m_{li} m_{si} \rangle$$

Now, over a closed shell $\langle D | f_i^M | D \rangle = 0$ unless $L=0$, $M=0$. We see:

$$(x^2+y^2) = \underbrace{\frac{2}{3} r^2}_{Y_0^0} - \underbrace{\frac{1}{3}(3z^2 - r^2)}_{Y_2^0}$$

or spherical invariant

, and hence $\langle D | Y_2^0 | D \rangle \to 0$?

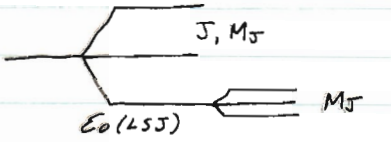
Then: $\varepsilon_{dia} = \frac{e^2}{12m^2c^2} \sum_{m_{li} m_{si}} \langle m_{li} m_{si} | r^2 | m_{li} m_{si} \rangle H^2$

$$= \frac{e^2}{12m^2c^2} 2(2l+1) \langle nl | r^2 | nl \rangle H^2$$

Finally, the diamagnetic susceptibility due to all closed shells is:

$$\chi_{dia} = -\frac{\partial^2 F}{\partial H^2} = -\sum_{\substack{ln\\\text{all closed}\\\text{shells}}} \frac{Ne^2}{3m^2c^2} \langle nl | r^2 | nl \rangle (2l+1)$$

We now consider the paramagnetic problem. Recall $\mathcal{H}_z = g\mu_0 \vec{J}\cdot\vec{H}$ which is a perturbation so that $\vec{J}$ is still a good quantum number and we have no coupling with higher J terms:



However, now we will include inter-J coupling in the second order Zeeman effect:

$$E = E_0(LSJ) + E_1(LSJM_J) + E_2(LSJM_J)$$

where: $E_0(LSJ)$ = unperturbed J term energy.

$$E_1(LSJM_J) = g\mu_0 M_J H$$

$$E_2(LSJM_J) = \sum_{J'M_J'} \frac{|\langle LSM_J J|\mathcal{H}_Z|LSJ'M_J'\rangle|^2}{E_0(LSJ) - E_0(LSJ')}$$

$$E_0(LSJ) = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

Now: $\mathcal{H}_Z = g\mu_0 \vec{J}\cdot\vec{H} \sim T_1^0$ and using the WE theorem:

$$\langle J'M_J'|T_L^M|JM_J\rangle = (J\|T_L\|J')\; C(JLJ'|M_J M M_J')$$

and recalling the condition on the CG coefficients that the M's must add to give M_J and the only possible values of J are $L+J', \ldots, |L-J'|$, we see that the only possible matrix elements of T_1^0 are of the form:

$$\langle JM_J|T_1^0|J\pm1\; M_J\rangle$$

Hence E_2 becomes:

$$E_2(LSJM_J) = \frac{|\langle LSJM_J|\mathcal{H}_Z|LSM_J, J+1\rangle|^2}{E_0(LSJ) - E_0(LS,J+1)} + \frac{|\langle LSJM_J|\mathcal{H}_Z|LSM_J, J-1\rangle|^2}{E_0(LSJ) - E_0(LS,J-1)}$$

We will use the following relation from Condon and Shortley:

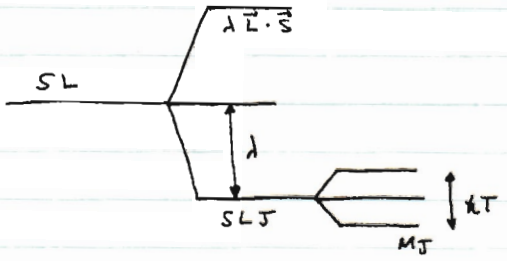
$$\langle LSJM_J|L_Z|LSM_J, J+1\rangle = \left[\frac{(J+1+S-L)(J+1+L-S)(L+S+J+2)\{(J+1)^2 - M_J^2\}}{4(J+1)^2(2J+1)(2J+3)}\right]^{1/2}\sqrt{L+S-J}$$

We get the negative of this expression for J-1, but this is trivial since we want $|\langle\rangle|^2$.

We now consider the calculation of the paramagnetic free energy:

$$F = -NkT \ln \sum_{M_J} e^{-(\varepsilon_0 + \varepsilon_1 + \varepsilon_2)/kT}$$

We first consider the case:



$kT \ll \lambda$ or less than the J-J spacing

$kT \gg H_z$ or greater than the Zeeman splitting

Note: If we are dealing with a normal multiplet, we need only the $J+1$ term in ε_2 since the Hund's Rule ground state is $J = |L-S|$; but, if the multiplet is inverted, use the $J-1$ term of ε_2 since $J = L+S$ is the Hund's Rule ground state.

For $kT \gg H_z$, we may expand the exponential in F, and need only keep to second order in H:

$$F = -NkT \ln \sum_{M_J} \left\{ 1 - (\varepsilon_1 + \varepsilon_2)/kT + \tfrac{1}{2}(\varepsilon_1 + \varepsilon_2)^2/(kT)^2 \right\}$$

$$= -NkT \ln \sum_{M_J} \left\{ 1 - (\varepsilon_1 + \varepsilon_2)/kT + \tfrac{1}{2}\varepsilon_1^2/(kT)^2 \right\}$$

Note that we have dropped the constant ε_0 term. Now $\sum_{M_J} = 2J+1$ so multiply and divide by $2J+1$ inside the ln and then drop $\ln(2J+1)$ term. We get:

$$F = -NkT \ln \left\{ 1 + \sum_{M_J} \left[\frac{-(\varepsilon_1 + \varepsilon_2)/kT}{2J+1} + \frac{\tfrac{1}{2}\varepsilon_1^2/(kT)^2}{2J+1} \right] \right\}$$

Expanding the ln:

$$F = -NkT \sum_{M_J} \left[\frac{-(\varepsilon_1 + \varepsilon_2)/kT}{2J+1} + \frac{\tfrac{1}{2}\varepsilon_1^2/(kT)^2}{2J+1} \right]$$

LECTURE 6 : 2-19-62

In what follows, we shall need the following expressions:

$$\mathcal{H}_z = \mu_0 H (L_z + 2S_z)$$

$$\langle LS\,J\,M_J \left| \begin{matrix} L_z \\ S_z \end{matrix} \right| LS\,M_J, J+1 \rangle = \pm f(J, M_J)$$

$$= \pm \left[\frac{(J+1+S-L)(L+S+J+2)(L-S+J+1)\{(J+1)^2 - M_J^2\}}{4(J+1)^2(2J+1)(2J+3)} \right]^{1/2} \left[L+S-J \right]^{1/2}$$

with opposite signs for $J-1$.

$$\sum_{M_J=-J}^{J} M_J = 0 \quad ; \quad \sum_{M_J=-J}^{J} M_J^2 = \frac{J(J+1)(2J+1)}{3}$$

$$F_{para} = -NkT \sum_{MJ} \left\{ \frac{-(\varepsilon_1+\varepsilon_2)/kT}{2J+1} + \frac{\frac{1}{2}\varepsilon_1^2/(kT)^2}{2J+1} \right\}$$

Since $\varepsilon_1 = g\,\mu_0 M_J H$; $\sum_{MJ} \varepsilon_1 = 0$ and

$$\sum_{MJ} \varepsilon_1^2 = g^2 \mu_0^2 H^2 \frac{J(J+1)(2J+1)}{3}$$

Now evaluate $\sum_{MJ} \varepsilon_2$ for a shell less than 1/2 full, $J = |L-S|$, and also assume $L > S$: Then:

$$\sum_{MJ} \varepsilon_2 = \frac{\mu_0^2 H^2}{\varepsilon_0(LSJ) - \varepsilon_0(LS,J+1)} \left[\frac{(2J+1)(L+S+J+2)(L+S-J)}{4(J+1)^2(2J+1)(2J+3)} \right]$$

$$\cdot \left[(J+1)^2(2J+1) - \frac{J(J+1)(2J+1)}{3} \right]$$

$$= \frac{\mu_0^2 H^2}{\varepsilon_0(LSJ) - \varepsilon_0(LS,J+1)} \left[\frac{(L+S+J+2)(L+S-J)(2J+1)}{4(J+1)(2J+3)} \left(\frac{2J+3}{3} \right) \right]$$

$$= \frac{\mu_0^2 H^2}{\varepsilon_0(LSJ) - \varepsilon_0(LS,J+1)} \left[\frac{(L+S+J+2)(L+S-J)(2J+1)}{12(J+1)} \right] = -a(LSJ)\,\mu_0^2 H^2$$

In summary, we then have:

$$a(LSJ) = \frac{(2J+1)(L+S+J+2)(L+S-J)}{12(J+1)\left[E_0(LSJ+1) - E_0(LSJ)\right]} \quad ; \text{ shell} < 1/2 \text{ full} \; ; \; L>S, \; L<S$$

$$a(LSJ) = \frac{(2J+1)(J+S-L)(J+L-S)}{12J\left[E_0(LSJ-1) - E_0(LSJ)\right]} \quad ; \text{ shell} > 1/2 \text{ full} \; ; \; L>S, \; L<S$$

Finally we obtain, for $kT \gg \mathcal{H}_z$; $kT \ll \lambda$:

$$F_{para} = -NkT\left[\frac{1}{kT}\,\frac{\mu_0^2 H^2 a(LSJ)}{2J+1} + \frac{g^2\mu_0^2 H^2 J(J+1)}{6(kT)^2}\right]$$

and:

$$\chi_{para} = \underbrace{\frac{N\mu_0^2 g^2 J(J+1)}{3kT}}_{\text{Curie's Law}} + \underbrace{\frac{2N\mu_0^2 a(LSJ)}{2J+1}}_{\text{Van Vleck temperature independent paramagnetism}}$$

Now consider the case where $\lambda \gg kT$, but $\mathcal{H}_z \sim kT$ and neglect the second order energy E_2. This is the case of low temperature. However the solution will be exact to E_1 as long as E_2 is neglected. This is usually so because J-J coupling will generally be very weak. We have:

$$F_{para} = -NkT \ln \sum_{M_J=-J}^{J} e^{-g\mu_0 H M_J/kT}$$

$$= -NkT \ln \left\{ \frac{e^{-g\mu_0 JH/kT}\left(1 - e^{g\mu_0 H(2J+1)/kT}\right)}{1 - e^{g\mu_0 H/kT}} \right\}$$

$$= -NkT \ln \left\{ \frac{e^{-g\mu_0 H(2J+1)/kT} + e^{g\mu_0 H(2J+1)/kT}}{e^{-g\mu_0 H/kT} - e^{g\mu_0 H/kT}} \right\}$$

Now, $M_{para} = -\frac{\partial F}{\partial H}$ and let $x = \frac{gJ\mu_0 H}{kT}$.

Then:

$$M_{para} = N g \mu_0 J \left\{ \coth\left(\frac{2J+1}{2J} x\right) \cdot \left(\frac{2J+1}{2J}\right) - \frac{1}{2J} \coth\frac{x}{2J} \right\}$$

$$= N g \mu_0 J B_J(x)$$

Now, it can be shown that $\lim_{T \to 0} B_J(x) = 1$, so at $T = 0$ we have perfect ordering or $M_{para} = N g \mu_0 J$. In the high temperature limit, we obtain the Curie result.

In the limit of large J, we obtain Langevin's result if we define:

$$\mu = \lim_{\substack{\mu_0 \to 0 \\ J \to \infty}} g \mu_0 J$$

Then:

$$M_{para} = N\mu \left(\coth x - \frac{1}{x} \right) = N\mu L(x)$$

This concludes the discussion of the magnetic susceptibilities of free atoms.

LECTURE 7 : 2-21-62

Nuclear Magnetism : Hyperfine Interactions

We recall the one-electron $\mathcal{H}_{HFS}$ and now generalize to the many electron case:

$$\mathcal{H}_{HFS} = \sum_i \left\{ \frac{\vec{\mu}_N}{r_i^3} \cdot (\vec{\mu}_{Si} - 2\vec{\mu}_{Li}) - \frac{3}{r_i^5} (\vec{\mu}_{Si} \cdot \vec{r}_i)(\vec{\mu}_N \cdot \vec{r}_i) \right\}$$

We take as electronic quantum numbers J and M_J and for nuclear quantum numbers I and M_I. We could combine J and I into a total quantum number F. We will only be interested in matrix elements diagonal in J and I so we can derive effective operators with the use of the WE theorem. (We could include the contact interaction in $\mathcal{H}_{HFS}$ above) Using the WE theorem:

$$\langle I\, J\, M_I' M_J' \,|\, \mathcal{H}_{HFS} \,|\, I\, J\, M_I M_J \rangle = K(J) \langle M_J' \,|\, \vec{J} \,|\, M_J \rangle \cdot K(I) \langle M_I' \,|\, \vec{I} \,|\, M_I \rangle$$

Then: $$\mathcal{H}_{HFS\,eff} = A\, \vec{I} \cdot \vec{J}$$

We can include Zeeman terms and obtain generally:

$$\mathcal{H}_{eff} = A\, \vec{I} \cdot \vec{J} + g(LSJ)\, \mu_0\, \vec{J} \cdot \vec{H} + g_I\, \mu_{0N}\, \vec{I} \cdot \vec{H}$$

A can be evaluated for some cases. Consider Mn^{++}:
$3s^2\, 3p^6\, 3d^5 \rightarrow {}^6S_{5/2}$ as Hund's Rule ground state. Now, the d shell is half filled and from simple physical arguments, the net hyperfine structure should vanish or $A = 0$ as can be seen from simple physical arguments.

To see this, return to a discussion of the many electron wave function, considering only unfilled shells. The one-electron functions are:

$$u_{nl m_l} = R_{nl}(r)\, Y_l^{m_l}(\theta, \phi)$$

R_{nl} and the energy can be determined by Hartree-Fock methods. Begin the many electron problem by writing the product of all the one-electron orbital and spin wave functions:

$$\Pi = u_1(1)\chi_1(1)\,u_2(2)\chi_2(2)\cdots u_N(N)\chi_N(N)$$

Now, completely antisymmetrize this product by taking the determinant:

$$D = \begin{vmatrix} u_1(1)\chi_1(1) & \chi_1(2)u_1(2) & \cdots \\ u_2(1)\chi_2(1) & u_2(2)\chi_2(2) & \cdots \\ \vdots & \vdots & \end{vmatrix}$$

Now, we want determinants as eigenfunctions of a state labeled by LSM_LM_S. This is true for M_SM_L states, but not for LS states in which case we must take a linear combination of determinants.

$$\Psi(LSM_LM_S) = \sum_i a_i D_i(M_LM_S)$$

Evaluate the following matrix element over a closed shell: $\Psi_c = D_c$

$$F = \langle \Psi_c | \sum_i f_i^{M}(r_i, p_i)\, f_i^{M'}(s_i) | \Psi_c \rangle$$

$$D_c = u_1(1)\cdots u_N(N)\chi_N(N) - u_1(2)\chi_1(2)\,u_2(1)\chi_2(1)\cdots$$

Assume all the wave functions are orthogonal:

$$\int u_i^*(\vec{r})\,u_2(\vec{s})\,d\tau = 0$$

$$F = \sum_{\text{occupied}} \langle m_{s_i} m_{s_i} | \xi_i^{M}(\vec{r})\,\xi_i^{M'}(\vec{s}) | m_{s_i} m_{s_i} \rangle$$

Apply the WE theorem:

$$F = \sum_i (l \| f_i \| l)\; C(lLl \mid m_{l_i} M m_{s_i})$$

$$\cdot \left[\langle \alpha | f_i^{M'}(\vec{s}) | \alpha \rangle + \langle \beta | f_i^{M'}(\vec{s}) | \beta \rangle \right]$$

Now, the rule on the CG coefficients says that $L=0$ and $M=0$ so that:

$$F = \delta_{L0}\,\delta_{M0}\,(l\|f_L\|l)\left[\langle\alpha|f_i^{M'}|\alpha\rangle + \langle\beta|f_i^{M'}|\beta\rangle\right]$$

Thus for a closed shell $L=0$ and $M=0$

On account of the Pauli principle, "parallel" spins tend to "push" each other away while "antiparallel" ones tend to "attract". This causes the orbit to be no longer symmetrical and the inner shell contact energy part of $\mathcal{H}_{HFS}$ will not vanish. This is called the exchange polarization.

What has this to do with $A=0$ for $1s$ shell

Quadrapole Interaction: Nuclear Magnetism

The quadrapole interaction is:

$$\mathcal{H}_Q = -\frac{e}{2} \sum_{\alpha\beta} \left\{ \frac{3 x_\alpha' x_\beta' - r_i'^2 \delta_{\alpha\beta}}{r_i'^5} \right\} \int \rho \cdot (x_\alpha' x_\beta') \, d\tau'$$

where the primes refer to nuclear coordinates. $\rho \cdot (x_\alpha' x_\beta')$ is then an operator with respect to the nuclear variables $x_\alpha' x_\beta'$. When we change to operator form, we replace the charge density $\rho(\vec{r})$ by the number of charged nuclear particles. We want to use the WE theorem to get an effective nuclear operator. Form:

$$x_\alpha' x_\beta' = \underbrace{\left(x_\alpha' x_\beta' - \tfrac{1}{3} r'^2 \delta_{\alpha\beta} \right)}_{L=2} + \underbrace{\tfrac{1}{3} r'^2 \delta_{\alpha\beta}}_{\text{spherical invariant, } L=0,\ \text{which just leads to a constant so we ignore it.}}$$

Then:

$$\langle I M_I' | \mathcal{H}_Q | I M_I \rangle = -\frac{e^2}{6} \sum_{\alpha\beta}' q_{\alpha\beta} \langle I M_I' | Q_{\alpha\beta} | I M_I \rangle$$

where: $q_{\alpha\beta} = \sum_i \frac{3 x_{i\alpha} x_{i\beta} - r_i^2 \delta_{\alpha\beta}}{r_i^5}$

$$Q_{\alpha\beta} = Z (3 x_\alpha' x_\beta' - r'^2 \delta_{\alpha\beta}) \quad ; \quad Z = \text{charge number}$$

Then, by the WE theorem:

$$\langle I M_I' | \mathcal{H}_Q | I M_I \rangle = -\frac{e^2}{6} \left\{ \frac{Q}{I(2I+1)} \right\} \sum_{\alpha\beta}' q_{\alpha\beta} \langle I M_I' | I_{\alpha\beta} | I M_I \rangle$$

where: $I_{\alpha\beta} = \frac{3}{2} \{ I_\alpha, I_\beta \} - \vec{I}^2 \delta_{\alpha\beta} \quad ; \quad \{ I_\alpha, I_\beta \} = I_\alpha I_\beta + I_\beta I_\alpha$

Look at the case $M_I' = M_I = I$ to find Q.

$$\langle II | Z (3z^2 - r^2) | II \rangle = \frac{Q}{I(2I-1)} \underbrace{\langle II | (3 I_z^2 - I^2) | II \rangle}_{3I^2 - I(I+1) \;=\; I(2I-1)}$$

Then: $Q = \langle II | Z (3z^2 - r^2) | II \rangle$

LECTURE 8 : 2-23-62

We have found the effective nuclear part of the quadrapole interaction. For the electronic part, we use the $J M_J$ representation. Since H_Q is much smaller than any other fine structure, we can neglect J-J coupling and use the WE theorem.

$$\langle J M_J' | q_{kl} | J M_J \rangle = \frac{q}{J(2J-1)} \langle J M_J' | J_{kl} | J M_J \rangle$$

where $J_{kl} = 3\{J_k, J_l\} - J^2 \delta_{kl}$; $\{J_k, J_l\} = \frac{1}{2}(J_k J_l + J_l J_k)$

We find q by proceeding as before: $M_J = M_J' = J$; $k = l$

$$\langle JJ | \sum_i \frac{1}{r_i^3} (3\cos^2\theta_i - 1) | JJ \rangle = \frac{q}{J(2J-1)} \langle JJ | (3J_z^2 - J^2) | JJ \rangle = q$$

We see that q and Q are representative of maximum alignment. Combining results gives the effective quadrapolar interaction:

$$H_{Q\,eff} = \frac{-e^2 q Q}{6I(2I-1)J(2J-1)} \sum_{kl} I_{kl} J_{kl}$$

Using the relations $[J_i, J_k] = i \epsilon_{ijk} J_k$, we obtain:

$$H_{Q\,eff} = \frac{-e^2 q Q}{2I(2I-1)J(2J-1)} \left\{ 3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I^2 J^2 \right\}$$

Note the invariance of the direction of the nuclear moment. There is no H_Q interaction for $I = 0, 1/2$; $J = 0, 1/2$ but only for values greater than these.

Note that this follows from $\langle J M_J' | T_2^M | J M_J \rangle$ since only $J > 1/2$ statisfies the restriction $J+2, \ldots, J-2$.

A useful identity is given by:

$$e q_{kl} = \lim_{r \to 0} \sum_i -\frac{\partial^2}{\partial x_i^k \partial x_i^l} \left\{ \frac{-e}{|\vec{r}_i - \vec{r}|} \right\} = -V_{kl}$$

Quadrapole Interaction in Solids

J is no longer a good quantum number, but we can still work within the lowest electronic state. We define a crystal quantum number γ:

$$\langle \gamma I M_I' | \mathcal{H}_Q | \gamma I M_I \rangle = \frac{-e^2 Q}{6I(2I-1)} \sum_{kl} \langle \gamma | q_{kl} | \gamma \rangle \langle I M_I' | I_{kl} | I M_I \rangle$$

Call $\langle \gamma | e q_{kl} | \gamma \rangle = - V_{kl}$

Now choose a crystal system in which V_{kl} is diagonal with $V_{zz} \geq V_{xx} \geq V_{yy}$. Then:

$$\mathcal{H}_{Q\,eff} = \frac{eQ}{6I(2I-1)} \left\{ V_{zz} (3I_z^2 - I^2) + V_{xx} (3I_x^2 - I^2) + V_{yy} (3I_y^2 - I^2) \right\}$$

Now, since V is a potential, it must satisfy a Laplace equation:

$$\frac{\partial^2 V}{\partial x_k \partial x_l} = 0$$

Using this, and writing:

$$\mathcal{H}_{Q\,eff} = \frac{eQ}{2I(2I-1)} \left[V_{zz} I_z^2 + \left\{ \frac{V_{xx} + V_{yy}}{2} + \frac{V_{xx} - V_{yy}}{2} \right\} I_x^2 + \left\{ \frac{V_{xx} + V_{yy}}{2} - \frac{V_{xx} - V_{yy}}{2} \right\} I_y^2 \right]$$

Now define: $eq = - V_{zz}$; $\eta = \dfrac{V_{xx} - V_{yy}}{V_{zz}}$

which in conjunction with Laplace's equation yields:

$$\mathcal{H}_{Q\,eff} = \frac{-e^2 q Q}{4I(2I-1)} \left\{ 3I_z^2 - I^2 + \eta (I_x^2 - I_y^2) \right\}$$

q, Q, and η are empirical parameters determined by experiment.

III. Paramagnetic Ions in Crystal Fields

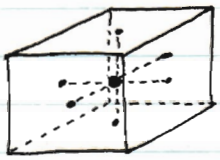
We now consider ions in crystals where the effect of the host lattice is to produce an electric field which disturbs the usual many body or electron atomic configuration. We do not consider here the effect of wave function overlap among nearest neighbors. We assume the following hierarchy of interactions:

$$\mathcal{H}_{coulomb} >> \mathcal{H}_{crystal} >> \mathcal{H}_{so} >> \mathcal{H}_z >> \mathcal{H}_{NZ} + \mathcal{H}_{HFS} + \mathcal{H}_Q$$

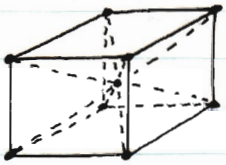
We assume that $\mathcal{H}_{crystal}$ or $V_{crystal}$ does mix in other term levels and only acts to split the lowest term level. Then L and S are still good quantum numbers (but not M_L or M_S) and we can still take $\mathcal{H}_{so} = \lambda \vec{L} \cdot \vec{S}$. Note that $V_{crystal}$ will not affect anything that does with spin.

We take as an example Cu^{++} in octahedral and tetragonal symmetry. Cu^{++} has the configuration $3d^9$ which is a one hole configuration.

Some of the terminology of cubic structures:



Octahedral Symmetry:
Octahedral Coordination
(If we pull along an axis, we get a tetragonal distortion)



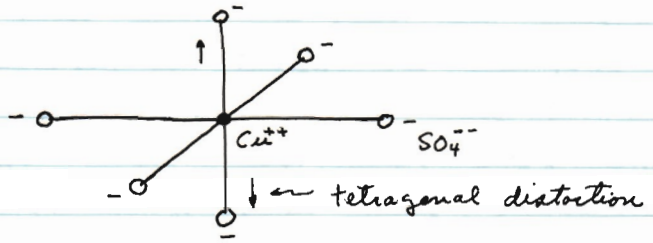
Octahedral Symmetry:
Cubic Coordination

LECTURE 9 : 2-26-62

We consider the effective interaction Hamiltonian for the single hole, crystal field problem of Cu^{++} ($3d^9 \rightarrow {}^2D$) in the octahedral, tetragonally distorted, host crystal $CuSO_4$ neglecting nuclear terms:

$$\mathcal{H} = \mathcal{E}_{term}(LS) + e V_{crystal} - \lambda \vec{L}\cdot\vec{S} + \mu_0(\vec{L}+2\vec{S})\cdot\vec{H}$$

The ligand arrangement of $CuSO_4$ has octahedral coordination with tetragonal distortion: $V_{crystal} = V_{cubic} + V_{tet}$



If we assume no wave function overlap and that the effect of the crystal is to exert an electric field, then the potential of this field obeys Laplace's equation and we can hence make a power series expansion of the potential:

$$V_{crystal} = \sum_{lm} A_l^m r^l Y_l^m(\theta,\phi)$$

Since we are only concerned with term effects, we want matrix elements diagonal in L of $V_{crystal}$. If we use the WE theorem and take $L=2$, we cannot couple with anything in $V_{crystal}$ higher than $l=4$. Odd values of l contribute nothing because $V_{crystal}$ has inversion symmetry. Also, there will be no contribution from $l=2$ for a cubic potential since $x^2+y^2+z^2$ does not satisfy Laplace's equation. However, we will have something for V_{tet}. We have then:

$$V_{tet} = A_2^0 r^2 Y_2^0 = A_2^0 \left(\frac{5}{4\pi}\right)^{1/2} \frac{1}{2}(3z^2 - r^2)$$

$$V_{cubic} = -A_4^0 r^4 \left[Y_4^0 + \left(\frac{5}{14}\right)^{1/2} \{ Y_4^4 + Y_4^{-4} \} \right]$$

$$= -A_4^0 \left(\frac{9}{4\pi}\right)^{1/2} \frac{5}{2}\left(x^4 + y^4 + z^4 - \frac{3}{5} r^4 \right)$$

We will make use of the formula:

$$\int Y_{l_3}^{m_3 *} Y_{l_2}^{m_2} Y_{l_1}^{m_1} \, d\Omega = \left\{ \frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)} \right\}^{1/2} C(l_1 l_2 l_3 | m_1 m_2 m_3) \; C(l_1 l_2 l_3 | 000)$$

Recall a result of the WE theorem:

$$\langle L M_L' | L_\ell^m | L M_L \rangle = (L \| L_\ell \| L) \; C(L \ell L | M_L m M_L')$$

Now: $\int Y_L^{M_L' *} Y_\ell^m Y_L^{M_L} d\Omega = \left\{ \frac{(2\ell+1)}{4\pi} \right\}^{1/2} C(L\ell L 1000) \; C(L\ell L | M_L m M_L')$

and:

$$\langle L 0 | L_\ell^0 | L 0 \rangle = (L \| L_\ell \| L) \; C(L \ell L 1000)$$

so we can replace spherical harmonics by angular momentum vectors by writing:

$$\int Y_L^{M_L' *} Y_\ell^m Y_L^{M_L} d\Omega = \left\{ \frac{(2\ell+1)}{4\pi} \right\}^{1/2} \frac{C^2(L\ell L 1000)}{\langle L 0 | L_\ell^0 | L 0 \rangle} \langle L M_L' | L_\ell^m | L M_L \rangle$$

Then:

$$Y_2^0 \sim (3z^2 - r^2) \longrightarrow 3L_z^2 - L^2$$

$$Y_4^0 \sim \frac{1}{8}(35z^4 - 30 z^2 r^2 + 3r^4) \longrightarrow \frac{1}{8}\left(35 L_z^4 - 30 \{L^2, L_z^2\} + 3\{L^2, L^2\}\right)$$

$$Y_4^4 \sim \frac{\sqrt{70}}{16}(x + iy)^4 \longrightarrow \frac{\sqrt{70}}{16}(L_+)^4 = L_4^4$$

$$Y_4^{-4} \sim \frac{\sqrt{70}}{16}(x - iy)^4 \longrightarrow \frac{\sqrt{70}}{16}(L_-)^4 = L_4^{-4}$$

Examples of symmetrized operators:

$$r^2 x \longrightarrow \{(L_x^2 + L_y^2 + L_z^2), L_x\} = L_x^3 + \frac{1}{3}(L_y^2 L_x + L_x L_y^2 + L_y L_x L_y)$$

$$+ \frac{1}{3}(L_z^2 L_x + L_x L_z^2 + L_z L_x L_z)$$

We make use of the angular momentum commutation rules:

$$L_y L_x L_y = \frac{1}{2}(L_y^2 L_x + i L_y L_z) + \frac{1}{2}(L_x L_y^2 - i L_z L_y)$$

$$= \frac{1}{2}(L_y^2 L_x + L_x L_y^2) - \frac{1}{2} L_x$$

Then:

$$r^2 x \rightarrow L_x^3 + \tfrac{1}{3} L_y^2 L_x + \tfrac{1}{3} L_x L_y^2 - \tfrac{1}{6} L_y^2 L_x + \tfrac{1}{6} L_x L_y^2 - \tfrac{1}{6} L_x$$

$$= L_x^3 + \tfrac{1}{2} L_y^2 L_x + \tfrac{1}{2} L_x^2 L_y - \tfrac{1}{6} L_x + \tfrac{1}{2} L_z^2 L_x + \tfrac{1}{2} L_x^2 L_z - \tfrac{1}{6} L_x$$

$$= \tfrac{1}{2} L_x (L^2) + \tfrac{1}{2} (L^2) L_x - \tfrac{1}{3} L_x = L_x (L^2 - 1/3)$$

In the same way: $\{L^2, L^2\} \rightarrow \{L^4\} \rightarrow L^2 (L^2 - \tfrac{1}{3})$

$\{L^2 L_z^2\} \rightarrow L^2 L_z^2 + \tfrac{1}{6} L^2 - \tfrac{5}{6} L_z^2$

The $\{\}$ symbol means take the symmetrized product and this is more general than the anticommutation symbol $\{,\}$.

The results for this problem of $L = 2$, $M_L = 0, \pm 1, \pm 2$ and taking the matrix element of $V_{cubic} + V_{tet}$ is:

$M_L \rightarrow$ / $M_L \downarrow$	0	+1	−1	+2	−2
0	$-6D_q + 2P$				
+1		$4D_q + P$			
−1			$4D_q + P$		
+2				$-D_q - 2P$	$-5D_q$
−2				$-5D_q$	$-D_q - 2P$

Upon diagonalization, we have:

$\mathcal{E} = -6D_q + 2P$: $\psi \sim \frac{1}{2}(3z^2 - r^2)$

$\mathcal{E} = -6D_q + 2P$: $\psi \sim \frac{1}{\sqrt{2}}(\psi_2 + \psi_{-2}) \sim \frac{\sqrt{3}}{2}(x^2 - y^2)$

$\mathcal{E} = 4D_q + P$: $\psi \sim z(x + iy)$

$\mathcal{E} = 4D_q + P$: $\psi \sim z(x - iy)$

$\mathcal{E} = 4D_q - 2P$: $\psi \sim \frac{1}{\sqrt{2}}(\psi_2 - \psi_{-2}) \sim \sqrt{3}\, i\, xy$

where $D_q = e A_4^0 \langle r^4 \rangle \left(\frac{9}{4\pi}\right)^{1/2} \frac{C^2(2\,42\,1000)}{6}$

$P = e A_2^0 \langle r^2 \rangle \left(\frac{5}{4\pi}\right)^{1/2} C^2(2221000)$

It is easily seen that in cubic field alone we would have split into a 2 fold and 3 fold degenerate level because P would be zero. In calculating the above, we have used the relations:

$$L_+ \psi(L M_L) = \sqrt{(L - M_L)(L + M_L + 1)}\, \psi(L, M_L + 1)$$
$$L_- \psi(L M_L) = \sqrt{(L + M_L)(L - M_L + 1)}\, \psi(L, M_L - 1)$$
$$L_z \psi(L M_L) = M_L \psi(L M_L)$$

$\psi_2 \sim \frac{\sqrt{6}}{4}(x + iy)^2$ $\qquad$ $\psi_{-2} \sim \frac{\sqrt{6}}{4}(x - iy)^2$

$\psi_1 \sim -\frac{\sqrt{6}}{2} z(x + iy)$ $\qquad$ $\psi_{-1} \sim \frac{\sqrt{6}}{2} z(x - iy)$

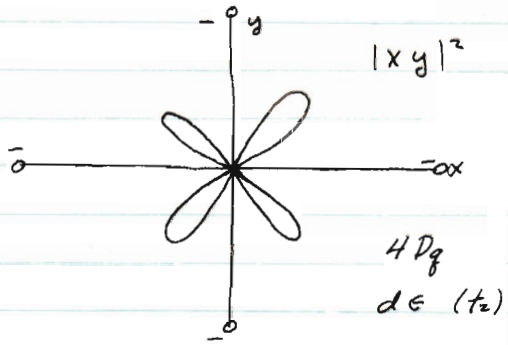
$\psi_0 \sim \frac{1}{2}(3z^2 - r^2)$

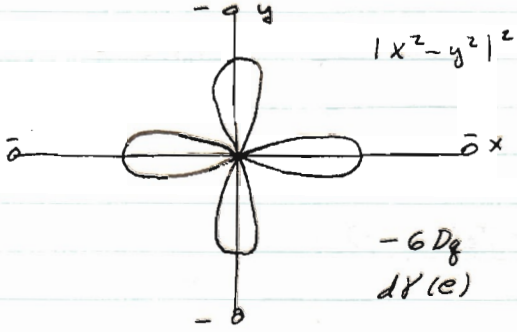
LECTURE 10 : 2-28-62

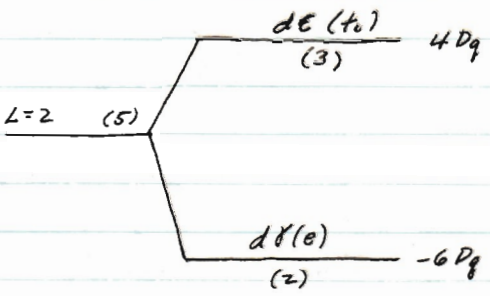
Without the tetragonal distortion, the cubic crystal field results in a 2 x 3 degeneracy. The wave functions have the form:

$$\left.\begin{matrix}(y^2-z^2)\\(x^2-y^2)\end{matrix}\right\} \mathcal{E} = -6Dq \quad ; \quad \left.\begin{matrix}xy\\yz\\zx\end{matrix}\right\} \mathcal{E} = 4Dq$$

An amplitude plot of the wave functions around the Cu^{++} ions with respect to the ligands looks like:

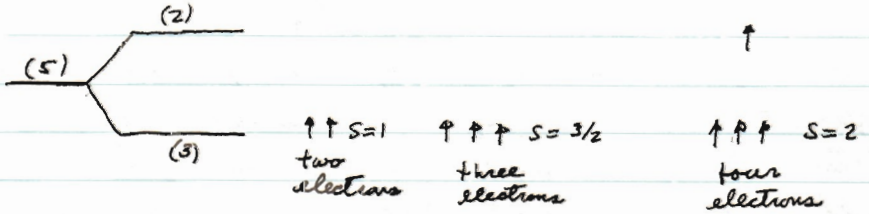






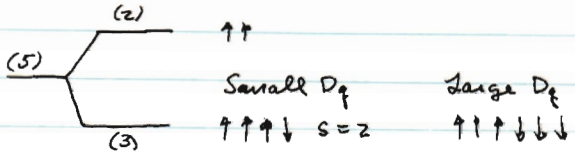
$CuSO_4$ gives the one hole problem and hence gives rise to only one term, ie, ^2D. For more than one particle, we get more than one term. V crystal can mix terms of different L, but same S, but if it is small, we can always work diagonal in L of the Hund's Rule ground state.

We examine the meaning of Hund's rule in a crystal field. Consider cubic field on ^2D and fill ground state with electrons:

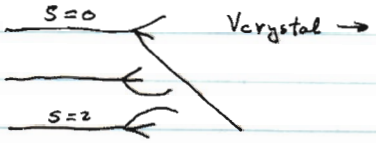


If we consider only parallel spins, when we add the fourth electron, it must go into an excited state. This happens until the top state is filled and then the ground state begins filling up with antiparallel spins. This happens in a strong crystal field and demonstrates Hund's Rule (however, not too strong a crystal field).

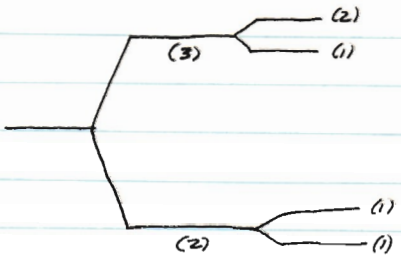
In the Co^{3+} ion, there can be two ground states, $S=2$ and $S=0$ and both are observed.



In weak fields, Hunds rule holds, but may break down in a strong field as shown in the diagram:



Jahn-Teller Theorem:

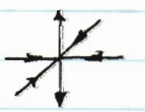


The result on the left is for cubic plus tetragonal fields. Note that the ground state degeneracy has been completely lifted.

The Jahn-Teller theorem says that a given symmetry configuration will distort itself so as to lift any remaining orbital degeneracies. However, the splitting is usually very small compared to kT so it is usually not noticed and we can speak of the degeneracy as still remaining.

Suppose that we can describe the state of an electron in terms of harmonic oscillators:

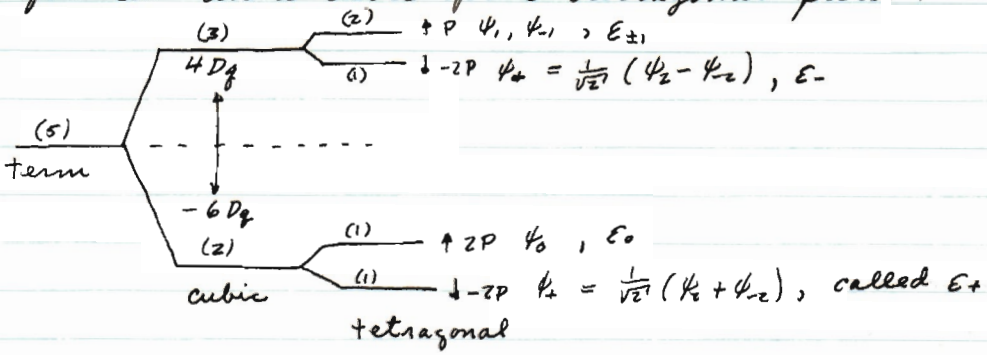
$$E_i = \sum_j \left(\frac{1}{2} \dot{q}_j^2 + \nu_j^2 q_j^2 \right) + E_i^0 + \underbrace{\sum_j \left(\frac{\partial E_i}{\partial q_j} \right) q_j}_{\text{distortion}}$$

One of the normal modes is like:  . We see that a distortion developes. However, at high temperatures the contributions from different modes averages out while at low temperatures the distortion locks in and we get the Jahn-Teller effect. In the Cu salts, it is believed that V_{tet} is due to this effect.

LECTURE 11 : 3-2-62

Spin Orbit Interaction in the Crystal Field

Recall for Cu^{++} in a cubic plus tetragonal field:



We now consider the spin-orbit interaction. For this case, the problem is simple because the ground state is non-degenerate. Assume $\mathcal{H}_{so} < 2P$.

$$\mathcal{H}_{so} = -\lambda \vec{L}\cdot\vec{S} = -\lambda \left(L_z S_z + \tfrac{1}{2}\{L_+ S_- + L_- S_+\}\right)$$

where $L_+ = L_x + iL_y$; $L_- = L_x - iL_y$ and are the raising and lowering operators.

Previously we have not considered spin. Therefore each state above is still two fold degenerate and spin-orbit coupling should have some effect. However, note that the orbital angular momentum of the ground state above is quenched because $\psi_+ = \frac{1}{\sqrt{2}}(\psi_2 + \psi_{-2})$ and this makes:

$$\langle \psi_+ | L_x, L_y, L_z | \psi_+ \rangle = 0$$

Hence:

$$\left.\begin{aligned} \langle \psi_+\alpha | -\lambda \vec{L}\cdot\vec{S} | \psi_+\alpha\rangle &= 0 \\ \langle \psi_+\alpha | -\lambda \vec{L}\cdot\vec{S} | \psi_+\beta\rangle &= 0 \\ \langle \psi_+\beta | -\lambda \vec{L}\cdot\vec{S} | \psi_+\beta\rangle &= 0 \end{aligned}\right\}$$

Therefore, there is no first order effect of $\mathcal{H}_{so}$ on the ground state.

However, there is a second order effect. Consider:

Ground state: ——— $\psi_+\alpha = \psi_1$, ε_1
——— $\psi_+\beta = \psi_2$, ε_2

in the second order.

Now we have:

$$E_1 = -6Dq - 2P + \sum_i \frac{|\langle \psi_+ \alpha | -\lambda \vec{L}\cdot\vec{S} | \psi_i \sigma_i \rangle|^2}{E_+ - E_i}$$

$$E_2 = -6Dq - 2P + \sum_i \frac{|\langle \psi_+ \beta | -\lambda \vec{L}\cdot\vec{S} | \psi_i \sigma_i \rangle|^2}{E_+ - E_i}$$

Let us examine the various matrix elements involved:

$$\langle \psi_+ \alpha | -\lambda L_z S_z | \psi_- \alpha \rangle = -\lambda$$
$$\langle \psi_+ \beta | -\lambda L_z S_z | \psi_- \beta \rangle = \lambda$$
$$\langle \psi_+ \beta | -\tfrac{\lambda}{2} L_+ S_- | \psi_1 \alpha \rangle = -\lambda/\sqrt{2}$$
$$\langle \psi_+ \alpha | -\tfrac{\lambda}{2} L_- S_+ | \psi_{-1} \beta \rangle = -\lambda/\sqrt{2}$$

This all resolves to:

$$E_1 = E_+ + \frac{\lambda^2}{10Dq} + \frac{\lambda^2/2}{10Dq + 3P}$$

$$E_2 = E_+ + \frac{\lambda^2}{10Dq} + \frac{\lambda^2/2}{10Dq + 3P}$$

We see that H_{SO} has not lifted the degeneracy of the ground state to the second order but has just shifted E_+ by a constant amount. The new wave functions are:

$$\psi_1 = \psi_+ \alpha - \frac{\lambda}{E_+ - E_-}\psi_+ \alpha - \frac{\lambda/\sqrt{2}}{E_+ - E_{-1}}\psi_- \beta$$

$$\psi_2 = \psi_+ \beta + \frac{\lambda}{E_+ - E_-}\psi_- \beta - \frac{\lambda/\sqrt{2}}{E_+ - E_{+1}}\psi_+ \alpha$$

or:

$$\psi_1 = \frac{1}{\sqrt{2}}\left\{\left(1 + \frac{\lambda}{10Dq}\right)\psi_{+2} + \left(1 - \frac{1}{10Dq}\right)\psi_{-2}\right\}\alpha + \left\{\frac{1}{\sqrt{2}}\frac{\psi_{-1}}{10Dq + 3P}\right\}\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left\{\left(1 + \frac{\lambda}{10Dq}\right)\psi_{-2} + \left(1 - \frac{\lambda}{10Dq}\right)\psi_{+2}\right\}\beta + \left\{\frac{\lambda}{\sqrt{2}}\frac{\psi_{+1}}{10Dq + 3P}\right\}\alpha$$

Kramer's Theorem

Suppose we have the following Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2m} + eV(\vec{r}) - \frac{\mu_0}{mc} \nabla V(\vec{r}) \times \vec{p} \cdot \vec{S}$$

Kramer's theorem states that if $\mathcal{H}\psi_1 = E\psi_1$, then there also is $\mathcal{H}\psi_2 = E\psi_2$ or the state is two fold degenerate. These states will be given by:

$$\psi_1 = \psi_a \alpha + \psi_b \beta$$
$$\psi_2 = -\psi_b^* \alpha + \psi_a^* \beta$$

What is connection between Kramer's degeneracy and spin?

Note that this form checks against the above results for the spin orbit second-order wave functions of the two fold degenerate ground state, ie, ψ_1 and ψ_2. Check by looking up the spherical harmonics for $\psi_{\pm 2}$, $\psi_{\pm 1}$. Hence, this ψ_1, ψ_2 satisfy Kramer's Theorem.

For further developments with spin, it is convenient to introduce the spinor formalism so that we may use the properties of the Pauli matrices:

$$\vec{S} = \frac{1}{2}\vec{\sigma} \quad ; \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Then, if $\psi_1 = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$, we easily see:

$$\psi_2 = \begin{pmatrix} -\psi_b^* \\ \psi_a^* \end{pmatrix} = -i\sigma_y C \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} = (-i\sigma_y C)\psi_1 = T\psi_1$$

The antilinear operator $T = -i\sigma_y C$ is called the Time Reversal Operator. Operate with T on the Schroedinger equation:

$$T(\mathcal{H}\psi_1) = T(E\psi_1) = E\psi_2$$

Now: $$T(\mathcal{H}\psi_1) = -i\sigma_y H^* C\psi_1 = \sigma_y H^* \sigma_y \underbrace{(-i\sigma_y C\psi_1)}_{\psi_2} = E\psi_2$$

We must show $\sigma_y \mathcal{H}^* \sigma_y = \mathcal{H}$. We need only look at the SO term.

Then:

$$\sigma_y (\mathcal{H}_{so})^* \sigma_y = -\frac{\mu_0}{mc} \nabla V \times \vec{p}^* \cdot (\sigma_y \vec{s}^* \sigma_y)$$

$$= -\frac{\mu_0}{mc} \nabla V \times \vec{p} \cdot (-\sigma_y \vec{s}^* \sigma_y)$$

Thus we have resolved to showing:

$$-\sigma_y \vec{s}^* \sigma_y = \vec{s} \quad \text{or} \quad -\sigma_y \vec{\sigma}^* \sigma_y = \vec{\sigma}$$

$$-\sigma_y \sigma_x^* \sigma_y = -\sigma_y \sigma_x \sigma_y = \sigma_x$$
$$-\sigma_y \sigma_y^* \sigma_y = \sigma_y$$
$$-\sigma_y \sigma_z^* \sigma_y = -\sigma_y \sigma_z \sigma_y = \sigma_z$$

using the anticommutation relations $\{\sigma_x, \sigma_y\} = 2\delta_{xy}$

However, for completeness sake, we must ask if the trivial result $\psi_2 = A\psi_1$, where A is a phase factor, is possible. If so, we must have:

$$\psi_a = -A\psi_b^* = -AA^*\psi_a = -|A|^2\psi_a$$

which is impossible so a two fold degeneracy does exist.

The above discussion rigourously demonstrates that $\mathcal{H}_{so}$ will never split the two-fold degeneracy of the ground state. Note also that any electric field is invariant under the operation of T so no electric field will remove the degeneracy, but a magnetic field will.

LECTURE 12 : 3-5-62

We now consider Kramer's Theorem for many electrons.

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i eV(\vec{r}_i) - \frac{\mu_0}{mc} \sum_i \nabla V(\vec{r}_i) \times \vec{p}_i \cdot \vec{S}_i$$

$$\mathcal{H}\, \psi_1(\vec{r}_1, \vec{\sigma}_1 \cdots) = E\, \psi_1(\vec{r}_1, \vec{\sigma}_1 \cdots)$$

$$\psi_2 = (-i\sigma_{y1})(-i\sigma_{y2}) \cdots C\, \psi_1 = T\psi_1$$

thus extending the one electron definition. The argument then proceeds exactly as before, and we can show:

$$\sigma_{y1}\sigma_{y2} \cdots \mathcal{H}^* \sigma_{y1}\sigma_{y2} \cdots = \mathcal{H}$$

and $\mathcal{H}\psi_2 = E\psi_2$. However, we must examine whether or not ψ_2 is linearly independent of ψ_1. Assume $\psi_2 = A\psi_1$

$$T\psi_2 = A^*\psi_2 = A^* T\psi_1 = |A|^2 \psi_1$$

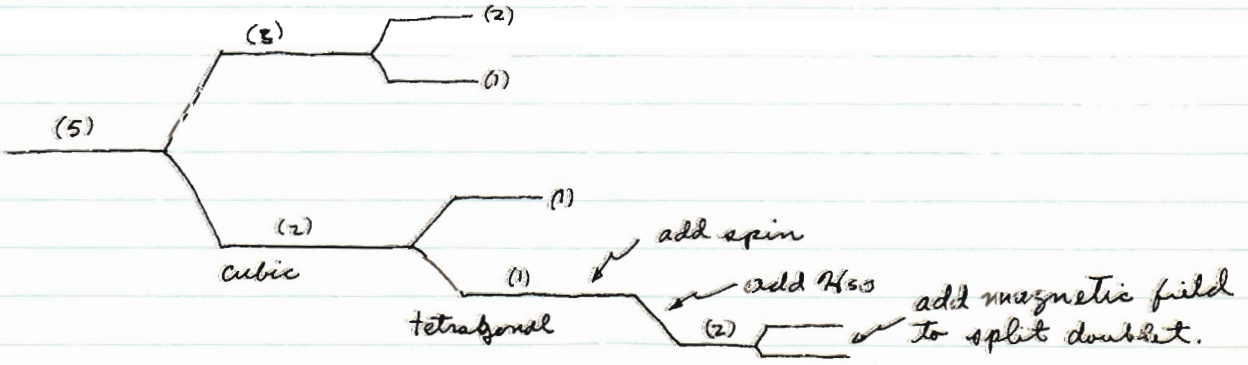
$$(-i\sigma_{y1}) \cdots C\,(-i\sigma_{y1}) \cdots C\, \psi_1 = (-i\sigma_{y1}) \cdots (i\sigma_{yi}^*) \cdots \psi_1 = |A|^2 \psi_1$$

or: $(-1)^N \psi_1 = |A|^2 \psi_1$

If N is even, $\psi_2 = A\psi_1$, but if N is odd, $\psi_2 \neq A\psi_1$ and we have a degeneracy present.

Note: If we have more than a two-fold Kramers degeneracy due to some number of odd electrons, the most $\mathcal{H}_{SO}$ can do is to split it up into a series of two fold degenerate levels.

The ^2D cubic problem looks like:



Let us consider the splitting of this Kramers doublet by a magnetic field. Recall:

$$\psi_1 = \frac{1}{\sqrt{2}}\left[\left(1+\frac{\lambda}{10Dq}\right)\psi_{+2} + \left(1-\frac{\lambda}{10Dq}\right)\psi_{-2}\right]\alpha + \left[\frac{\lambda}{\sqrt{2}}\,\frac{\psi_{-1}}{10Dq+3P}\right]\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left[\left(1+\frac{\lambda}{10Dq}\right)\psi_{-2} + \left(1-\frac{\lambda}{10Dq}\right)\psi_{+2}\right]\beta + \left[\frac{\lambda}{\sqrt{2}}\,\frac{\psi_{+1}}{10Dq+3P}\right]\alpha$$

The Zeeman interaction is given by:

$$\mathcal{H}_z = \mu_0\,(\vec{L}+2\vec{S})\cdot\vec{H} = \mu_0\,(L_z+2S_z)H_z + \frac{\mu_0}{2}(L_+ + 2S_+)H_- + \frac{\mu_0}{2}(L_- + 2S_-)H_+$$

where $L_\pm$, $S_\pm$, $H_\pm$ have their usual meanings. Since Veet has lifted the isotropy of the problem, we will have to worry about the direction of H_z. In calculating the matrix element $\langle\psi_1|\mathcal{H}_z|\psi_2\rangle$ we will work only to first order in λ. We then find for the matrix element of the H_z or the matrix form of $\mathcal{H}_z$:

$$(\mathcal{H}_z) = \mu_0\begin{pmatrix} \left(1+\frac{4\lambda}{10Dq}\right)H_z & \left(1+\frac{\lambda}{10Dq+3P}\right)H_- \\ \left(1+\frac{\lambda}{10Dq+3P}\right)H_+ & -\left(1+\frac{4\lambda}{10Dq}\right)H_z \end{pmatrix}$$

$$= \frac{\mu_0}{2}\begin{pmatrix} g_\parallel H_z & g_\perp H_- \\ g_\perp H_+ & -g_\parallel H_z \end{pmatrix}$$

The secular determinant is clearly:

$$\begin{vmatrix} \tfrac{1}{2}\mu_0 g_\parallel H_z - E & \tfrac{1}{2}\mu_0 g_\perp H_- \\ \tfrac{1}{2}\mu_0 g_\perp H_+ & -\tfrac{1}{2}\mu_0 g_\parallel H_z - E \end{vmatrix} = 0$$

Define: $H_\perp^2 = H_+ H_- = H_x^2 + H_y^2$

Then:

$$\mathcal{E} = \pm \frac{\mu_0 H}{2} \left[g_{11}^2 \cos^2\theta + g_\perp^2 \sin^2\theta \right]^{1/2}$$

These results are essentially verified by resonance experiments.

When we try to correlate the g factors with experiment, we find that λ is reduced by as much as 25% from its free ion value. This may be due to:

(1) The expansion of the orbitals by $V_{crystal}$, or:

(2) covalent bonding

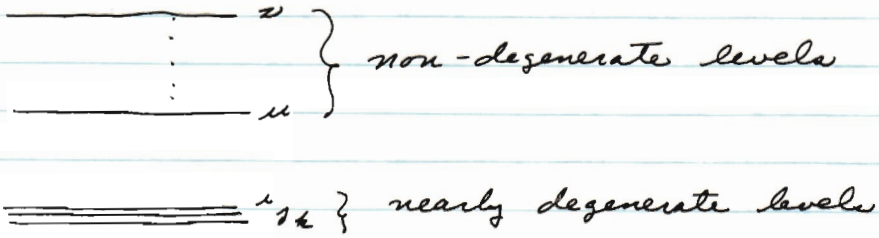
Both of these effects reduce $\left\langle \frac{1}{r^3} \right\rangle$ which is involved in $\mathcal{H}_{SO}$.

We next consider the Spin Hamiltonian.

LECTURE 13 : 3-7-62

The Spin Hamiltonian

We first consider Brillouin-Wigner Perturbation Theory (BWPT). Consider the following energy scheme:



We consider $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$ and the matrix element of $\mathcal{H}$ with respect to ι, φ, κ, etc with $\mathcal{H}'$ and the states $\mu, \ldots, \nu$ treated as perturbations. BWPT says that we can write an effective matrix element as:

$$(\mathcal{H}_{eff})_{\iota\varphi} = \mathcal{E}_\iota^\circ \delta_{\iota\varphi} + \langle \iota | \mathcal{H}' | \varphi \rangle + \sum_\mu \frac{\langle \iota | \mathcal{H}' | \mu \rangle \langle \mu | \mathcal{H}' | \varphi \rangle}{\mathcal{E} - \mathcal{E}_\mu^\circ}$$

$$+ \sum_{\mu\nu} \frac{\langle \iota | \mathcal{H}' | \mu \rangle \langle \mu | \mathcal{H}' | \nu \rangle \langle \nu | \mathcal{H}' | \delta \rangle}{(\mathcal{E} - \mathcal{E}_\nu^\circ)(\mathcal{E} - \mathcal{E}_\mu^\circ)} + \cdots$$

where $\mathcal{E}$ is the final energy which is close to the usually found $\mathcal{E}_\iota^\circ$.

Consider the matrix element between two spin states with $M_L = 0$ (actually, any orbitally non-degenerate ground state):

$$\langle 0 M_S' | \mathcal{H}_{eff} | 0 M_S \rangle = \langle 0 M_S' | -\lambda \vec{L} \cdot \vec{S} + \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} | 0 M_S \rangle$$

$$+ \sum_{\substack{\mu \\ M_S''}} \frac{\langle 0 M_S' | -\lambda \vec{L} \cdot \vec{S} + \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} | \mu M_S'' \rangle \langle \mu M_S'' | -\lambda \vec{L} \cdot \vec{S} + \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} | 0 M_S \rangle}{\mathcal{E}_0 - \mathcal{E}_\mu^\circ}$$

Now $\langle 0 | \vec{L} | 0 \rangle = 0$ so that only $\langle 1 | \vec{S} \cdot \vec{H} | 1 \rangle$ contributes in the first term.

On the second term, use the relation:

$$\sum_{M_S''} \langle M_S' | \vec{S} | M_S'' \rangle \langle M_S'' | \vec{S} | M_S \rangle = \langle M_S' | \vec{S}\,\vec{S} | M_S \rangle$$

Then we can write an effective Hamiltonian, diagonal in $M_L = 0$ and removing the brackets $\langle M_S'|$ and $|M_S\rangle$:

$$\mathcal{H}_{eff} = 2\mu_0 \vec{S}\cdot\vec{H} + \vec{S}\cdot\left\{\lambda^2 \sum_\mu \frac{\langle 0|\vec{L}|\mu\rangle\langle\mu|\vec{L}|0\rangle}{E_0 - E_\mu^0}\right\}\cdot\vec{S}$$

$$+ \mu_0 \vec{S}\cdot\left\{-\lambda \sum_\mu \left[\frac{\langle 0|\vec{L}|\mu\rangle\langle\mu|\vec{L}|0\rangle + \langle\mu|\vec{L}|0\rangle\langle 0|\vec{L}|\mu\rangle}{E_0 - E_\mu^0}\right]\right\}\cdot\vec{H}$$

$$+ \mu_0^2 \vec{H}\cdot\left\{\sum_\mu \frac{\langle 0|\vec{L}|\mu\rangle\langle\mu|\vec{L}|0\rangle}{E_0 - E_\mu}\right\}\cdot\vec{H}$$

There are no spin-spin terms because $\vec{S}$ cannot connect states of orbital angular momentum that are different.

The spin Hamiltonian thus has the general form:

$$\mathcal{H}_{eff} = \underbrace{\mu_0 \vec{S}\cdot\vec{\vec{g}}\cdot\vec{H}}_{\text{Zeeman Term}} + \underbrace{\vec{S}\cdot\vec{\vec{D}}\cdot\vec{S}}_{\substack{\text{this gives zero field splitting from SO, but does not remove the Kramer's doublet. No degeneracy is lifted in a cubic field}}} + \underbrace{\mu_0^2 \vec{H}\cdot\vec{\vec{T}}\cdot\vec{H}}_{\substack{\text{second Order Zeeman term. This is the analog to the term in atoms or ions that gives rise to Van Vleck paramagnetism.}}}$$

We now construct the spin Hamiltonian for nuclear hyperfine interactions, assuming diagonal in L and S and without the assumption of $\vec{L}\cdot\vec{S}$ coupling. Recall:

$$\mathcal{H}_{HFS} = \sum_n \left[\frac{\vec{\mu}_{Sn}\cdot\vec{\mu}_N}{r_n^3} - \frac{3}{r_n^5}(\vec{\mu}_{Sn}\cdot\vec{r}_n)(\vec{\mu}_N\cdot\vec{r}_n) - \underbrace{2\frac{\vec{\mu}_{Ln}\cdot\vec{\mu}_N}{r_n^3}}_{A_L\,\vec{I}\cdot\vec{L}} - \underbrace{\frac{8\pi}{3}\vec{\mu}_{Sn}\cdot\vec{\mu}_n\,\delta(\vec{r})}_{A_S\,\vec{I}\cdot\vec{S}}\right]$$

Look at the dipole - dipole term:

$$\mathcal{H}_{d\text{-}d} = \sum_i \left[\frac{\vec{\mu}_{Si} \cdot \vec{\mu}_N}{r_i^3} - \frac{3}{r_i^5} (\vec{\mu}_{Si} \cdot \vec{r}_i)(\vec{\mu}_N \cdot \vec{r}_i) \right]$$

Use the WE Theorem:

$$\mathcal{H}_{d\text{-}d} = \sum_{ikl} \underbrace{\mu_{Si}^k}_{C(S)\, S_k} \underbrace{\frac{1}{r_i^5} \left(r_i^2 \delta_{kl} - 3 r_i^k r_i^l \right)}_{C(L)\left(L^2 \delta_{kl} - \frac{3}{2}\{L_k L_l + L_l L_k\}\right) C(I)\, I_k} \mu_N^l$$

Hence:

$$\mathcal{H}_{d\text{-}d} = B \left[L^2 \vec{S} \cdot \vec{I} - \frac{3}{2} (\vec{S} \cdot \vec{L})(\vec{L} \cdot \vec{I}) - \frac{3}{2} (\vec{I} \cdot \vec{L})(\vec{L} \cdot \vec{S}) \right]$$

We will be concerned with the effective Hamiltonian corresponding to $\langle L S I M_L' M_S' M_I' | \mathcal{H}_{HFS} | L S I M_L M_S M_I \rangle$ which is:

$$\mathcal{H}_{HFS} = A_S \vec{I} \cdot \vec{S} + A_L \vec{I} \cdot \vec{L} + B \left[L^2 \vec{S} \cdot \vec{I} - \frac{3}{2} (\vec{S} \cdot \vec{L})(\vec{L} \cdot \vec{I}) - \frac{3}{2} (\vec{S} \cdot \vec{L})(\vec{L} \cdot \vec{I}) \right]$$

LECTURE 14: 3-9-62

We will be concerned with matrix elements of $\mathcal{H}_{HFS}$ with respect to the $L=0$ ground state.

First we must show $\langle 0|\vec{L}|0\rangle = 0$ for an orbitally non-degenerate state with no magnetic field applied. Consider the Schroedinger equation:

$$\mathcal{H}\psi_n^n = E_n \psi_n^n \quad \text{where } n \text{ indexes degeneracy.}$$

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_i eV(r_i) + \sum_{i<j} \frac{e^2}{r_{ij}}$$

so that $\mathcal{H}^* = \mathcal{H}$

$$\mathcal{H}^* C\psi_n^n = E_n C\psi_n^n \quad ; \quad \mathcal{H}(C\psi_n^n) = E_n (C\psi_n^n)$$

Thus: $C\psi_n^n = \sum_m a_{nm}\psi_n^m$

If ψ_n is non-degenerate, then we have simply $C\psi_n = a\psi_n$. Form:

$$C^2\psi_n = a^* C\psi_n = |a|^2\psi_n = \psi_n \quad , \text{ hence } |a|^2 = 1$$

or $a = e^{i\phi}$, then:

$$\psi_n^* = e^{i\phi_n}\psi_n$$

Now take the expectation value of some operator O, with O Hermitean (NB: L^+, L^- are not Hermitean) and assume further that $O^* = -O$ ($\vec{L}$ is an operator of this type):

$$\int \psi_n^* O \psi_n \, d\tau = \langle n|O|n\rangle = \int \psi_n^* O^* \psi_n \, d\tau = -\int \psi_n^* O \psi_n \, d\tau$$
$$= 0$$

Hence: $\langle 0|\vec{L}|0\rangle = 0$

We now return to calculating the spin Hamiltonians for $\mathcal{H}_{HFS}$ with $M_L = 0$. However, $M_L = 0$ is misleading because the state need only be orbitally non-degenerate and hence may not be a state of spherical symmetry but just a state of crystal symmetry as well, hence the "$|0\rangle$" means orbitally non-degenerate ground state, not $M_L = 0$.

We get:

$$\mathcal{H}_{HFS} = A_s \vec{I}\cdot\vec{S} + B\,L(L+1)\,\vec{I}\cdot\vec{S} - \frac{3}{2} I_z S_z \langle 0|L_z^2|0\rangle$$

$$= \vec{I}\cdot\overleftrightarrow{A}\cdot\vec{S}$$

If we deal with tetragonal symmetry, $\overleftrightarrow{A}$ has the form:

$$\overleftrightarrow{A} = \begin{pmatrix} A_1 & & \\ & A_1 & \\ & & A_2 \end{pmatrix}$$

We have above the lowest order spin Hamiltonian. To find second order we have to consider along with $\mathcal{H}_{HFS}$ terms like $-\lambda\vec{L}\cdot\vec{S} + \mu_0(\vec{L}+2\vec{S})\cdot\vec{H} + \mathcal{H}_{NZ}$ in combination which would lead to contributing terms in the $\overleftrightarrow{A}$ tensor like:

$$\sum_{\mu} \frac{\langle 0|-\lambda\vec{S}\cdot\vec{L}|\mu\rangle\langle\mu|\vec{L}\cdot\vec{I}|0\rangle}{E_0 - E_\mu^0}$$

Now consider the spin Hamiltonian form of the nuclear Zeeman effect.

$$\mathcal{H}_{ZN} = g_I \mu_N \vec{I}\cdot\vec{H}$$

$$(\mathcal{H}_{NZ})_{eff} = \langle 0|g_I\mu_N\vec{I}\cdot\vec{H}|0\rangle + \sum_{\mu}\frac{\langle 0|\vec{I}\cdot\vec{L}|\mu\rangle\langle\mu|\vec{L}\cdot\vec{H}|0\rangle}{E_0 - E_\mu^0}$$

This does not seem to yield anything drastically new as far as a spin Hamiltonian is concerned.

Considering the Quadrapole interaction, we recall.

$$\mathcal{H}_Q = \frac{-e^2Q}{6I(2I-1)} \sum_{kl} q_{kl} I_{kl}$$

where $I_{kl} = \frac{3}{2}\{I_k I_l + I_l I_k\} - I^2\delta_{kl}$

$$q_{kl} = \sum_{\mu} \frac{3x_k^{\mu}x_l^{\mu} - r_\mu^2\delta_{kl}}{r_\mu^5}$$

Previously, when we did the quadrupole interaction, we obtained the operator equivalent for $\mathcal{H}_Q$ in terms of J, but now J is not a good quantum number and we are using L and I instead. We obtain for the effective $\mathcal{H}_Q$:

$$\mathcal{H}_Q = \kappa \left[3(\vec{I}\cdot\vec{L})^2 + \frac{3}{2}(\vec{I}\cdot\vec{L}) - I^2 L^2 \right]$$

Like $\mathcal{H}_{NZ}$, this contains nothing of interest from the viewpoint of spin.

We now generalize the spin Hamiltonian concept to the case where we may have a degenerate ground state before $-\lambda \vec{L}\cdot\vec{S} + \mu_0 (\vec{L} + 2\vec{S})\cdot\vec{H}$ is turned on. Suppose we start with a 2 fold degenerate problem so that we have to describe it by some linear combination of 2×2 matrices. Such a problem can be described by a linear combination of 2×2 matrices, four of them precisely, so that we can form a general eigenvalue equation of the form (to first order in H):

$$(D + E_x H_x + E_y H_y + E_z H_z)\psi = \varepsilon \psi$$

This expression is good for any-fold degeneracy because D, E_x, E_y and E_z can themselves be linear combinations of matrices. We must have enough matrices on hand to form a complete set, that is, we must have n^2 linearly independent matrices available.

For the 2×2 problem, we can take the Pauli matrices $\vec{S} = \frac{1}{2}\vec{\sigma}$ plus the 2×2 identity. For a 2×2 problem with cubic symmetry, the only form the spin Hamiltonian can take is obviously:

$$E I + g \vec{S}\cdot\vec{H}$$

LECTURE 15 : 3-16-62

If we have a 6×6 problem, we need 36 linearly independent matrices. This problem could arise from a 3 fold fold orbitally degenerate problem.

We have said that for a 2 fold problem we can use I and the pauli matrices. Consider:

S_x, S_y, S_z, I : $S_x = \frac{1}{2}\sigma_x$, etc ; $S_x^2 + S_y^2 + S_z^2 = S(S+1)I$

$[S_x, S_y] = i S_z$

Now consider the 2×2 problem in a tetragonal field: The general Spin Hamiltonian is:

$$\mathcal{H} = g_{\parallel} \mu_0 S_z H_z + g_{\perp} \mu_0 (S_x H_x + S_y H_y) + AI$$

For a 3×3 problem, we must generate some more linearly independent matrices of dimension 3. For now, we assume that we can form these matrices out of some new matrices I, S_x', S_y', S_z'. We need nine:

S_x', S_y', S_z', I
$S_x'^2, S_y'^2, S_z'^2$
$S_x' S_y', S_y' S_z', S_z' S_x'$

} We have ten already and need 9. Eliminate $S_x'^2$ as not being linearly independent.

The Spin Hamiltonian for a tetragonal field is:

$$\mathcal{H} = g_{\parallel} \mu_0 S_z' H_z + g_{\perp} \mu_0 (S_x' H_x + S_y' H_y) + A S_z^2 + \underbrace{B(S_x'^2 + S_y'^2)}_{\text{can write this as } B[S^2 I - S_z'^2]}$$

For the 4×4 problem, keep the 3×3 matrices (in 4×4 form) and add the following:

$S_x'^3$, $\underbrace{S_y'^3, S_z'^3}_{\text{eliminate}}$; $S_x'^2 S_y'$, $S_y'^2 S_z'$, $S_z'^2 S_x'$; $S_x' S_y' S_z'$

$S_x'^2 S_z'$, $\underbrace{S_y'^2 S_x'}_{\text{eliminate}}$, $S_z'^2 S_y'$

All elimination is done on the basis of linear independence.

The most general 4×4 spin Hamiltonian is:

$$\mathcal{H} = g_{\parallel}\mu_0 S'_z H_z + g_{\perp}\mu_0 (S'_x H_x + S'_y H_y) + A S'^2_z + B(S'^2_x + S'^2_y)$$

$$+ \eta S'^3_z H_z + \xi (S'^3_x H_x + S'^3_y H_y) + \underbrace{\mu S'_z H_z (S'^2_x + S'^2_y)}_{\text{can be put in } g_{\parallel}\mu_0 \text{ term}}$$

$$+ \underbrace{J(S'^2_x H_y S'_y + S'^2_y H_x S'_x)}_{\text{can be put in existing terms}} + \underbrace{\rho (S'_x H_x + S'_y H_y) S'^2_z}_{\text{can be put in } g_{\perp}\mu_0 \text{ term}}$$

We now consider an example of a rare earth ion in a crystal field. We assume that $V_{crystal}$ retains J but splits M_J so everything is still diagonal in J. This is reasonable because in the rare earths, the effect of the crystal field on the active shell of the ion is screened out by two complete shells. This enables the hierarchy of interactions:

$$E_{term} > V_{crystal} < \mathcal{H}_{SO} > \mathcal{H}_Z > \mathcal{H}_{nuclear}$$

$$\mathcal{H}_{SO} \rightarrow \frac{1}{2}\{J(J+1) - L(L+1) - S(S+1)\}$$

$$\mathcal{H}_Z = g_J \mu_0 \vec{J}\cdot\vec{H}$$

$$g_J = \left[\frac{2\{J(J+1) + S(S+1) - L(L+1)\}}{2J(J+1)} + \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)}\right]$$

We can use the WE theorem for J:

$$\langle J M'_J | V_{crystal} | J M_J \rangle \rightarrow \langle J M'_J | V_{\substack{\text{operator} \\ \text{equivalent}}}(J) | J M_J \rangle$$

We will consider the case of a 4f ion in ethyl sulphate which has trigonal symmetry. Since $L = 3$ and the shell is less than half full, we can couple no higher than Y_6^m in an expansion of $V_{crystal}$.

The potential that has the correct trigonal or 3-fold symmetry is:

$$V_{crystal} = A_0 + A_2^0 r^2 Y_2^0 + A_4^0 r^4 Y_4^0 + A_6^0 r^6 Y_6^0 + A_6^6 r^6 (Y_6^6 + Y_6^{-6})$$

Now we will have:

$$Y_6^6 \sim (x+iy)^6 \sim (J^+)^6 \quad ; \quad Y_6^{-6} \sim (x-iy)^6 \sim (J^-)^6$$

The other operator equivalents we shall just give their structure without going through the tedium of calculation:

$$Y_2^0 \sim (3z^2 - r^2) \rightarrow J_z^2, J^2$$

$$Y_4^0 \sim (35 z^6 - 30 z^2 r^2 + 3 r^4) \rightarrow J_z^2, J^2$$

$$Y_6^0 \sim (231 z^6 - 315 z^4 r^2 + 105 z^2 r^4 - 5 r^6) \rightarrow J_z^2, J^2$$

The reference to this work is:

Elliot and Stevens, Proc. Roy. Soc. A215, 437
A218, 553
A219, 387

LECTURE 16: 3-14-62

The Hund's Rule ground states for the rare earths go as:

$J = 0, 4, 6, 8, \cdots$ for an even number of electrons
$J = 5/2, 7/2, 9/2, \cdots$ for an odd number of electrons

We will do $J = 5/2$ for Ce^{3+} in ethyl sulphate and $J = 4$ for Pr^{3+} in same.

Do the Zeeman effect only in first order; $\mathcal{H}_z = g_J \mu_0 \vec{J} \cdot \vec{H}$, and take matrix elements of $V_{crystal} + \mathcal{H}_z$.

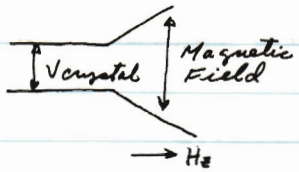
For $J = 4$, $M_J = -4, \cdots, 4$, the only off-diagonal connections for $V_{crystal}$ are: $4 \leftrightarrow -2$, $3 \leftrightarrow -3$, $2 \leftrightarrow -4$

because of $(L_+)^6$, $(L_-)^6$;

M_J \ M_J	4	-2	3	-3	2	-4	1	-1	0
4	$B_4 + 4g_J\mu_0 H_z$	C_1							
-2	C_1^*	$B_2 - 2g_J\mu_0 H_z$							
3			$B_3 + 3g_J\mu_0 H_z$	C_2					
-3			C_2^*	$B_3 - 3g_J\mu_0 H_z$					
2					$B_2 + 2g_J\mu_0 H_z$	C_3			
-4					C_3^*	$B_4 - 4g_J\mu_0 H_z$			
1							$B_1 + g_J\mu_0 H_z$		
-1								$B_1 - g_J\mu_0 H_z$	
0									B_0

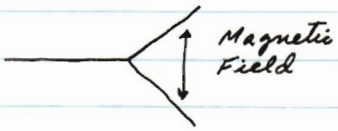
$J = 4$
$\vec{H} = H_z$

For the 2×2 boxes, the splitting is like:



The gap here is too wide for microwave resonance.

For the 1×1 part:



One cannot induce transitions here because $g_\perp \mu_0 h_x S'_x = 0$ and $g_{||} \mu_0 H_z S'_z$ is already diagonal in S_z.

However, experimentally we have a broad line here which suggests the interaction:

$$\mathcal{H} = g_{||} \mu_0 H_z S'_z + \Delta_x S_x' + \Delta_y S'_y$$

giving:

$$\mathcal{E} = \pm \left\{ \left(\frac{\mu_0}{2}\right)^2 g_{||}^2 H_z^2 + \frac{1}{4} (\Delta_x^2 + \Delta_y^2) \right\}^{1/2}$$

For $J = 5/2$, the crystal field connects no states and we will take:

$$\mathcal{H}_z = g_J \mu_0 \left\{ J_z H_z + \frac{1}{2} (J_+ H_- + J_- H_+) \right\}$$

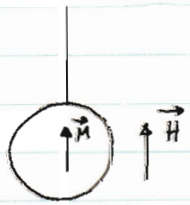
M_J \ M'_J	5/2	−5/2	3/2	−3/2	1/2	−1/2
5/2	$B_{5/2}$ $+\frac{5}{2} g_J \mu_0 H_z$					
−5/2		$B_{5/2}$ $-\frac{5}{2} g_J \mu_0 H_z$				
3/2			$B_{3/2}$ $+\frac{3}{2} g_J \mu_0 H_z$			
−3/2				$B_{3/2}$ $-\frac{3}{2} g_J \mu_0 H_z$		
1/2					$B_{1/2}$ $\frac{1}{2} g_J \mu_0 H_z$	$\frac{3}{2} g_J \mu_0 H_+$
−1/2					$\frac{3}{2} g_J \mu_0 H_-$	$B_{1/2}$ $-\frac{1}{2} g_J \mu_0 H_z$

We now consider briefly the Einstein - de Haas effect. We take as a model crystals of the iron group with a ground state of $S = 1/2$ and $\vec{H}$ along the tetragonal axis. The resultant energy levels can be written:

$$\mathcal{E} = \pm \frac{\mu_0}{2} H (2+\epsilon) \quad \text{from} \quad \mathcal{E} = \underset{\uparrow \text{spin } g}{2} \mu_0 H \left(\tfrac{1}{2}\right) + \underset{\uparrow \text{orbital } g}{1} \mu_0 H \left(\tfrac{\epsilon}{2}\right)$$

This suggests an average angular momentum in the z direction of $\bar{L}_z = \epsilon/2$. From a resonance experiment, the g factor would be $2+\epsilon$ and the splitting would be $\Delta\mathcal{E} = \mu_0 H (2+\epsilon)$.

The Einstein - de Haas effect is as follows: We suspend a body on a thread and propose to measure the average angular momentum or $\vec{M}$ by conservation requirements.



We apply $\vec{H}$ and let system come to equilibrium. Now drop $\vec{H}$ suddenly. There will be no torque as $\vec{H}$ and $\vec{M}$ are in the same direction ($\vec{T} \sim \vec{M} \times \vec{H}$). However, in order to conserve angular momentum the sphere must rotate and hence we can measure $\bar{L}$ directly which is the angular momentum the system had when magnetized. Now we can get an effective g factor by noticing:

$$\mu_0 g' = \frac{\overline{M}}{\overline{L}} = \frac{\overline{n\uparrow}\left(2\mu_0 \tfrac{1}{2} + \mu_0 \tfrac{\epsilon}{2}\right) (= \overline{M})}{\overline{n\uparrow}\left(\tfrac{1}{2} + \tfrac{\epsilon}{2}\right) (= \overline{L})}$$

where $\overline{n\uparrow}$ is the average number of spins up. Hence:

$$g' = \frac{1+\frac{\epsilon}{2}}{\frac{1}{2}(1+\epsilon)} = \frac{2+\epsilon}{1+\epsilon} \simeq (2+\epsilon)(1-\epsilon) \simeq (2-\epsilon)$$

for small ϵ. We get the same result obtained by Kittel and Van Vleck.

$$g - 2 = 2 - g'$$

LECTURE 17 : 3-16-62

The reference for this lecture is Van Vleck's book. We reproduce here a table of rare earth ions for convenience.

Number of f electrons		L	S	gJ	Meff (Hund's Rule)
Ce^{3+}	$4f^1$ $^2F_{5/2}$	3	1/2	6/7	2.54
Pr^{3+}	$4f^2$ $^3H_4$	5	1	4/5	3.58
Nd^{3+}	$4f^3$ $^4I_{9/2}$	6	3/2	8/11	3.62
Pm^{3+}	$4f^4$ $^5I_4$	6	2	3/2	2.68
Sm^{3+}	$4f^5$ $^6H_{5/2}$	5	5/2	2/7	.84
Eu^{3+}	$4f^6$ $^7F_0$	3	3	0	0
Tb^{3+}	$4f^8$ $^7F_6$	3	3	3/2	9.7
Dy^{3+}	$4f^9$ $^6H_{15/2}$	5	5/2	4/3	10.6
Ho^{3+}	$4f^{10}$ $^5I_8$	6	2	5/4	10.6
Er^{3+}	$4f^{11}$ $^4I_{15/2}$	6	3/2	6/5	9.6
Tm^{3+}	$4f^{12}$ $^3H_6$	5	1	7/6	7.6
Yb^{3+}	$4f^{13}$ $^2F_{7/2}$	3	1/2	3/7	4.5
	$4f^7$	0	7/2	2	7.94

Susceptibility in Crystal Fields

We will consider the two cases:

(1) $\mathcal{E}(LS) > V_{crystal} > \mathcal{H}_{so} > \mathcal{H}_z$ (3d ions, decouple L and S)

(2) $\mathcal{H}_{so} > V_{crystal} > \mathcal{H}_z$ (4f ions, couple L and S to form J)

We will use the Boltzmann Free Energy:

$$F = -NkT \ln \sum_i e^{-E_i/kT}$$

We will assume tetragonal symmetry, $S = 1/2$ and take for the spin Hamiltonian:

$$\mathcal{H} = g_{\parallel} \mu_0 H_z S_z + g_{\perp} \mu_0 (H_x S_x + H_y S_y) - \frac{\mu_0}{2} \vec{H} \cdot \vec{\vec{a}} \cdot \vec{H}$$

The eigenvalues of the problem are then:

$$\epsilon = \pm g(\theta) \frac{\mu_0}{2} H - \frac{\mu_0^2}{2} a(\theta) H^2$$

Recall the solution of the free ion case:

$$\chi_{para} = \frac{N g^2 \mu_0^2 J(J+1)}{3kT} + \frac{2N a \mu_0^2}{(2J+1)} \quad ; \quad a \sim \frac{|\langle 1|\mathcal{H}_z|1\rangle|^2}{\mathcal{H}_{so}}$$

We can take over this result exactly for our 2×2 problem here, obtaining:

$$\chi_{para} = \frac{N g^2(\theta) \mu_0^2 (\frac{1}{2})(\frac{3}{2})}{3kT} + \frac{2N a(\theta) \mu_0^2}{2} \quad ; \quad a(\theta) \sim \frac{|\langle 1|\mathcal{H}_z|1\rangle|^2}{V_{crystal}}$$

or:

$$\chi_{para} = \frac{N g^2(\theta) \mu_0^2}{4kT} + N a(\theta) \mu_0^2$$

Here g and a have angular dependence because of the crystal field.

Rare Earth Ions in Crystal Fields

Here the hierarchy of interactions is:

$$\mathcal{E}(LS) > \mathcal{H}_{so} > V_{crystal} > \mathcal{H}_z$$

Consider the free ion case first:

Shell > ½ full

Shell < ½ full

For most rare earth ions we can neglect the Van Vleck term in χ_{para} and get:

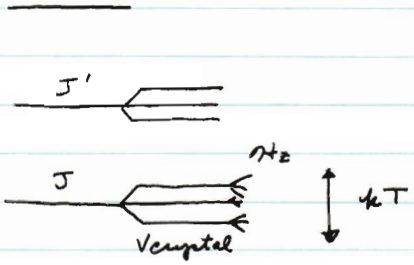
$$\chi_{curie} = \frac{N g_J^2 \mu_0^2 J(J+1)}{3kT} = \frac{N \mu_{eff}^2}{3kT}$$

Sm^{3+} and Eu^{3+} depart from a simple Curie's law because of a second order effect arising from the closeness of neighboring levels to the ground state, the separation being given essentially by:

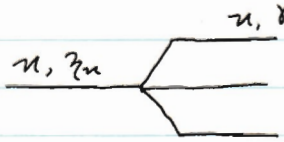
$$\lambda = \frac{\langle nl | \sum \mathcal{H}_{so} | nl \rangle}{2\delta}$$

In Eu^{3+} and Sm^{3+}, several of the lower levels are populated as well as the ground state.

Why are free ion values of μ_{eff} observed in crystal fields for the rare earth ions? The reason is that kT is greater than the splitting caused by $V_{crystal}$ and the net degrees of freedom when H is applied remain essentially the same as if there were no $V_{crystal}$.



The effect of $V_{crystal}$ is averaged out by the spread of kT. To see this, consider a hypothetical problem where we consider the abstract quantum numbers n, γ_n and γ_n.



n, γ_n could be crystal field quantum numbers.

$$F = NkT \sum_{n\gamma_n} e^{-\varepsilon(n,\gamma_n)/kT}$$

We have the eigenvalue problems: $\mathcal{H}_0 \psi(n,\gamma_n) = E_0(n)\psi(n,\gamma_n)$ and:

$$\{\mathcal{H}_0 + \mathcal{H}_1\}\psi(n,\gamma_n) = \varepsilon(n,\gamma_n)\psi(n,\gamma_n)$$

Using BWPT we obtain an effective Hamiltonian for $E(n, \gamma_n)$:

$$\langle n, \eta_n' | H_{eff} | n, \eta_n \rangle = E_0(n)\, \delta_{\eta_n \eta_n'} + \langle n, \eta_n' | H_1 | n, \eta_n \rangle + \sum_{n'' \eta_n''} \frac{\langle n, \eta_n' | H_1 | n'', \eta_n'' \rangle \langle n'', \eta_n'' | H_1 | n, \eta_n \rangle}{E_0(n) - E_0(n'')}$$

Now take into account that the spread of the split levels is small compared to kT. Then we can write F as:

$$F = -NkT \ln \sum_{n \gamma_n} e^{-E(n\gamma_n)/kT} = -NkT \ln \sum_n e^{-E_0(n)/kT} \sum_{\gamma_n} e^{-\{E(n\gamma_n) - E_0(n)\}/kT}$$

We can expand the $\sum_{\gamma_n}$ term around $E_0(n)$ because $\{E(\gamma_n n) - E_0(n)\}/kT \ll 1$. This term becomes:

$$\sum_{\gamma_n} \left[1 - \underbrace{\frac{\{E(\gamma_n n) - E_0(n)\}}{kT}}_{\text{This is essentially the trace of } E(\gamma_n n) \text{ and can be taken in the } \eta_n \text{ representation.}} + \frac{1}{2} \underbrace{\frac{\{E(n\gamma_n) - E_0(n)\}^2}{(kT)^2}}_{\text{Trace argument applies here also.}} \right]$$

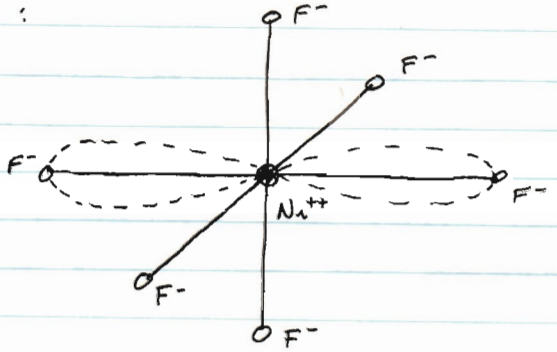
We can split off $V_{crystal}$ and H_Z and get a structure like:

$$\sum_{\eta_n} \left[1 + \sim \frac{V_{crystal}}{\Delta E} + \sim H + \sim H^2 \right]$$

which gives free ion result as $\frac{V_{crystal}}{\Delta E} \ll 1$.

Covalence Effects

Discrepancies appear in the crystal field theory when studies are made of the nuclear resonance in $KNiF_3$:



A hyperfine F^- structure due to the overlap of Ni^{++} electrons near the F nucleus is observed. Thus some extension of the ligand theory is required. Once overlap occurs, the Ni^{++} and F^- wave functions are no longer separately orthogonal and we must write wave functions that are linear combinations of Ni^{++} and F^- with enough arbitrary parameters in order to normalize. The wave functions used are 3d orbitals from Ni^{++} and the 2s, 2p orbitals from F^-. The linear combinations must be consistent with the crystal symmetry which involves finding wave functions for a group theoretical representation of the problem. We fill up these states with the required number of electrons and have empty states left over. We now must take into account exchange and correlation. This has been done by Sugano and Shulman, Proceedings of the Magnetism Conference, Kyoto, 1961.

LECTURE 18 : 3-19-62

Exchange Coupling of Ions in a Crystal

We will be interested in the interaction between neighboring paramagnetic ions in a crystal. The electron - election interaction or coulomb interaction is:

$$\sum_{i<j} \frac{e^2}{r_{ij}}$$

This will involve interactions between determinants.

Consider the product wave function:

$$\pi = u_1(1)\,\chi_1(1) \cdots u_N(N)\,\chi_N(N)$$

where the u's are orthonormal. The determinant formed from π can be written:

$$D = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P\pi$$

We can always write P in terms of pair permutations and these in terms of orbital and spin permutations:

$$P_{ij} = P_{ij}^{q} P_{ij}^{\sigma}$$

Now form $\langle D | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle$ and just consider the term:

$$\int \{ u_1(1)\chi_1(1) \cdots u_N(N)\chi_N(N) \}^* \sum_{i<j} \frac{e^2}{r_{ij}} (-1)\, u_1(2)\chi_1(2)\, u_2(1)\chi_2(1) \cdots d\tau$$

We see that this gives zero unless we have the term r_{12}. That is, we get a contribution only when we have the same π's or just one exchange difference between π's. Thus we can deduce the important relation:

$$\langle D | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle = \langle \pi | \sum_{i<j} \frac{e^2}{r_{ij}} \left[1 - P_{ij}^{q} P_{ij}^{\sigma} \right] | \pi \rangle$$

What about non-diagonal matrix elements? We can write the same expression:

$$\langle D' | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle = \langle \pi' | \sum_{i<j} \frac{e^2}{r_{ij}} \left[1 - P_{ij}^{q} P_{ij}^{\sigma} \right] | \pi \rangle$$

Now consider the matrix elements:

$$\left.\begin{aligned} \langle \alpha(i)\alpha(j) | P_{ij}^{\sigma} | \alpha(i)\alpha(j) \rangle &= 1 \\ \langle \beta(i)\beta(j) | P_{ij}^{\sigma} | \beta(i)\beta(j) \rangle &= 1 \\ \langle \alpha(i)\beta(j) | P_{ij}^{\sigma} | \alpha(j)\beta(i) \rangle &= 1 \end{aligned}\right\} \text{ These are the only non-vanishing spin matrix elements.}$$

Now consider the matrix elements of the operator: $\frac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j)$:

$$\langle \alpha(i)\alpha(j) | \tfrac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j) | \alpha(i)\alpha(j) \rangle = \tfrac{1}{2}(1+1) = 1$$

$$\langle \alpha(i)\beta(j) | \tfrac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j) | \alpha(j)\beta(i) \rangle = \tfrac{1}{2}\Big(4\underbrace{s_i^{+} s_j^{-}}_{1/2} + 4\underbrace{s_i^{-} s_j^{+}}_{0}\Big) = 1$$

Hence we can make the replacement: $P_{ij}^{\sigma} = \frac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j)$ and:

$$\langle D' | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle = \langle \pi' | \sum_{i<j} \frac{e^2}{r_{ij}} \left[1 - P_{ij}^{q} \tfrac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j) \right] | \pi \rangle$$

or, for the diagonal element we get:

$$\langle D | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle = \sum_{i<j} K_{ij} - \sum_{i<j} J_{ij} \tfrac{1}{2}(1 + 4\,\vec{s}_i \cdot \vec{s}_j)$$

removing the orbital part and leaving a spin operator.

$$K_{ij} = \int \psi_i^{*}(1)\,\psi_i(1)\,\frac{e^2}{r_{12}}\,\psi_j^{*}(2)\,\psi_j(2)\,d\tau$$

$$J_{ij} = \int \psi_i^{*}(1)\,\psi_i(2)\,\frac{e^2}{r_{12}}\,\psi_j^{*}(2)\,\psi_j(1)\,d\tau$$

This explains Hund's Rule and also ferromagnetic behaviour because spin alignment lowers energy.

Now consider two neighboring paramagnetic ions:

u ion, N electrons
Crystal q-numbers:
γ_u, S_u, $M_{Su} \to \psi_u(\gamma_u S_u M_{Su})$
Free ion q-numbers:
L_u, M_{Lu}, S_u, M_{Su}

v ion, M electrons
Crystal q-numbers
γ_v, S_v, $M_{Sv} \to \psi_v(\gamma_v S_v M_{Sv})$
Free ion q-numbers
L_v, M_{Lv}, S_v, M_{Sv}

Assume the wave functions of u, v to be orthogonal among themselves and each other. We want to form an antisymmetric linear combination of ψ_u, ψ_v assuming ψ_u, ψ_v to be previously antisymmetric among their own electrons so that permutations are now only between u and v:

$$\psi_{uv} = \eta \sum_{P_{uv}} (-1)^{P_{uv}} P_{uv}\, \psi_u \psi_v$$

Now consider: $\langle \psi_{u'v'} | \sum_{i_u j_v} \frac{e^2}{r_{i_u j_v}} | \psi_{uv} \rangle$

$$= \langle \psi_{u'} \psi_{v'} | \sum_{i_u j_v} \frac{e^2}{r_{i_u j_v}} \left[1 - P^q_{i_u j_v} \tfrac{1}{2} (1 + 4\, \vec{s}_{i_u} \cdot \vec{s}_{j_v}) \right] | \psi_u \psi_v \rangle$$

$$\Rightarrow \langle S_u S_v M_{Su'} M_{Sv'} | K(\gamma_{u'} \gamma_{v'}; \gamma_u \gamma_v) - J'(\gamma_{u'} \gamma_{v'}; \gamma_u \gamma_v)$$

$$- J(\gamma_{u'} \gamma_{v'}; \gamma_u \gamma_v)\, \vec{S}_u \cdot \vec{S}_v | S_u S_v M_{Su} M_{Sv} \rangle$$

using the WE Theorem. $J \vec{S}_u \cdot \vec{S}_v$ is the effective exchange interaction. If we consider the diagonal interaction of the ground states, we have an exchange contribution to the ground state energy of $-J(\gamma_u^0 \gamma_v^0; \gamma_u^0 \gamma_v^0) \vec{S}_u \cdot \vec{S}_v$. This is a direct, ferromagnetic type interaction.

Now consider the effective interaction including so coupling using BWPT. The interaction term is:

$$\sum_{i \in u} \frac{e^2}{r_{i_u j_v}} + \lambda_u \vec{L}_u \cdot \vec{S}_u + \lambda_v \vec{L}_v \cdot \vec{S}_v$$

In third order BWPT, we have structures like:

$$\frac{\langle \gamma_u^0 \gamma_x^0 | \lambda_u \vec{L}_u \cdot \vec{S}_u | \gamma_u' \gamma_x^0 \rangle \langle \gamma_u' \gamma_x^0 | -J \vec{S}_u \cdot \vec{S}_x | \gamma_u^0 \gamma_x'' \rangle \langle \gamma_u^0 \gamma_x'' | \lambda_x \vec{L}_x \cdot \vec{S}_x | \gamma_u^0 \gamma_x^0 \rangle}{\text{Energy Denominator}}$$

These structures give rise to anisotropic pseudo-dipole-dipole and pseudo-quadropole interactions. The final form of the effective interaction is:

$$\mathcal{H}_{\substack{\text{anisotropic} \\ \text{exchange}}} = \sum_{kl} \left\{ \Gamma_u^{kl} S_u^k (\vec{S}_u \cdot \vec{S}_x) S_u^l + \Gamma_x^{kl} S_x^k (\vec{S}_u \cdot \vec{S}_x) S_x^l + \Gamma_{ux}^{kl} S_u^k (\vec{S}_u \cdot \vec{S}_x) S_x^l + \Gamma_{xu}^{kl} S_x^k (\vec{S}_u \cdot \vec{S}_x) S_u^l \right\}$$

The direct exchange is: $\mathcal{H}_{\substack{\text{direct} \\ \text{exchange}}} = -J(\gamma_u^0 \gamma_x^0; \gamma_u^0 \gamma_x^0) \vec{S}_u \cdot \vec{S}_x$

From second order BWPT, we have structures like:

$$\frac{\lambda_u \vec{L}_u(\gamma_u^0 \gamma_u') \cdot \vec{S} \{ -J(\gamma_u' \gamma_x^0; \gamma_u^0 \gamma_x^0) \vec{S}_u \cdot \vec{S}_x \}}{\mathcal{E}(\gamma_u^0 \gamma_x^0) - \mathcal{E}(\gamma_u' \gamma_x^0)}$$

which can be written in effective form as:

$$\mathcal{H}^{(2)} = \vec{C}_u \cdot \vec{S}_u (\vec{S}_u \cdot \vec{S}_x) + (\vec{S}_u \cdot \vec{S}_x) \vec{C}_u^* \cdot \vec{S}_u + \text{terms in } x$$

If we define: $\lambda \vec{D}_u = \frac{1}{2}(\vec{C}_u - \vec{C}_u^*)$

$\vec{E}_u = \frac{1}{2}(\vec{C}_u + \vec{C}_u^*)$

then we can write:

$$\mathcal{H}^{(2)} = \lambda \vec{D}_u \cdot \vec{S}_u (\vec{S}_u \cdot \vec{S}_x) - \lambda (\vec{S}_u \cdot \vec{S}_x) \vec{D}_u \cdot \vec{S}_u + \vec{E}_u \cdot \vec{S}_u (\vec{S}_u \cdot \vec{S}_x) + (\vec{S}_u \cdot \vec{S}_x) \vec{E}_u \cdot \vec{S}_u + \text{terms in } x$$

$\vec{D}_u \cdot \vec{S}_u (\vec{S}_u \cdot \vec{S}_x) - (\vec{S}_u \cdot \vec{S}_x) \vec{D}_u \cdot \vec{S}_u \Rightarrow \vec{D}_u \cdot (\vec{S}_u \times \vec{S}_x)$, this type of interaction has been recently discovered in antiferromagnets.

LECTURE 19 : 3-21-62

Paramagnetic Resonance

We will now develop the density matrix methods appropriate to the subject. We sketch time dependent perturbation theory:

$i\hbar\dot{\psi} = \mathcal{H}\psi$; $\mathcal{H}_0\psi_n = E_n\psi_n$; $\mathcal{H}_0$ time independent.

Use: $\psi = \sum_n a_n(t)\psi_n \rightarrow i\hbar\sum_n \dot{a}_n\psi_n = \sum_n \mathcal{H}a_n\psi_n$

Operate with: $\int \psi_j^* d\tau$ getting:

$$i\hbar\dot{a}_k = \sum_l a_l \mathcal{H}_{kl} \quad \text{or} \quad i\hbar\dot{a}_j = \sum_l a_l \mathcal{H}_{jl}$$

We want the equation for the density matrix, defined as $\rho_{kj} \equiv a_k^* a_j$, hence we form:

$$i\hbar\dot{a}_j a_k^* = \sum_l a_l a_k^* \mathcal{H}_{jl}$$

and: $i\hbar a_j\dot{a}_k^* = -\sum_l a_j a_k^* \mathcal{H}_{lk}$, and get:

$$i\hbar\dot{\rho}_{jk} = \sum_l (\rho_{lk}\mathcal{H}_{jl} - \rho_{jl}\mathcal{H}_{lk}) = (\mathcal{H}\rho - \rho\mathcal{H})_{jk}$$

or: $i\hbar\dot{\rho} = [\mathcal{H}, \rho]$

For equilibrium, we expect $\dot{\rho}^\circ_{kj} = 0$, $\rho_{nn} = e^{-E_n/kT}$.

Consider the terms that should comprise $\mathcal{H}$:

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_B + \mathcal{H}'$

- $\mathcal{H}_0$: time independent and independent of thermal background. Includes DC fields.
- $\mathcal{H}_1$: energy conserving term - elastic scattering.
- $\mathcal{H}_B$: Bath - could be spin-lattice interaction with phonons or nucleus - conduction electron interaction.
- $\mathcal{H}'$: time dependent perturbation by external rf field.

Consider the Liouville equation with H_0 first:

$$i\hbar \dot{\rho}_{aa} = \mathcal{H}^{\circ}_{aa}\rho_{aa} - \rho_{aa}\mathcal{H}^{\circ}_{aa} = 0$$

$$i\hbar \dot{\rho}_{ab} = \mathcal{H}^{\circ}_{aa}\rho_{ab} - \mathcal{H}^{\circ}_{bb}\rho_{ab} = 0 \text{ for thermal equilibrium.}$$

In certain systems where the period of observation is shorter than the relaxation time of the system (in nuclear resonance, the time of measurements is μsec while $\tau \sim$ msec), we can neglect H_1 and H_B and write:

$$H = H_0 + H'$$

Consider a simple spin system (two levels) obeying these conditions. We have:

$$H_0 = g\mu_0 S_z H_z \Rightarrow \pm \frac{g\mu_0}{2} H_z$$

Apply a rotating magnetic field:

$$H' = g\mu_0 (S_x h\cos\omega t + S_y h \sin\omega t) \quad \text{(See Abragham)}$$

or: $$H' = g\mu_0 \left[\frac{S_+ + S_-}{2} h\cos\omega t + \frac{S_+ - S_-}{2i} h \sin\omega t \right]$$

$$H' = \frac{g\mu_0 h}{2}\left[S_+ e^{-i\omega t} + S_- e^{i\omega t} \right]$$

Hence we will have only off-diagonal matrix elements of H': Then:

$$i\hbar \dot{\rho}_{aa} = \mathcal{H}'_{ab}\rho_{ba} - \rho_{ab}\mathcal{H}'_{ba}$$

$$i\hbar \dot{\rho}_{ab} = \mathcal{H}^{\circ}_{aa}\rho_{ab} - \rho_{ab}\mathcal{H}^{\circ}_{bb} + \mathcal{H}'_{ab}\rho_{bb} - \rho_{aa}\mathcal{H}'_{ab}$$

Call $a \rightarrow$ spin up and $b \rightarrow$ spin down. Then:

$$\mathcal{H}'_{ab} = \frac{g\mu_0 h}{2} e^{-i\omega t} \quad ; \quad \mathcal{H}'_{ba} = \frac{g\mu_0 h}{2} e^{i\omega t}$$

Form:

$$i\hbar\,(\dot{\rho}_{aa} - \dot{\rho}_{bb}) = 2\,\mathcal{H}'_{ab}\,\rho_{ba} - 2\,\mathcal{H}'_{ba}\,\rho_{ab}$$

$$i\hbar\,\dot{\rho}_{ab} = \hbar\,\omega_{ab}\,\rho_{ab} - \mathcal{H}'_{ab}\,(\rho_{aa} - \rho_{bb})$$

Now assume the solutions:

$$(\rho_{aa} - \rho_{bb}) = A\,e^{i\Omega t} + B\,e^{-i\Omega t} + E$$

$$\rho_{ab} = e^{-i\omega t}\left\{C\,e^{i\Omega t} + D\,e^{-i\Omega t} + F\right\}$$

We obtain on substitution:

$$F = F^* \;;\quad E = \frac{\hbar(\omega_{ab} - \omega)}{|\mathcal{H}'_{ab}|}\,F \;,\quad A = B \;;$$

$$C = \frac{-|\mathcal{H}'_{ab}|\,A}{\hbar(\omega - \Omega - \omega_{ab})} \;;\quad D = \frac{-|\mathcal{H}'_{ab}|\,A}{\hbar(\omega + \Omega - \omega_{ab})}$$

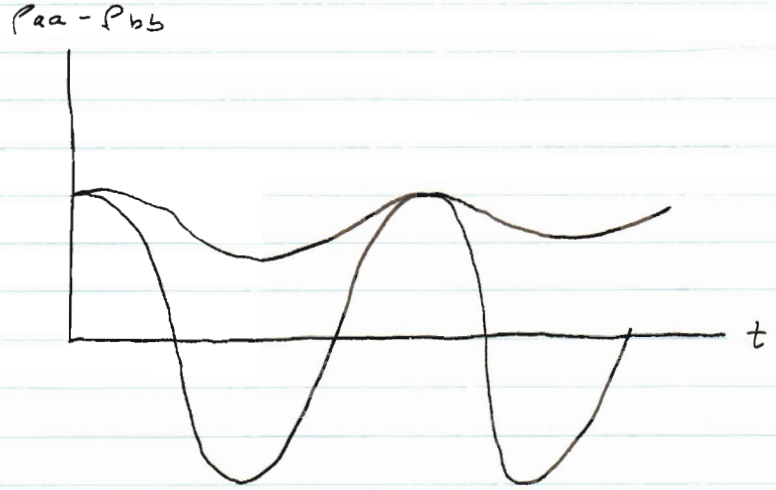
with:

$$\Omega = \left\{(\omega - \omega_{ab})^2 + \frac{4\,|\mathcal{H}'_{ab}|^2}{\hbar^2}\right\}^{1/2}$$

Using the boundary conditions: $\left.\begin{aligned}\rho_{aa} - \rho_{bb} &= \mathring{\rho}_{aa} - \mathring{\rho}_{bb}\\ \rho_{ab} &= 0\end{aligned}\right\}\ t = 0$

we find:

$$\rho_{aa} - \rho_{bb} = \frac{\mathring{\rho}_{aa} - \mathring{\rho}_{bb}}{\Omega^2}\left\{\frac{4\,|\mathcal{H}'_{ab}|^2}{\hbar^2}\cos\Omega t + (\omega - \omega_{ab})^2\right\}$$



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Consider another property of ρ involved in the expectation value of some operator v :

$$\int \psi^*(t)\, v\, \psi(t)\, d\tau = \int \sum_i a_i^* \psi_i^*\, v \sum_j a_j \psi_j\, d\tau = \sum_{ij} v_{ij} \rho_{ji}$$

$$= \mathrm{Tr}\{v\rho(t)\} = \langle v(t) \rangle$$

Returning to the spin doublet problem, we assumed that time of observation << relaxation time and obtained an oscillatory $\rho_{aa} - \rho_{bb}$. We can include bath effects thru $\mathcal{H}_B$ in the second order. Here we replace the Liouville equation by:

$$i\hbar \dot{\rho} = [\mathcal{H}_0 + \mathcal{H}', \rho] - i\hbar R\rho$$

$$i\hbar R\rho \rightarrow -i\hbar \sum_{kl} R_{ij}^{kl} \rho_{kl}$$

R_{ij}^{kl} is called the relaxation matrix, which can be reduced by some assumptions to a form coupling only two levels :

$$i\hbar \dot{\rho}_{ij} = [\mathcal{H}_0 + \mathcal{H}', \rho]_{ij} - i\hbar R_{ij} \rho_{ij} \quad \text{(off diagonal)}$$

and $i\hbar \dot{\rho}_{ii} = [\mathcal{H}_0 + \mathcal{H}', \rho]_{ii} - i\hbar \sum_j R_{i\to j} \rho_{ii} + i\hbar \sum_j R_{j\to i} \rho_{jj}$

(diagonal)

The relaxation is proportional to the initial density motivating the about to follow relation:

$$\frac{R_{j\to i}}{R_{i\to j}} = \frac{\rho_{ij}^0}{\rho_{jj}^0} \quad ?$$

We apply these results to the two level problem.

$$\imath\hbar\,\dot{\rho}_{ab} = \hbar\,\omega_{ab}\,\rho_{ab} + \mathcal{H}'_{ab}(\rho_{bb} - \rho_{aa}) - \imath\hbar\,R_{ab}\,\rho_{ab}$$

$$\imath\hbar\,(\dot{\rho}_{aa} - \dot{\rho}_{bb}) = 2\,\mathcal{H}'_{ab}\,\rho_{aa} - 2\,\mathcal{H}'_{ba}\,\rho_{ab} - \imath\hbar\,2\,R_{a\to b}\,\rho_{aa} + \imath\hbar\,2\,R_{b\to a}\,\rho_{bb}$$

Using $\rho_{aa} + \rho_{bb} = 1$, we get a structure like:

$$-(R_{a\to b} + R_{b\to a})\,\imath\hbar\left[(\rho_{aa} - \rho_{bb}) - (\rho^{\circ}_{aa} - \rho^{\circ}_{bb})\right]$$

This allows us to define:

$$(R_{a\to b} + R_{b\to a}) = \frac{1}{T_1} \quad ; \qquad R_{ab} = \frac{1}{T_2}$$

We take for solutions the same expressions as last time except now we anticipate that $e^{\pm\imath\omega t}$ will disappear from the steady state solution. We find:

$$(\rho_{aa} - \rho_{bb}) = \frac{(\rho^{\circ}_{aa} - \rho^{\circ}_{bb})\left[(\omega - \omega_{ab})^2 + \frac{1}{T_2^2}\right]}{(\omega - \omega_{ab})^2 + \frac{1}{T_2^2} + 4\,\frac{|\mathcal{H}'_{ab}|}{\hbar^2}\,\frac{T_1}{T_2}}$$

Note that $\frac{4|\mathcal{H}'_{ab}|}{\hbar^2}\frac{T_1}{T_2}$ is the saturation term giving equilibrium when $h = 0$. Also:

$$\rho_{ab} = \frac{-e^{-\imath\omega t}\,|\mathcal{H}'_{ab}|/\hbar\;\;(\rho_{aa} - \rho_{bb})}{(\omega - \omega_{ab}) + \frac{\imath}{T_2}}$$

Now the power absorbed is given by:

$$P_{abs} = -\vec{h}\cdot\frac{d\vec{m}(t)}{dt}$$

where $\vec{m}(t) = \rho_{ab}\,\vec{m}_{ba} + \rho_{ba}\,\vec{m}_{ab}$; $\vec{m} = -\gamma\,\mu_0\,\vec{S}$

Hence:

$$P_{abs} = \frac{\gamma\,\mu_0\,h^2\,\frac{\omega}{T_2}\,\langle M_z\rangle}{(\omega - \omega_{ab})^2 + \frac{1}{T_2^2}}$$

The Bloch - Bloembergen Relaxation Equation

Take $i\hbar\dot{\rho} = [\mathcal{H}, \rho] - i\hbar R\rho$ and $\mathcal{H} = g\mu_0 \vec{S}\cdot\vec{H}$

Now write the equations of motion for $\langle \vec{S}(t)\rangle = \vec{S}_{ab}\rho_{ba} + \vec{S}_{ba}\rho_{ab}$, use the Liouville equation for $\dot{\rho}_{ba}$ and $\dot{\rho}_{ba}$ and get:

$$\frac{d\langle S_z\rangle}{dt} = -\frac{g\mu_0}{\hbar}\left[\langle\vec{S}\rangle \times \vec{H}\right]_z - \frac{\langle S_z\rangle - \langle S_z^0\rangle}{T_1}$$

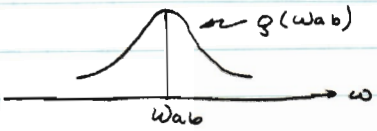
$$\frac{d\langle S_x\rangle}{dt} = -\frac{g\mu_0}{\hbar}\left[\langle\vec{S}\rangle \times \vec{H}\right]_x - \frac{\langle S_x\rangle}{T_2}$$

in which we have used: $-i\hbar\frac{d\vec{S}}{dt} = [\mathcal{H}, \vec{S}]$

Now include $\mathcal{H}_1$ which could be a dipole-dipole or exchange interaction. This gives line broadening and instead of ω_{ab} (sharp line), we have a line width given by $g(\omega_{ab})$ so that $\int g(\omega_{ab})\, d\omega_{ab} = 1$. Then the power absorbed is:

$$P_{abs} = \int_{-\infty}^{\infty} \frac{g(\omega_{ab})\, g\mu_0 h^2 \frac{\omega}{T_2}\langle M_z\rangle\, d\omega_{ab}}{(\omega-\omega_{ab})^2 + \frac{1}{T_2^2}}$$

If $g(\omega_{ab})$ is slowly varying; then $g(\omega_{ab}) \to g(\omega)$ and:



$$P_{abs} = g(\omega)\, g\mu_0 h^2 \frac{\omega}{T_2}\langle M_z\rangle \int_{-\infty}^{\infty} \frac{d\omega_{ab}}{(\omega-\omega_{ab})^2 + \frac{1}{T_2^2}}$$

or:

$$P_{abs} = g\mu_0 h^2 \omega \langle M_z\rangle\, g(\omega)$$

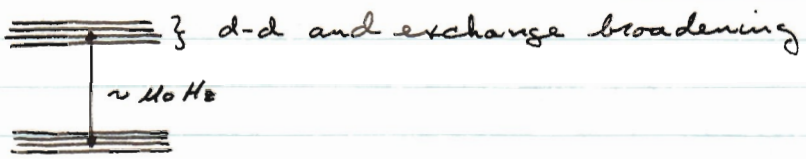
Note that there is no longer any T_2 and we have lumped line breadth effects into $g(\omega)$.

Van Vleck's Method of Moments

Suppose we write down a Hamiltonian that includes dipole-dipole and exchange broadening:

$$\mathcal{H} = \underbrace{\sum_i g_i \mu_0 \vec{S}_i \cdot \vec{H}}_{\mathcal{H}_0} + \underbrace{\sum_{i<j} \frac{g_i g_j \mu_0^2}{r_{ij}^3}\left[\vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij})\right] + \sum_{i<j} J_{ij}\, \vec{S}_i \cdot \vec{S}_j}_{\mathcal{H}_1}$$

Take $\vec{H} = H_z$ and $\mathcal{H}' = \sum_i g_i \mu_0 S_{ix} h = -M_x h$. The spin doublet looks something like:



Now, instead of getting $g(\omega)$ we try to calculate the moments $\langle\omega^2\rangle$, $\langle\omega^4\rangle$, ... of the frequency distribution. This would be given by:

$$\langle\omega^2\rangle = \frac{\sum_{ij} \omega_{ij}^2 |M_{xij}|^2}{\sum_{ij} |M_{xij}|^2}$$

where:

$|M_{xij}|^2$ is the matrix element of the transition:

$$M_{xij} = \langle i | g \mu_0 h S_x | j \rangle.$$

Now we can write:

$$\langle\omega^2\rangle = \frac{1}{\hbar^2} \frac{\sum_{ij} (E_i - E_j)^2 M_{xij} M_{xji}}{\sum_{ij} M_{xij} M_{xji}}$$

$$= \frac{1}{\hbar^2} \frac{\sum_{ij} [\mathcal{H}, M_x]_{ij} [\mathcal{H}, M_x]_{ji}}{\sum_{ij} M_{xij} M_{xji}}$$

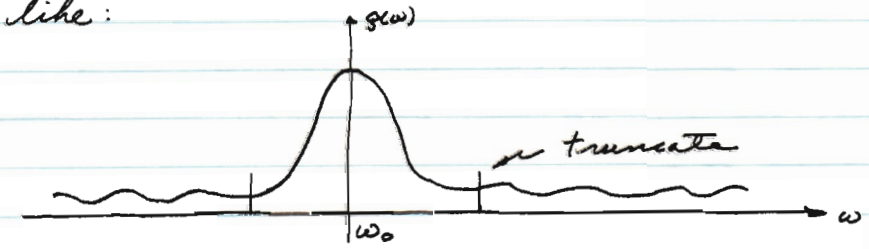
$$\text{or:} \quad \langle \omega^2 \rangle = \frac{\frac{1}{\hbar^2} \mathrm{Tr}\left\{ [\mathcal{H}, M_x]^2 \right\}}{\mathrm{Tr}\, M_x^2}$$

Now we can evaluate the trace in any convenient representation and the easiest one to choose is one in which S_z is diagonal.

Similarly:

$$\langle \omega^4 \rangle = \frac{\frac{1}{\hbar^4} \mathrm{Tr}\left\{ [\mathcal{H}, [\mathcal{H}, M_x]]^2 \right\}}{\mathrm{Tr}\, M_x^2}$$

Now the second moment, $\langle \Delta\omega^2 \rangle$, and the fourth moment, $\langle \Delta\omega^4 \rangle$, of the line distributions can be obtained from the above. The recorder trace of $g(\omega)$ looks like:



One has to truncate the tails because we would get too much of a weighting from $\mathcal{H}_1$, which is not observed experimentally, due to weak transitions to other levels. That is, consider the dipole-dipole part of $\mathcal{H}_1$:

$$\mathcal{H}_{d\text{-}d} \sim \underbrace{S_{iz} S_{jz}}_{U} + \underbrace{S_i^+ S_i^-}_{V} + \underbrace{S_{iz} S_j^+,\ S_i^+ S_{jz}^+,\ S_i^- S_j^-}_{W}$$

Consider a W term. Each would give a weak line far from ω_0. Thus we must cut off $\mathcal{H}'$ to get rid of weighting to $g(\omega)$ from lines far from ω_0. This amounts to throwing out W from $\mathcal{H}_{d\text{-}d}$. Therefore:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{truncated}}$$

Reference: J. H. Van Vleck, PR 74, 1168 (1948).

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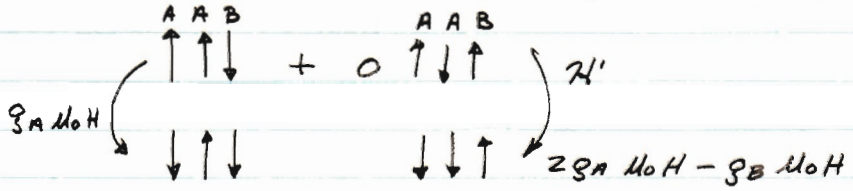
We have seen that we have had to truncate the dipole-dipole interaction term in order to prevent undue weighting of $g(\omega)$. What about exchange interaction? Note:

$$\left[J_{12}\, \vec{S}_1 \cdot \vec{S}_2 ,\ (S_{1x} + S_{2x}) \right] = 0$$

so that exchange does not contribute to $\langle \omega^2 \rangle$ for identical spins, however, it does effect $\langle \omega^4 \rangle$ and it actually narrows the line. This is called exchange narrowing and occurs for identical spins only.

For more than one species of spin:



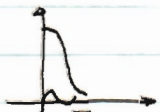
We cannot include the term V in $\mathcal{H}$ truncated. The exchange term no longer commutes with S_x so that we can have a contribution to $\langle \omega^2 \rangle$ and get exchange broadening.

Applying this theory to NMR, taking $\mathcal{H}_1 (U+V)$ with no exchange (polycrystalline material), one finds:

$$\frac{\langle \Delta\omega^4 \rangle^{1/4}}{\langle \Delta\omega^2 \rangle^{1/2}} = 1.25$$

For a gaussian line, this ratio is 1.32. Experimentally this ratio is about 1.22.

Low Magnetic Field:



wings now fall close to ω_0 so cannot truncate $\mathcal{H}_1$

$$\frac{\langle \Delta\omega^2 \rangle_{\text{no truncation}}}{\langle \Delta\omega^2 \rangle_{U+V}} = \frac{10}{3} \quad \left(\frac{10}{3} \text{ effect} \right)$$

High Magnetic Field; Non Identical Spins:

What are identical spins?

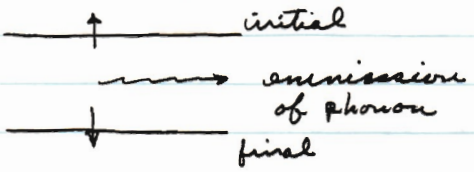
$$\frac{\langle \Delta\omega^2 \rangle_U \text{ (non-identical)}}{\langle \Delta\omega^2 \rangle_{U+V}} = \frac{4}{9} \quad \left(\frac{4}{9} \text{ effect} \right)$$

Relaxation Mechanisms

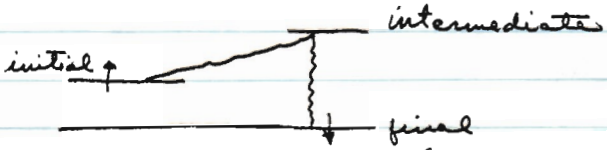
Nuclear spins relax thru coupling with electron spins via the $A\vec{I}\cdot\vec{S}$ interaction. The non-thermal equilibrium of nuclear spins causes a non-thermal equilibrium of electron spins which is then dissapated by the usual means thru electron-phonon interaction.

Usually, the thermal equilibrium of the electrons is restored thru one or two phonon processes.

1 phonon process



2 phonon process



Raman process (2 phonons)

In the crystal field theory:

$$\mathcal{H} = V^{\circ}_{crystal} + \lambda\vec{L}\cdot\vec{S} + \mathcal{H}_Z + \underbrace{V'_{crystal}\, e^{i\omega t}}_{\text{lattice vibration term}}$$

Suppose we have excited transitions thru an rf field. How is equilibrium restored? For a one-phonon process, we can modify the Spin Hamiltonian.

$$\mathcal{H} = \mu_0\, \vec{S}\cdot\overleftrightarrow{g}\cdot\vec{H} + D S_z^2$$

with $\overleftrightarrow{g} = \overleftrightarrow{g}_0 + \frac{\partial \overleftrightarrow{g}}{\partial\, strain}\, strain\, e^{i\omega t}$

One cannot decribe the two phonon process by a modification of the Spin Hamiltonian when the intermediate state is another crystal field state.

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IV. Magnetic Properties of Bloch Electrons

The complete Hamiltonian is:

$$\mathcal{H} = \sum_i \frac{1}{2m}\left(\vec{p}_i + \frac{e}{c}\vec{A}_i(\vec{r}_i)\right)^2 + \sum_i -eV_0(\vec{r}_i) + \sum_{i<j}\frac{e^2}{r_{ij}}$$

$$- \frac{\mu_0}{mc}\sum_i \vec{S}_i \cdot \nabla V(\vec{r}_i) \times \vec{p}_i + \sum_i 2\mu_0 \vec{S}_i \cdot \vec{H}$$

$$+ \mathcal{H}_{HFS} + \mathcal{H}_{NZ} + \mathcal{H}_Q$$

Even when we ignore the magnetic field and nuclear interactions the problem is still difficult to handle. We can approach it by Hartree-Fock methods, and convert to a one electron problem by considering an average periodic potential. The one electron Hamiltonian is:

$$\mathcal{H} = \frac{p^2}{2m} + (-eV(\vec{r})) - \frac{\mu_0}{mc}\vec{s}\cdot\nabla V(\vec{r}) \times \vec{p}$$

The proper representation is:

$$\mathcal{H}\, b_{n\vec{k}}(\vec{r}) = \varepsilon_n(\vec{k})\, b_{n\vec{k}}(\vec{r})$$

where $b_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$; $u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{R})$

Operating with the crystal translation operator gives:

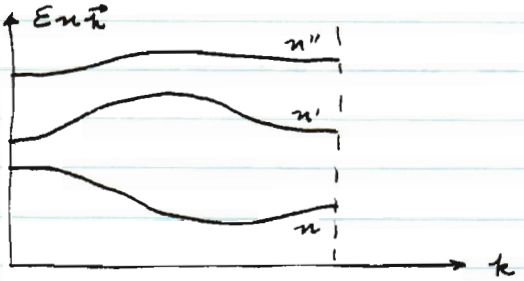
$$T\mathcal{H}\psi = T\varepsilon\psi \quad ; \quad \mathcal{H}(T\psi) = \varepsilon(T\psi)$$

or $T\psi = c\psi$ if ψ is non-degenerate. For Bloch functions:

$$T\, b_{n\vec{k}}(\vec{r}) = b_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r}+\vec{R})\, e^{i\vec{k}\cdot(\vec{r}+\vec{R})}$$

$$= e^{i\vec{k}\cdot\vec{R}}\, b_{n\vec{k}}(\vec{r})$$

The plot of the dispersion relation is:



Each band can be thought of as retaining some of the characteristics of the orbital from which the band is comprised.

In going from this one-electron model to many electrons, we use a determinantial wave functions of Bloch functions for all electrons that fill a band to a given level. We will get some exchange and correlation effects upon using the coulomb interaction term of the original Hamiltonian.

Application of Magnetic Field:

Consider that $\vec{k}$ behaves as a crystal momentum. This allows us to devise a band Hamiltonian from $E_n(\vec{k})$, that is:

$$\mathcal{H}_n\left(\frac{\vec{p}}{\hbar}\right) \rightarrow E_n(\vec{k})$$

Then in the presence of a magnetic field we are motivated to write:

$$\mathcal{H}_n^{\text{symmetrized}}\left(\frac{1}{\hbar}\left\{\vec{p}+\frac{e}{c}\vec{A}\right\}\right)\psi + \mu_0 \vec{S}\cdot\vec{\vec{g}}\cdot\vec{H}\,\psi = \mathcal{E}\psi$$

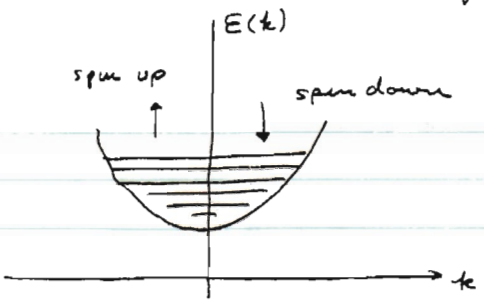
We will justify this form later.

Pauli Paramagnetism

We consider just the spin part of the band Hamiltonian.

$$\mu_0 \vec{S}\cdot\vec{\vec{g}}\cdot\vec{H}\,\psi = \mathcal{E}\psi \quad ; \quad \mathcal{E} = \pm g(\theta,\varphi)\frac{\mu_0 H}{2}$$

The band occupancy is governed by Fermi statistics:



$$f(\mathcal{E}_i) = \frac{1}{1 + e^{\beta(\mathcal{E}_i - \xi)}} \; ; \; \beta = \frac{1}{kT}$$

and ξ = Fermi energy

$$\sum_n f(\mathcal{E}_i) = N$$

The total band Hamiltonian eigenvalues are:

$$\mathcal{E}_n(\Gamma, H) \pm \frac{\mu_0}{2} g(\theta, \varphi) H$$

We take the liberty of replacing $\mathcal{E}_n(\Gamma, H)$ by $\mathcal{E}_n(\vec{k})$ for small H. This allows us to separate the diamagnetic and paramagnetic parts. Thus the eigenvalues are:

$$\mathcal{E} = \mathcal{E}_n(\vec{k}) + g\frac{\mu_0 H}{2} \; ; \; \mathcal{E} = \mathcal{E}_n(\vec{k}) - \frac{g\mu_0 H}{2}$$

The total magnetic moment is:

$$M = \int \left[f\left\{\mathcal{E}(\vec{k}) + \frac{g\mu_0 H}{2}\right\}\left\{-\frac{g\mu_0}{2}\right\} + f\left\{\mathcal{E}(\vec{k}) - \frac{g\mu_0 H}{2}\right\}\left\{\frac{g\mu_0}{2}\right\}\right] \frac{V}{2} n(\vec{k})\, d\vec{k}$$

For simple spherical energy surfaces:

$$dn(\vec{k}) = \frac{2V}{h^3} d\vec{p} = \frac{2}{h^3} V h^3 d\vec{k} = \frac{2V}{(2\pi)^3} d\vec{k}$$

or $n(\vec{k}) = \frac{2}{(2\pi)^3}$.

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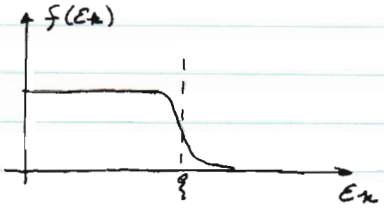
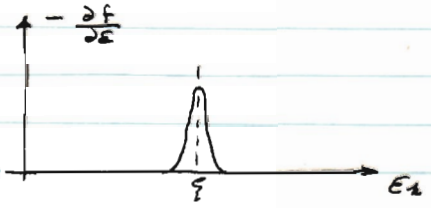
Now, for small fields we can expand the Fermi functions in M, the magnetic moment, and obtain:

$$M = \left(-\frac{g\mu_0}{2}\right)\int\left[f(\varepsilon_k) + \frac{\partial f}{\partial \varepsilon}\left(g\frac{\mu_0 H}{2}\right) - f(\varepsilon_k) + \frac{\partial f}{\partial \varepsilon}\left(\frac{g\mu_0 H}{2}\right)\right]\frac{V n(\vec{k})\, d\vec{k}}{2}$$

$$= -\left(\frac{g\mu_0}{2}\right)^2 H V \int \frac{\partial f}{\partial \varepsilon}\, n(\vec{k})\, d\vec{k}$$

Recall some of the properties of $f(\varepsilon_k)$:





We now want to change the independent variable from $\vec{k}$ to energy.

$$d\vec{k} = dA\, dk_\perp \qquad (\perp \text{ to constant } \varepsilon \text{ surface})$$

$$d\vec{k} = dA\, \frac{dk_\perp}{d\varepsilon}\, d\varepsilon$$

Then:

$$M = -\left(\frac{g\mu_0}{2}\right)^2 H V \int \frac{\partial f}{\partial \varepsilon}\, n(\varepsilon)\, d\varepsilon$$

If $n(\varepsilon)$ is slowly varying with respect to $\frac{\partial f}{\partial \varepsilon}$:

$$M = -\left(\frac{g\mu_0}{2}\right)^2 H V\, n(\zeta) \underbrace{\int \frac{\partial f}{\partial \varepsilon}\, d\varepsilon}_{f(\varepsilon)\Big|_0^\infty} = \left(\frac{g\mu_0}{2}\right)^2 H V\, n(\zeta)$$

and the Pauli paramagnetic susceptibility is:

$$\chi_{para} = \left(\frac{g\mu_0}{2}\right)^2 n(\zeta)$$

We can also approach Pauli Paramagnetism through the Helmholtz free energy in a more exact manner. Let ε^L denote the Landau levels energy.

$$\varepsilon_L = \varepsilon_L^L(H) \pm \frac{\mu_0 g H}{2}$$

$$F = N\xi - kT \sum_L' \ln\left\{1 + e^{-(\varepsilon_L - \xi)\beta}\right\}$$

$$= N\xi - kT \sum_L' \ln\left\{1 + e^{-(\varepsilon_L^L(H) - \xi)\beta}\, e^{-\frac{\mu_0}{2} g H \beta}\right\}$$

$$- kT \sum_L' \ln\left\{1 + e^{-(\varepsilon_L^L(H) - \xi)\beta}\, e^{\frac{\mu_0}{2} g H \beta}\right\}$$

Assume low magnetic fields so that we may expand the spin exponentials. Let $x_L = e^{-(\varepsilon_L^L(H) - \xi)\beta}$, $y = \frac{\mu_0}{2} g H \beta$.

$$F = N\xi - kT \sum_L' \left\{\ln\left[1 + x_L\left(1 - y + \tfrac{1}{2}y^2 + \cdots\right)\right]\right\}$$

$$- kT \sum_L' \left\{\ln\left[1 + x_L\left(1 + y + \tfrac{1}{2}y^2 + \cdots\right)\right]\right\}$$

$$= N\xi - kT \sum_L' \ln\left\{(1 + x_L)\left(1 + \frac{x_L}{1 + x_L}\left[-y + \tfrac{1}{2}y^2\right]\right\}\right.$$

$$- kT \sum_L' \ln\left\{(1 + x_L)\left(1 + \frac{x_L}{1 + x_L}\left[y + \tfrac{1}{2}y^2\right]\right\}\right.$$

$$F = N\xi - 2kT \sum_L' \ln(1 + x_L) + \sum_L' \ln\left\{1 + f(\varepsilon_L^L)\left[-y + \tfrac{1}{2}y^2\right]\right\}$$

$$\cdot \left\{1 + f(\varepsilon_L^L)\left[y + \tfrac{1}{2}y^2\right]\right\}$$

Now $N\xi - 2kT \sum_L' \ln(1 + x_L)$ is the diamagnetic part while the rest is paramagnetic. The paramagnetic part to order H^2 can be written:

$$\sum_L' \ln\left\{1 + y^2 f(\varepsilon_L^L) - f^2(\varepsilon_L^L) y^2\right\}$$

Use the relation: $\ln(1 + \epsilon) \approx \epsilon$ for small ϵ, and:

$$f(\varepsilon_L^L) - f^2(\varepsilon_L^L) = -\frac{1}{\beta}\frac{\partial f}{\partial \varepsilon_L^L} \qquad \text{(exact)}$$

Then:

$$\sum_{\nu} \ln\left\{1 - \frac{y^2}{\beta}\frac{\partial f}{\partial \varepsilon_\nu^2}\right\} \rightarrow -\frac{y^2}{\beta}\sum_{\nu}\frac{\partial f}{\partial \varepsilon_\nu^2}\Big|_{H=0}$$

and:

$$F_{para} = \left(\frac{\beta \mu_0 H}{2}\right)^2 \sum_{\nu}\frac{\partial f}{\partial \varepsilon_\nu^2}\Big|_{H=0}$$

$$M = -\frac{\partial F}{\partial H} = -2\left(\frac{\beta\mu_0}{2}\right)^2 H \sum_{\nu}\frac{\partial f}{\partial \varepsilon_\nu}$$

which is identical to the previous result on changing $\sum_\nu \rightarrow \int d\varepsilon$.

A reference on the many body effects in Pauli Paramagnetism is the review papers of Pines.

Landau Levels:

This problem can be solved completely only for spherical energy surfaces: $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$. The band Hamiltonian is then:

$$\left[\frac{1}{2m^*}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2\right]\psi = \varepsilon\psi$$

Choose the asymmetric gauge $\vec{A} = (0, xH, 0)$ so that $\nabla \times \vec{A} = H\hat{z}$.

$$\left[\frac{1}{2m^*}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{eH}{m^*c}p_y x + \frac{e^2H^2}{2m^*c^2}x^2\right]\psi = \varepsilon\psi$$

Try the solution: $\psi = e^{ik_z z}e^{ik_y y}f(x)$ and get:

$$\frac{1}{2m^*}\left\{\hbar^2\left(k_y^2 + k_z^2\right) - \hbar^2\frac{\partial^2}{\partial x^2} + \frac{2eHx}{c}\hbar k_y + \frac{e^2H^2x^2}{c^2}\right]f(x) = \varepsilon f(x)$$

Let $x' = x + \hbar k_y\left(\frac{c}{eH}\right)$:

$$\frac{1}{2m^*}\left[-\hbar^2\frac{\partial^2}{\partial x'^2} + \frac{e^2H^2}{c^2}x'^2\right]f(x') = \left[\varepsilon - \frac{\hbar^2 k_z^2}{2m^*}\right]f(x')$$

which is the harmonic oscillator with solutions:

$$\varepsilon = (n+1/2)\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m^*}; \quad \psi = u_n\left\{\left(\frac{\hbar c}{eH}\right)\left(x + \frac{c}{eH}\hbar k_y\right)\right\}e^{ik_z z}e^{ik_y y}$$

Since ε is independent of k_y, it is degenerate with respect to it. Note: $\omega_c = \frac{eH}{m^*c}$

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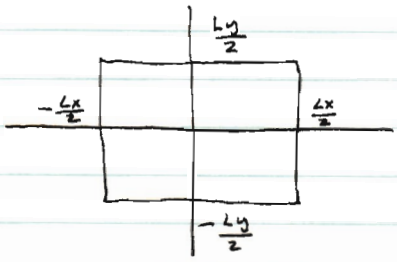
We have noted that the Landau levels are degenerate in k_y. To handle this huge degeneracy conveniently, put the problem in a box and use BVK boundary conditions.



$$\left.\begin{aligned} k_y &= \pm n_y \left(\frac{2\pi}{L_y}\right) \\ k_z &= \pm n_z \left(\frac{2\pi}{L_z}\right) \\ k_x &= \pm n_x \left(\frac{2\pi}{L_x}\right) \end{aligned}\right\} \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \cdots$$

Now the zero value of x has to be in the box, that is:

$$-\frac{L_x}{2} < x_0 < \frac{L_x}{2} \qquad \text{or:} \qquad -\frac{L_x}{2} < -\hbar k_y \frac{c}{eH} < \frac{L_x}{2}$$

This gives immediately: $|n_y|_{max} = \frac{eH}{2\hbar c} L_x L_y$, the total degeneracy then being:

$$N(n, k_y) = \frac{eH}{\hbar c} L_x L_y$$

Van Leeuwen's Theorem

This theorem says that the total magnetic susceptibility of an electron gas vanishes, both the diamagnetic and the paramagnetic (Reference: Van Vleck). Consider the classical free energy:

$$F = -NkT \ln \iint d\vec{p}\, d\vec{r}\; e^{-\frac{1}{2m}(\vec{p} + \frac{e}{c}\vec{A})^2/kT}$$

On making the substitution $\vec{P} \to \vec{p} + \frac{e}{c}\vec{A}$ and $\vec{p}, \vec{r} \to \vec{P}, \vec{r}$ whose Jacobian is one, we obtain:

$$F = -NkT \ln \iint d\vec{P}\, d\vec{r}\; e^{-\frac{1}{2m}P^2/kT}$$

which is independent of the magnetic field, so classically χ_{dia} should vanish. The same is true for χ_{para}. The Langevin derivation of χ_{para} does not vanish because we assume all the magnetic moments fixed at a point in space which quasi-quantizes the problem.

Landau - Peierls Diamagnetism ($\vec{H} \to 0$)

We recall the diamagnetic free energy:

$$F = N\xi - 2kT \sum_i \ln \left\{ 1 + e^{-(\varepsilon_i - \xi)\beta} \right\}$$

Remember the 2 came from the fact we had spin.
We will use the band Hamiltonian:

$$\mathcal{H}_n^{\text{symmetrized}} \left(\vec{p} + \frac{e}{c}\vec{A} \right)$$

We can then write:

$$F = N\xi - 2kT \sum_i \int \psi_i^*(\vec{r}) \ln \left\{ 1 + e^{-[\mathcal{H}(\vec{p} + \frac{e}{c}\vec{A}) - \xi]\beta} \right\} \psi_i(\vec{r})\, d\tau$$

$$= N\xi - 2kT \ \text{Trace} \left\{ \ln \left[1 + e^{-(\mathcal{H} - \xi)\beta} \right] \right\}$$

We now make use of the invariance property of the trace. We take the trace with respect to plane waves.

$$F = N\xi - 2kT \int e^{-i\vec{k}\cdot\vec{r}} \log \left[1 + e^{-(\mathcal{H} - \xi)\beta} \right] e^{i\vec{k}\cdot\vec{r}} \frac{d\vec{k}}{(2\pi)^3} \frac{d\vec{r}}{V}$$

We will work to order H^2 and neglect the dependence of ξ on H which must be even because if it is odd this would make ξ depend on the direction of $\vec{H}$; that is, $\xi = \xi_1 + \xi_2 H^2 + \cdots$.

We now examine the structure:

$$F = N\xi - 2kT \int e^{-i\vec{k}\cdot\vec{r}} \varphi(\mathcal{H})\, e^{i\vec{k}\cdot\vec{r}} \frac{d\vec{r}}{V} \frac{d\vec{k}}{(2\pi)^3}$$

where $\varphi(\mathcal{H}) = \log \left[1 + e^{-(\mathcal{H} - \xi)\beta} \right] = \sum_n a_n \mathcal{H}^n$

Let: $\mathcal{H}\left(\vec{p} + \frac{e}{c}\vec{A} \right) = \mathcal{H}(\vec{P})$

Use the repeated zone scheme: This makes $\mathcal{H}(\vec{P})$ periodic in $\vec{k}$ space and allows a Fourier expansion on the direct lattice:

$$\mathcal{H}(\vec{P}) = \int A(\vec{l})\, e^{i \frac{\vec{l}\cdot\vec{P}}{\hbar}}\, d\vec{l}$$

where we have taken the liberty of integrating instead of summing over the direct lattice. We now have:

$$\varphi(\mathcal{H}) = \sum_n a_n \int A(\vec{l}_1)\cdots A(\vec{l}_n)\, e^{i\vec{l}_1\cdot\vec{P}/\hbar}\cdots e^{i\vec{l}_n\cdot\vec{P}/\hbar}\, d\vec{l}_1\cdots d\vec{l}_n$$

Now, we will use the operator identity:

$$e^{(u+v)} = e^{-\frac{1}{2}[u,v]}\, e^{u}\, e^{v}$$

providing $\quad [[u,v],u] = [[u,v],v] = 0$

Check:

$$1 + (u+v) + \tfrac{1}{2}(u^2+v^2+uv+vu) + \cdots$$

$$= \left[1 - \tfrac{1}{2}(uv-vu)+\cdots\right]\left[1+u+\frac{u^2}{2}+\cdots\right]\left[1+v+\frac{v^2}{2}+\cdots\right]$$

We will also use another identity:

$$e^{a\frac{i}{\hbar}p_x}\, e^{bx} = e^{ab}\, e^{bx}\, e^{a\frac{i}{\hbar}p_x}$$

Use the repeated zone scheme: This makes $\mathcal{H}(\vec{P})$ periodic in $\vec{k}$ space and allows a Fourier expansion on the direct lattice:

$$\mathcal{H}(\vec{P}) = \int A(\vec{l})\, e^{i \frac{\vec{l}\cdot\vec{P}}{\hbar}}\, d\vec{l}$$

where we have taken the liberty of integrating instead of summing over the direct lattice. We now have:

$$\varphi(\mathcal{H}) = \sum_n a_n \int A(\vec{l}_1)\cdots A(\vec{l}_n)\, e^{i\vec{l}_1\cdot\vec{P}/\hbar}\cdots e^{i\vec{l}_n\cdot\vec{P}/\hbar}\, d\vec{l}_1\cdots d\vec{l}_n$$

Now, we will use the operator identity:

$$e^{(u+v)} = e^{-\frac{1}{2}[u,v]}\, e^{u}\, e^{v}$$

providing $\quad [[u,v],u] = [[u,v],v] = 0$

Check:

$$1 + (u+v) + \tfrac{1}{2}(u^2+v^2+uv+vu) + \cdots$$

$$= \left[1 - \tfrac{1}{2}(uv-vu)+\cdots\right]\left[1+u+\frac{u^2}{2}+\cdots\right]\left[1+v+\frac{v^2}{2}+\cdots\right]$$

We will also use another identity:

$$e^{a\frac{i}{\hbar}p_x}\, e^{bx} = e^{ab}\, e^{bx}\, e^{a\frac{i}{\hbar}p_x}$$

Define $Q = [(a_{n,n-1} + a_{n,1}) + \cdots + a_{2,1}]$

Finally:

$$F = N\xi - 2kT \sum_n a_n \int\cdots\int A(\vec{l}_1)\cdots A(\vec{l}_n)\, e^{\imath\pi H Q}\, e^{\frac{\imath}{\pi}(\vec{l}_1+\cdots+\vec{l}_n)\cdot(\pi\vec{k}+\frac{e}{c}\vec{A})}$$

$$\cdot\, d\vec{l}_1\cdots d\vec{l}_n\ \frac{d\vec{k}}{(2\pi)^3}\, V\, \frac{d\vec{r}}{V}$$

Now change the variables to $\vec{k}' = \pi\vec{k} + \frac{e}{c}\vec{A}$ and $\vec{r} = \vec{r}$ to eliminate $\vec{A}$ and perform the $\vec{r}$ integrations. Then let $\vec{k}' \to \vec{k}$ and expand $e^{\imath\pi HQ}$. The first term in F is then:

$$F_0 = N\xi - 2kT \int \log\left\{1 + e^{-\beta\{\varepsilon(k)-\xi\}}\right\} V\frac{d\vec{k}}{(2\pi)^3}$$

The second term vanishes, $F_1 = 0$, because:

$$-2kT \sum_n a_n \int\!\!\int A(\vec{l}_1)\cdots A(\vec{l}_n)\cdots A(\vec{l}_j)\cdots A(\vec{l}_n)\, \imath\pi H\cdots[l_n^y l_j^x - l_n^x l_j^y]\cdots$$

$$e^{\frac{\imath}{\pi}(\vec{l}_1+\cdots+\vec{l}_n)\cdot\pi\vec{k}}\, d\vec{l}_1\cdots d\vec{l}_n\ \frac{V\,d\vec{k}}{(2\pi)^3}$$

$$\to \int \varepsilon(\vec{k}) \int A(\vec{l}_n)\, A(\vec{l}_j)\,[l_n^y l_j^x - l_n^x l_j^y]\, e^{\frac{\imath}{\pi}\vec{l}_n\cdot\pi\vec{k}}\, e^{\frac{\imath}{\pi}\vec{l}_j\cdot\pi\vec{k}}$$

$$d\vec{l}_n\, d\vec{l}_j\ \frac{V\,d\vec{k}}{(2\pi)^3}$$

Now this gives rise to the structure:

$$\left[\left(\frac{1}{\imath}\right)^2 \frac{\partial\varepsilon(k')}{\partial k_y'}\,\frac{\partial\varepsilon(k'')}{\partial k_x''}\right] - \left[\left(\frac{1}{\imath}\right)^2 \frac{\partial\varepsilon(k'')}{\partial k_y''}\,\frac{\partial\varepsilon(k')}{\partial k_x'}\right]$$

which when added to the other combinations vanishes. Thus we are motivated to assert that there will be only even terms in F. In $F_2 \to -\frac{1}{2}\pi^2 H^2 Q^2$, there will be terms like:

(I) a_{lj}^2

(II) $a_{lj}a_{ik}$ $(j\neq k)$; $a_{jl}a_{kl}$ $(j\neq k)$

(III) $a_{lj}a_{jk}$ $(l\neq k)$

(IV) $a_{lj}a_{kl}$ $(l\neq k\neq l\neq j)$

These break down into:

$$(i)\quad kT\,H^2\,n^2 \sum_n \int a_n\, \varepsilon_{(k)}^{n-2} \left[2\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right) - 2\left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)^2 \right] \frac{d\vec{k}\,V}{(2\pi)^3}$$

$$(ii)\quad kT\,H^2\,n^2 \sum_n \int a_n\, \varepsilon_{(k)}^{n-3} \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial\varepsilon}{\partial k_y}\right)^2 + \left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right)\left(\frac{\partial\varepsilon}{\partial k_x}\right)^2 - 2\left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right) \cdot \left(\frac{\partial\varepsilon}{\partial k_x}\right)\left(\frac{\partial\varepsilon}{\partial k_y}\right) \right] \frac{V\,d\vec{k}}{(2\pi)^3}$$

(iii) Negative of (ii)

(iv) Zero

Combining together is a simple combinatorial problem of different i, j's:

$$(i)\ \frac{n(n-1)}{2}\ ;\ (ii)\ \frac{2}{3}(n)(n-1)(n-2)\ ;\ (iii)\ \frac{1}{3}n(n-1)(n-2)$$

We find:

$$F_z = kT\,n^2H^2 \left\{ \int_k \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right) - \left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)^2 \right] \frac{\partial^2\phi}{\partial\varepsilon^2}\ \frac{d\vec{k}\,V}{(2\pi)^3} \right.$$

$$\left. + \frac{1}{3}\int_k \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial\varepsilon}{\partial k_y}\right)^2 + \left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right)\left(\frac{\partial\varepsilon}{\partial k_x}\right)^2 - 2\left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)\left(\frac{\partial\varepsilon}{\partial k_x}\right)\left(\frac{\partial\varepsilon}{\partial k_y}\right) \right] \frac{\partial^3\phi}{\partial\varepsilon^3}\ \frac{V\,d\vec{k}}{(2\pi)^3} \right\}$$

Now: $\frac{\partial\phi}{\partial\varepsilon} = -\frac{1}{kT} f(\varepsilon)$ so that F_z reduces to:

$$F_z = -\frac{1}{3}\left(\frac{e}{2\pi c}\right)^2 H^2 \int_k \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right) - \left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)^2 \right] \frac{\partial f}{\partial\varepsilon}\ \frac{V\,d\vec{k}}{(2\pi)^3}$$

This is the expression obtained by Peierls. Now assume δ function behaviour for $\frac{\partial f}{\partial\varepsilon}$ and change to an integral over a constant energy surface via $d\vec{k} \to dS\,\frac{d\varepsilon}{|\nabla_k\varepsilon|}$. Then,

$$F_z = \frac{1}{3}\left(\frac{e}{2\pi c}\right)^2 H^2 \int_S \frac{V}{(2\pi)^3} \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right) - \left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)^2 \right] \frac{dS}{|\nabla_k\varepsilon|}$$

and:

$$\chi_{dia} = -\frac{1}{V}\frac{\partial^2 F_z}{\partial H^2} = -\frac{e^2}{48\pi^3\hbar^2c^2} \int_S \left[\left(\frac{\partial^2\varepsilon}{\partial k_x^2}\right)\left(\frac{\partial^2\varepsilon}{\partial k_y^2}\right) - \left(\frac{\partial^2\varepsilon}{\partial k_x\,\partial k_y}\right)^2 \right] \frac{dS}{|\nabla_k\varepsilon|}$$

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We will now evaluate χ_{dia} over a spherical energy surface at the fermi level. Take:

$$\mathcal{E} = \frac{\hbar^2 k^2}{2m^*} \quad ; \text{ the Fermi surface being given by: } \quad S = 4\pi k_F^2$$

$$\int_S \left[\frac{\partial^2 \mathcal{E}}{\partial k_x^2} \frac{\partial^2 \mathcal{E}}{\partial k_y^2} - \left(\frac{\partial^2 \mathcal{E}}{\partial k_x \partial k_y} \right)^2 \right] \frac{dS}{\nabla_u \mathcal{E}} = \left(\frac{\hbar^2}{m^*} \right)^2 \frac{4\pi k_F^2}{\frac{\hbar^2 k_F}{m^*}}$$

This gives:

$$\chi_{dia}^F = \frac{-e^2 k_F}{12\pi^2 c^2 m^*}$$

Now: $N = 2 \cdot \frac{4}{3} \cdot \frac{\pi \hbar^3 k_F^3}{h^3}$; $k_F = (3\pi^2 n)^{1/3}$

Hence: $\chi_{dia}^F = \frac{-e^2}{12\pi^2 c^2 m^*} (3\pi^2 n)^{1/3}$

Summarizing the various magnetic susceptibilities, we find:

$$\chi_{dia}^{core} = -\frac{1}{6} \left(\frac{e^2}{mc^2} \right) \sum_{core} \langle r^2 \rangle_{core} N_c n_A$$

$$\chi_{dia}^F = -\frac{1}{3} \frac{1}{4\pi^2} \left(\frac{e^2}{mc^2} \right) \left(\frac{m}{m^*} \right) (3\pi^2 n)^{1/3}$$

$$\chi_{para}^F = \left(\frac{g}{2} \right)^2 \frac{1}{4\pi^2} \left(\frac{e^2}{mc^2} \right) \left(\frac{m^*}{m} \right) (3\pi^2 n)^{1/3}$$

In Bismuth, $g \sim \frac{1}{m^*}$ so that χ_{dia} and χ_{para} should have the same behaviour, however, this is not observed.

The de Haas - Van Alphen Effect : Cyclotron Resonance

The de Haas - Van Alphen effect is observed at high fields and low temperatures and is the oscillations of the diamagnetic susceptibility. The classical treatment follows: We assume a band Hamiltonian:

$$\mathcal{E}(\vec{k}) = \mathcal{H} \left\{ \frac{1}{\hbar} \left(\vec{p} + \frac{e}{c} \vec{A} \right) \right\}$$

We can consider this as a classical Hamiltonian and then make contact with quantum mechanics thru the correspondence principle. Use:

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial p_x} \quad ; \quad \dot{p}_x = -\frac{\partial \mathcal{H}}{\partial x} \quad ; \quad \vec{v} = \nabla_p \mathcal{E}$$

If $\vec{A}$ is independent of time;

$$\frac{e}{c}\vec{v} \times \vec{H} = \dot{\vec{p}} + \frac{e}{c}(\vec{v}\cdot\nabla)\vec{A}$$

Define the "kinetic momentum" $\vec{P} = \vec{p} + \frac{e}{c}\vec{A}$, from which one can derive the velocity $\vec{P} = m\vec{v}$. We still have:

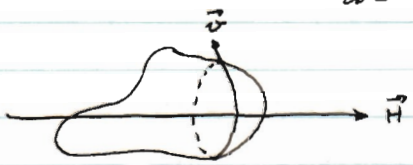
$$\vec{v} = \nabla_p \mathcal{E}(\vec{P}) = \nabla_p \mathcal{E}(\vec{p})$$

Now: $$\frac{d\vec{P}}{dt} = \frac{d\vec{p}}{dt} + \frac{e}{c}(\vec{v}\cdot\nabla)\vec{A}$$

Hence: $$\frac{d\vec{P}}{dt} = \frac{e}{c}\vec{v}(\vec{r},t) \times \vec{H} \quad ; \quad \vec{v} = \nabla_p \mathcal{E}(\vec{P})$$

are the appropriate equations of motion.

In kinetic momentum space the motion is periodic regardless of the shape of the constant energy surface and the component of $\vec{P}$ along $\vec{H}$ is a constant of the motion: $\frac{d(\vec{P}\cdot\vec{H})}{dt} = 0$



The period of the motion is:

$$T(p_z, \mathcal{E}) = \oint \frac{dP}{\left|\frac{e}{c}\vec{v} \times \vec{H}\right|}$$

We now introduce m^* as used in defining the cyclotron resonance frequency:

$$\omega_c = \frac{2\pi}{T} = \frac{eH}{m^* c} \quad ; \quad \therefore \quad m^* = \frac{1}{2\pi}\oint \frac{dP}{|\vec{v} \times \hat{H}|}$$

If we have a complicated $\mathcal{E}$ surface, m^* will be different depending on the path in $\vec{P}$ space and it only has a simple interpretation for spherical surfaces.

Take $\hat{H} = \hat{z}$ and $\vec{v} = \nabla_p \mathcal{E}$ and consider:

$$m^* = \frac{1}{2\pi} \oint \frac{dP}{\left| -\frac{\partial \mathcal{E}}{\partial P_x} \hat{y} + \frac{\partial \mathcal{E}}{\partial P_y} \hat{x} \right|} = \frac{1}{2\pi} \oint \frac{dP}{\frac{\partial \mathcal{E}}{\partial P_\perp}}$$

$$= \frac{1}{2\pi} \oint \frac{dP\, dP_\perp}{d\mathcal{E}} = \frac{1}{2\pi} \frac{\partial A}{\partial \mathcal{E}}$$

Hence: $$m^*(P_z, \mathcal{E}) = \frac{1}{2\pi} \frac{\partial A(P_z, \mathcal{E})}{\partial \mathcal{E}}$$

If we have an ellipsoidal surface:

$$\mathcal{E} = \frac{1}{2} \left[\frac{P_x^2}{m_1} + \frac{P_y^2}{m_2} + \frac{P_z^2}{m_3} \right]$$

$$m^* = \sqrt{\frac{m_1 m_2 m_3}{m_1 \alpha^2 + m_2 \beta^2 + m_3 \gamma^2}}$$

Some often used relations in cyclotron resonance (CR) are:

$$\frac{d\vec{P}}{dt} = \frac{e}{c} \vec{v} \times \vec{H}$$

$$\vec{P}(t) = \frac{e}{c} \vec{r}(t) \times \vec{H} + \vec{P}_0$$

$$\vec{P}_\perp(t) = \frac{e}{c} \vec{r}(t) \times \vec{H} = \frac{e}{c} \vec{r}_\perp(t) \times \vec{H}$$

$$\vec{P}_{||}(t) = \vec{P}_0 = \text{constant}$$

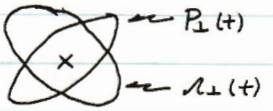
$$\vec{P}_\perp(t) \times \vec{H} = -\frac{e}{c} H^2 \vec{r}_\perp(t)$$

$$\vec{r}_\perp(t) = -\frac{c}{eH} \vec{P}_\perp(t) \times \hat{H}$$

If we have $\vec{H}$ along a non-symmetry axis of an ellipsoidal surface, we can have periodic motion along the field direction. However, we are usually more interested in the transverse motion.

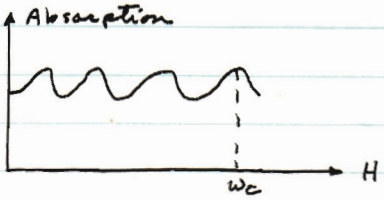
LECTURE 27 : 4-16-62

Recall : $\vec{r}_\perp(t) = -\frac{c}{eH}\vec{P}_\perp(t) \times \hat{H}$, This shows that the motion in real space is like that in $\vec{P}$ space rotated by 90° :

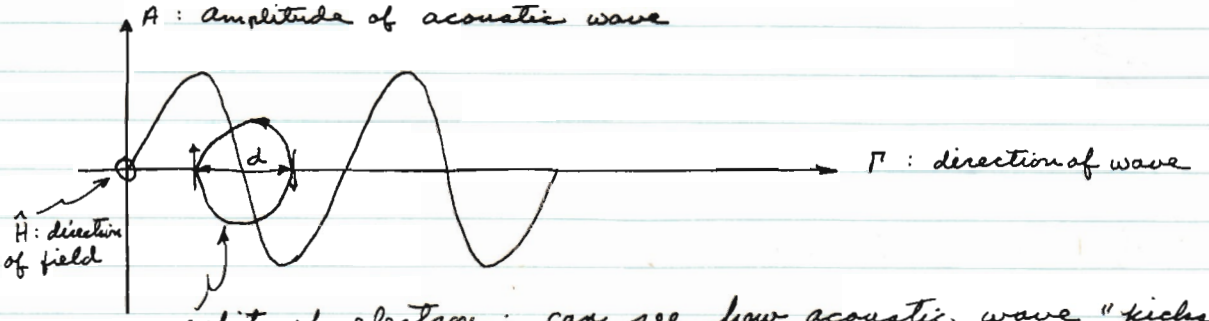


Recall that for an arbitrary $\mathcal{E}$ surface, $m^* = \frac{1}{2\pi}\frac{\partial A(\mathcal{E}, P_z)}{\partial \mathcal{E}}\Big|_F$

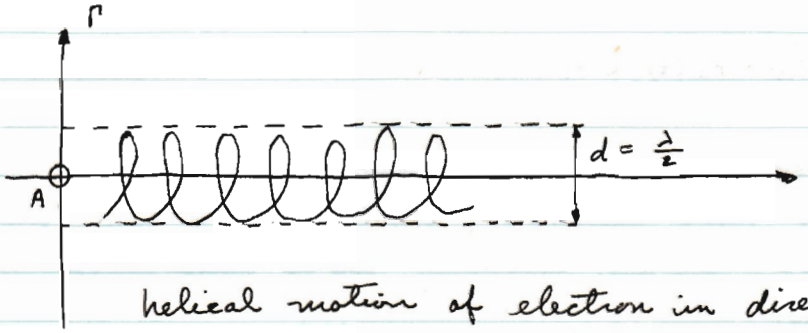
Resonance is observed at $\frac{\partial m^*}{\partial P_z} = 0$, $\omega_c = \frac{eH}{m^* c}$.
Peaks are seen at intervals of $\omega = n\omega_c$



Another technique of dealing with diamagnetic resonance is thru acoustic waves. The physics of the situation is in the following diagrams :

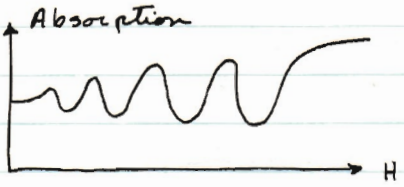


orbit of electron : can see how acoustic wave "kicks" it around cycle if frequency and wavelength are right, ie, $\lambda = 2d$.



helical motion of electron in direction of $\hat{H}$

We measure the absorbtion which looks like:

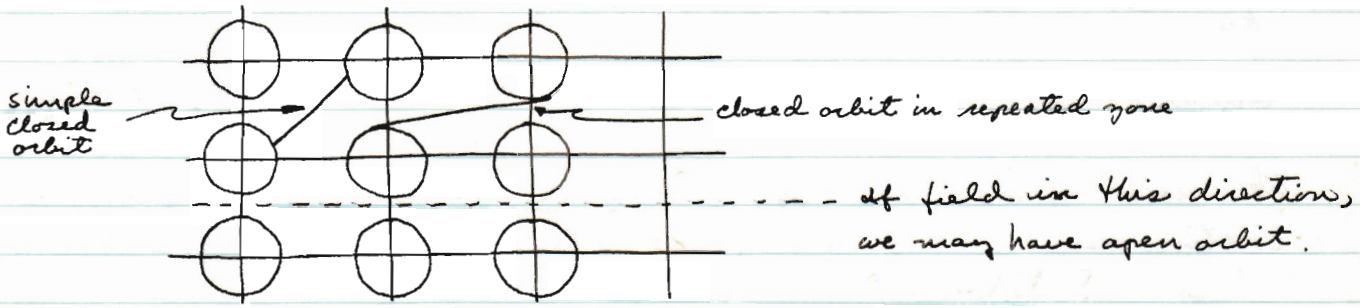


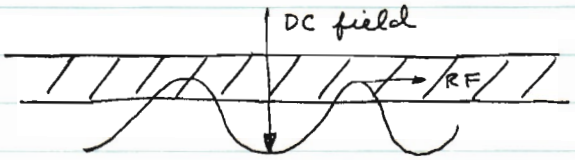
The resonance condition is obviously any odd number of wavelengths equal to the electronic orbit:

$d = (2n+1)\frac{\lambda}{2}$ where λ is the phonon wavelength.

The resonance appears at the stationary point d_p: $\frac{\partial d_p}{\partial P_z} = 0$. ?

Refer to the figure below of the repeated zone scheme. This is an example of a non-simply connected Fermi surface, however, one can still have cyclotron resonance or acoustic resonance for open orbits:





For acoustic resonance, $d_p = \frac{eH}{c} d = \frac{1}{2} P_{bz}$

In order to observe cyclotron resonance, we require that the orbit period T be less than the relaxation time τ, and this is also true for acoustic resonance. We have for acoustic resonance: $\tau > \frac{2\pi}{\omega_c}$

$(2n+1)\frac{\lambda}{2} = 2R = \frac{v_F}{\omega_c}$; $\frac{1}{\omega_c} = \frac{2R}{v_F}$; $2R = \frac{v_s}{\omega}$, then:

$\omega\tau > \left(\frac{v_s}{v_F}\right)$ so that the relaxation condition is much less stringent for acoustic resonance than for cyclotron resonance.

We now consider high field effects. Recall:

$$F = N\xi - kT \sum_{\nu} \ln \left\{ 1 + e^{-\beta(\epsilon_\nu - \beta)} \right\}$$

Use this with the correspondence principle:

$$\frac{\partial \mathcal{E}}{\partial n} \sim \hbar \omega_c \text{ (for } n \text{ large)} = \frac{\hbar e H}{c} \frac{2\pi}{\partial A / \partial \mathcal{E}} \; ; \quad \mathcal{E} = \mathcal{E}(n, P_z)$$

Inverting: $(n+\gamma) \Rightarrow \frac{c}{\hbar e H} A(\mathcal{E}, P_z)$ in the high quantum number limit where γ is a constant of integration.
Now the complete energy is:

$$\mathcal{E} = \mathcal{E}(n, P_z) \pm \tfrac{1}{2} \mu_0 H = \mathcal{E}(n, P_z) + \mu H$$

Then:

$$F = N\xi - kT \sum_{\mu} \sum_{n=0}^{\infty} \int \ln \left[1 + e^{-\beta \{ \mathcal{E}(n P_z) + \mu H - \xi \}} \right] \frac{eH}{\hbar^2 c} V \, dP_z$$

$\frac{eH}{\hbar c}$ comes from degeneracy in k_y.

Define: $\phi_\mu \{ \mathcal{E}(n P_z) \} = \ln \left[1 + e^{-\beta \{ \mathcal{E}(n P_z) + \mu H - \xi \}} \right]$; $B = \frac{eH}{\hbar^2 c} V$

We now make use of <u>Poisson's Theorem</u>: If $f(x)$ is continuous in $0 \to \infty$, and $f(x) \to 0$ as $x \to \infty$, then:

$$\sum_{s=1}^{\infty} f(s) + \tfrac{1}{2} f(0) = \sum_{\lambda=-\infty}^{\infty} \int_0^{\infty} f(s) \, e^{2\pi i \lambda s} \, ds$$

Thus we can write:

$$F = N\xi - \frac{B kT}{2} \sum_{\mu} \int_{-\infty}^{\infty} \left\{ \phi_\mu [\mathcal{E}(n P_z)] \right\}_{n=0} dP_z$$

$$- B kT \sum_{\mu} \sum_{\lambda=-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \phi_\mu [\mathcal{E}(n P_z)] \, e^{2\pi i n \lambda} \, dn \, dP_z$$

We will now separate into $F = N\xi + F_1 + F_{osc}$.

LECTURE 28: 4-18-62

Now: $F = N\xi + F_1 + F_{osc}$.

$$F_1 = -\frac{kTB}{2} \sum_\mu \int_{-\infty}^{\infty} [\phi_\mu]_{n=0}\, dP_z - kTB \sum_\mu \int_{-\infty}^{\infty}\int_0^{\infty} \phi_\mu\, dn\, dP_z$$

$$F_{osc} = -B \sum_\mu \sum_r{}' \int_{-\infty}^{\infty} f_\mu \left(\frac{\partial \varepsilon}{\partial n}\right) \frac{e^{2\pi i n r}}{2\pi i r}\, dn\, dP_z$$

where F'_{osc} is the derivative of F_{osc} with respect to n. Also:

$$\frac{\partial \phi_\mu(\varepsilon)}{\partial \varepsilon} = -\frac{1}{kT} f_\mu(\varepsilon) = -\frac{1}{kT} \frac{1}{1 + e^{\beta(\varepsilon - \xi + \mu H)}}$$

Recall our semiclassical result:

$$n = \frac{c}{heH} A(\varepsilon, P_z) - \gamma$$

where everything is now continuous. Then:

$$F'_{osc} = -B \sum_\mu \sum_r{}' \int_0^{\infty} \int_{P_{1z}(\varepsilon)}^{P_{2z}(\varepsilon)} f_\mu(\varepsilon) \frac{e^{2\pi i r}}{2\pi i r} \left[\frac{c}{heH} A(\varepsilon, P_z) - \gamma\right] dP_z\, d\varepsilon$$

Consider the P_z integration and do by the method of stationary phase, where $\frac{\partial A(\varepsilon)}{\partial P_z} = 0$. Now there may be more than one point of stationary phase, labelled by m. Expand $A(\varepsilon P_z)$:

$$A(\varepsilon P_z) = A(\varepsilon P_{zm}(\varepsilon)) + \frac{1}{2}\left(\frac{\partial^2 A}{\partial P_z^2}\right)_m (P_z - P_m)^2 + \cdots$$

Define: $y = (P_z - P_m)^2 \left\{\frac{rc}{2heH} \left|\frac{\partial^2 A}{\partial P_z^2}\right|_m\right\}$

Then:

$$F'_{osc} = -2B \sum_\mu \sum_r{}' \sum_m \int_0^{\infty} \frac{e^{2\pi i r \left[\frac{c}{heH} A\{P_m \varepsilon\} - \gamma\right]}}{2\pi i r} \cdot \left(\frac{2heH_z\pi}{rc}\right)^{1/2}$$

$$\cdot \frac{1}{\left|\frac{\partial^2 A}{\partial P_z^2}\right|^{1/2}} d\varepsilon \underbrace{\int_0^{\infty} e^{\pm 2\pi i y}\, y^{-1/2}\, dy}_{\frac{1}{\sqrt{2}}\, e^{\pm i\pi/4}}$$

Then:

$$F_{osc} = -2\left(\frac{heH}{c}\right)^{1/2} B \sum_{\mu} \sum_{r}{}' \sum_{m} \int_0^{\infty} \frac{e^{2\pi i r\left[\frac{c}{heH} A(\varepsilon P_m) - \gamma \pm \pi/4\right]}}{(2\pi i r)\, r^{1/2} \left|\frac{\partial^2 A}{\partial P_z^2}\right|_m^{1/2}} f_\mu(\varepsilon)\, d\varepsilon$$

Now F'_{osc} really doesn't mean derivative with respect to r as this is really a change of variable from r to ε. F'_{osc} differs from F_{osc} in that F'_{osc} contains non-oscillatory terms.

We now expand A around the Fermi energy.

Define $x = \dfrac{\varepsilon - \xi + \mu H}{kT}$

We now drop prime because we will drop non-oscillatory terms. $\mathbb{R}$ means real part.

$$F_{osc} = \frac{kT\left(\frac{eH}{c}\right)^{3/2} V}{4\pi^2 \hbar^{3/2}} \sum_m \sum_\mu \sum_{r=1}^{\infty} \mathbb{R}\left[\frac{1}{\left|\frac{\partial^2 A}{\partial P_z^2}\right|_m^{1/2}} \frac{e^{2\pi i r\left\{\frac{c}{heH} A(\xi P_m) - \eta \pm \pi/4\right\}}}{(2\pi i r)\, r^{1/2}}\right]$$

$$\cdot \int_{-\infty}^{\infty} \frac{e^{2\pi i r \theta x}}{1 + e^x}\, dx$$

where:

$$\theta = \frac{kT}{\hbar \omega_c(\xi P_m(\xi))} \; ; \; \hbar\omega_c = \frac{heH}{c\frac{\partial A}{\partial \varepsilon}} \; ; \; \eta = \gamma \pm \frac{g\mu_0 H}{\hbar\omega_c}$$

Now: $$\int_{-\infty}^{\infty} \frac{e^{i\delta x}}{1+e^x}\, dx = \frac{-\pi i}{\sinh \pi\delta}$$

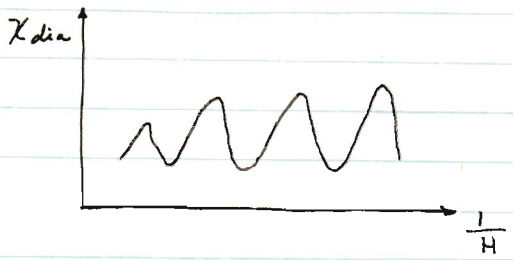
Use this in:

$$F_{osc} = \frac{kT\left(\frac{eH}{c}\right)^{3/2} V}{4\pi^2 \hbar^{3/2}} \sum_m \sum_\eta \frac{(2\pi)^{1/2}}{\left|\frac{\partial^2 A}{\partial P_z^2}\right|_m^{1/2}} \sum_{r=1}^{\infty} \frac{1}{r^{3/2}}$$

$$\cdot \frac{\cos 2\pi r\left[\frac{c}{heH} A\{\xi P_m(\xi)\} - \eta \pm \pi/4\right]}{\sinh\left(2\pi^2 r\, \theta_m(\xi)\right)}$$

It is clear that the diamagnetic susceptibility will oscillate with $\frac{1}{H}$:

$$\Delta\left(\frac{1}{H}\right) = \frac{eh}{c\, A_m(\xi)}$$



From the period we can get the cross-section of the Fermi surface.

There are some difficulties with finite line widths due to impurities or high temperatures. Assume some linewidth of $n \to n + \Delta$. Then:

$$F_{osc} = -B \sum_{\mu} \sum_{r}{}' \int_{-\infty}^{\infty} f_{\mu} \left(\frac{\partial \varepsilon}{\partial n}\right) \frac{e^{2\pi i (n+\Delta) r}}{2\pi i r} \, dn \, dP_z \, P(\Delta) \, d\Delta$$

This gives an effective temperature $\Theta = k(T + T')$ with T' goes as reciprocal lifetime. This concludes the discussion of the de Haas - von Alphen effect.

Spin Resonance in Metals

To observe the paramagnetic spin resonance of the conduction electrons in metals, we must use powder samples because of the skin effect. Some strange effects occur because of diffusion in and out of skin region. In the alkalli metals we find $g = 2$. However, in some materials (graphite) at low temperatures we observe a k dependence of g due to the shape of the Fermi surface.

LECTURE 29: 4-23-62

Nuclear Resonance in Metals: Knight Shift

Consider: $\mathcal{H} = g_I \mu_N I_z H + \mathcal{H}_Q + \mathcal{H}_{HFS}$

In cubic symmetry, $\mathcal{H}_Q = 0$.

$$\mathcal{H}_{HFS} = \sum_{\text{conduction electrons}} g_I \mu_N \mu_0 \vec{I} \cdot \left[\underbrace{\frac{-\vec{S}_{ic} + 3(\vec{S}_{ic} \cdot \vec{r}_{ic})(\hat{r}_{ic})}{r_{ic}^3}}_{\text{contributes a small amount for } p \text{ or higher states}} + \underbrace{\frac{8\pi}{3} \vec{S}_{ic} \delta(\vec{r}_{ic})}_{\text{Contact term is largest contribution}} + \underbrace{\frac{\vec{L}_{ic}}{r_{ic}^3}}_{\text{very small, zero for } s \text{ states}} \right]$$

To get the effective Hamiltonian we take the expectation value of the contact term with respect to the Bloch functions.

$$\mathcal{H} = g_I \mu_N I_z H + g_I \mu_N \mu_0 \frac{8\pi}{3} I_z \sum_i S_{ic} \left(\frac{\Omega}{V}\right) |u_{ni}(0)|^2$$

We neglect the k dependence of the cell-periodic function $u_{n\vec{k}}(\vec{r})$. Also, we use $M = -\mu_0 \langle S \rangle = \chi_{para} V H$

$$\mathcal{H} = g_I \mu_N I_z H - g_I \mu_N \frac{8\pi}{3} \left(\frac{\Omega}{V}\right) I_z (\chi_{para} V H) |u_{n0}(0)|^2$$

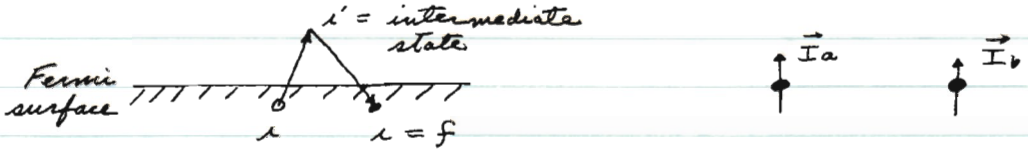
or: $$\mathcal{H} = g_I \mu_N I_z H \left\{ 1 - p \frac{8\pi}{3} \Omega \chi_{para} \right\}$$

For $I_z = 1$: $$\hbar\omega = g_I \mu_N H \left[1 - p \frac{8\pi}{3} \Omega \chi_{para} \right]$$

The last term gives the Knight shift. The Knight shift should be positive, $K = \frac{\Delta H}{H}$, as can be seen if we keep ω constant and vary H.

Note: $p = |u_n(0)|^2$

Consider second order effects and the two nucleus problem.



The second order transition is:

$$\frac{\langle \iota | \mathcal{H}^a_{HFS} | \iota' \rangle \langle \iota' | \mathcal{H}^b_{HFS} | \iota \rangle}{\mathcal{E}(\iota) - \mathcal{E}(\iota')}$$

This is known as the <u>Kittel - Ruderman - Yoshida Interaction</u>

From this we can generate an effective interaction between nuclei a and b thru the conduction electrons:

$$\mathcal{H}_{eff} = \sum_{\iota\iota'} \frac{\langle \iota | \mathcal{H}^a_{HFS} | \iota' \rangle \langle \iota' | \mathcal{H}^b_{HFS} | \iota \rangle}{\mathcal{E}(\vec{k}_\iota) - \mathcal{E}(\vec{k}_{\iota'})}$$

$$= (g_{Ia} g_{Ib}) \mu_N^2 \mu_0^2 \left(\frac{8\pi}{3}\right)^2 |u_{k_\iota}(0)|^2 |u_{k_{\iota'}}(0)|^2 \left(\frac{\Omega}{V}\right)^2$$

$$\cdot \sum_{\iota,\iota'} \frac{\langle \sigma_{\iota c} | \vec{S}_{\iota c} \cdot \vec{I}_a | \sigma_{\iota' c} \rangle \langle \sigma_{\iota' c} | \vec{S}_{\iota c} \cdot \vec{I}_b | \sigma_{\iota c} \rangle}{\mathcal{E}(\vec{k}_\iota) - \mathcal{E}(\vec{k}_{\iota'})}$$

We actually get another term because we actually take:

$$\langle u_{k_\iota}(\vec{r}) e^{i\vec{k}_\iota \cdot \vec{r}} | \delta(\vec{r} - \vec{R}_a) | u_{k_{\iota'}}(\vec{r}) e^{i\vec{k}_{\iota'} \cdot \vec{r}} \rangle$$

$$\rightarrow u^*_{k_\iota}(0) u_{k_{\iota'}}(0) e^{i(\vec{k}_{\iota'} - \vec{k}_\iota) \cdot \vec{R}_a}$$

so we actually have in the sum above the term:

$$e^{i(\vec{k}_{\iota'} - \vec{k}_\iota) \cdot (\vec{R}_a - \vec{R}_b)}$$

In the $\langle \iota | \; | \iota' \rangle \langle \iota' | \; | \iota \rangle$ we take $\iota = \iota'$ because the largest contributions comes from: $\mathcal{E}(k_\iota) \approx \mathcal{E}(k_{\iota'})$

$$\langle \sigma_{\iota c} | \vec{S}_{\iota c} \cdot \vec{I}_a \; \vec{S}_{\iota c} \cdot \vec{I}_b | \sigma_{\iota c} \rangle = \vec{I}_a \cdot \sum_{\alpha\beta} \langle \sigma | \vec{S}_{\iota c} \vec{S}_{\iota c} | \sigma \rangle \cdot \vec{I}_b = \frac{1}{4} \vec{I}_a \cdot \vec{I}_b$$

Then:

$$\mathcal{H}_{eff} = (g_{I_a} g_{I_b})(\mu_0 \mu_N)^2 (\mu_0)^2 \left(\frac{8\pi}{3}\right)^2 |u_{kF}(0)|^2 \frac{\Omega^2}{4} \cdot \sum_{\lambda,\lambda'} \frac{e^{i(\vec{k}_\lambda - \vec{k}_{\lambda'}) \cdot \vec{R}_{ab}}}{\varepsilon(\vec{k}_\lambda) - \varepsilon(\vec{k}_{\lambda'})} \vec{I}_a \cdot \vec{I}_b$$

Now assume $\varepsilon = \frac{\hbar^2 k^2}{2m^*}$. For the evaluation, see:

K. Yoshida, PR 106, 893 (1957)
M. Ruderman and C. Kittel in the Physical Review

We get:

$$\mathcal{H}_{eff} = (g_{I_a} g_{I_b})(\mu_0 \mu_N)^2 |u_{kF}(0)|^4 \left(\frac{8\pi}{3}\right)^2 \left(\frac{2m^*}{\hbar}\right) \frac{4 k_F^4}{(2\pi)^3} \cdot \frac{1}{x^4} \left[x \cos x - \sin x\right] \vec{I}_a \cdot \vec{I}_b$$

where $x = 2 k_F R_{ab}$

This expresses the long-range interaction of one nucleus on another nucleus due to the polarization of the conduction electrons by the $\mathcal{H}_{HFS}$ interaction. The same type of behaviour also occurs for magnetic impurities in metals, and we also have $\vec{I}_a \cdot \vec{I}_b$ long-range broadening in NMR. Charge fluctuations lead to long-range quadrapole broadening. Spin fluctuations due to impurities lead to fluctuations in the Knight shift. For two impurities in a metal, we have a long-range effect with an indirect exchange interaction given by $J \vec{S}_a \cdot \vec{S}_b$ (Found in Rare Earths).

LECTURE 30 : 4-25-62

The Effective Mass Approximation

The total crystal Hamiltonian is:

$$\left[\frac{1}{2m}\left(\vec{p}+\frac{e}{c}\vec{A}\right)^2 - eV(\vec{r}) - \frac{\mu_0}{mc}\vec{s}\cdot\nabla V\times\left(\vec{p}+\frac{e}{c}\vec{A}\right) + 2\mu_0\vec{s}\cdot\vec{H}\right.$$

$$\left. + eV'(r) + \hat{\mathcal{H}}_{HFS} + \hat{\mathcal{H}}_Q + \hat{\mathcal{H}}_{NZ}\right]\psi = \mathcal{E}\psi$$

where $V'(r)$ is an impurity potential. The Bloch Hamiltonian is:

$$\left[\frac{1}{2m}\vec{p}^2 - eV(\vec{r}) - \frac{\mu_0}{mc}\vec{s}\cdot\nabla V\times\vec{p}\right]\psi = \mathcal{E}\psi$$

The Bloch functions are: $\psi = u_{n\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$

In this problem, it is convenient to use the Kohn - Luttinger functions which form a complete set:

$$\chi_{n\vec{k}}(\vec{r}) = \sqrt{\frac{\Omega}{V}}\, u_{n0}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$

$$\int \chi^*_{n'\vec{k}'}(\vec{r})\,\chi_{n\vec{k}}(\vec{r})\,d\vec{r} = \delta_{nn'}\,\delta_{kk'}$$

$$\int_{WS} u^*_{n'0}(\vec{r})\, u_{n0}(\vec{r})\,d\vec{r} = \delta_{nn'}$$

$$\frac{1}{V}\int e^{i(\vec{k}'-\vec{k})\cdot\vec{r}}\,d\vec{r} = \delta_{k'k}$$

We can expand any ψ such that:

$$\psi = \sum_{n\vec{k}} A_n(\vec{k})\,\chi_{n\vec{k}}(\vec{r}) = \sum_{nk} A_n(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}\, u_{n0}(\vec{r})$$

Substituting in the original Schroedinger equation will give:

$$\sum_{nk} A_n(\vec{k}) \Big[e^{i\vec{k}\cdot\vec{r}} \Big(\frac{1}{2m}\vec{p}^2 + \frac{1}{m}\vec{p}\cdot\hbar\vec{k} + \frac{\hbar^2k^2}{2m} + \frac{e}{mc}\vec{A}\cdot\vec{p}$$

$$+ \frac{e}{mc}\vec{A}\cdot\hbar\vec{k} + \frac{1}{2m}\frac{e^2}{c^2}\vec{A}^2 - eV(\vec{r}) - \frac{\mu_0}{mc}\vec{S}\cdot\nabla V\times\vec{p}$$

$$- \frac{\mu_0}{mc}\vec{S}\cdot\nabla V\times\hbar\vec{k} - \frac{\mu_0}{mc}\vec{S}\cdot\nabla V\times\frac{e}{c}\vec{A}\Big)\sqrt{\frac{\Omega}{V}}\,u_{n0}(\vec{r})$$

$$+ \Big(\mathcal{H}^a_{HFS} + \mathcal{H}^a_Q + \mathcal{H}^a_{NZ} - eV'(r) - \varepsilon\Big)\sqrt{\frac{\Omega}{V}}\,e^{i\vec{k}\cdot\vec{r}}\,u_{n0}(\vec{r})\Big] = 0$$

Now use the relation:

$$\Big[\frac{p^2}{2m} - eV(\vec{r}) - \frac{\mu_0}{mc}\vec{S}\cdot\nabla V\times\vec{p}\Big]u_{n0}(\vec{r}) = \mathcal{E}^0_n\,u_{n0}(\vec{r})$$

Collect terms in the following fashion:

$$\sum_{nk} A_n(k)\Big[\Big\{\frac{1}{2m}\Big(\vec{p}+\frac{e}{c}\vec{A}\Big)^2 e^{i\vec{k}\cdot\vec{r}}\Big\}\sqrt{\frac{\Omega}{V}}\,u_{n0}(\vec{r})$$

$$+ \Big\{\Big(\vec{p}+\frac{e}{c}\vec{A}\Big)e^{i\vec{k}\cdot\vec{r}}\Big\}\Big\{\Big(\frac{\vec{p}}{m} - \frac{\mu_0}{mc}\nabla V\times\vec{S}\Big)\sqrt{\frac{\Omega}{V}}\,u_{n0}(\vec{r})\Big\}$$

$$+ \Big(2\mu_0\vec{S}\cdot\vec{H} - eV'(r) + \mathcal{H}^a_{HFS} + \mathcal{H}^a_Q + \mathcal{H}^a_{NZ} - (\varepsilon-\varepsilon^0_n)\Big)$$

$$\cdot\sqrt{\frac{\Omega}{V}}\,e^{i\vec{k}\cdot\vec{r}}\,u_{n0}(\vec{r})\Big] = 0$$

We have neglected previously the inclusion of the spin Zeeman interaction. Now form a matrix equation: Operate with $\int u^*_{n'0}(\vec{r})\,e^{-i\vec{k}'\cdot\vec{r}}\sqrt{\frac{\Omega}{V}}$.

Then use the approximation:

$$\langle\chi_{n'k'}|\,g(r)\,U(r)\,|\chi_{nk}\rangle \simeq g_{n'n}\,U_{k'k}$$

as long as $U(r)$ is a slowly varying function with respect to the lattice vector or interatomic distance.

$$g_{nn'} = \int_{WS} u^*_{n'0}(r)\,g(r)\,u_{n0}(\vec{r})\,d\tau$$

$$U_{kk'} = \frac{1}{V}\int e^{-i\vec{k}'\cdot\vec{r}}\,U(\vec{r})\,e^{i\vec{k}\cdot\vec{r}}\,d\tau$$

The motivation for this approximation follows:

$$\frac{\Omega}{V}\int u_{n'0}^{*}\, e^{-i\vec{k}'\cdot\vec{r}}\, g(r)\, U(r)\, u_{n0}\, e^{i\vec{k}\cdot\vec{r}}\, d\tau$$

$$\approx \sum_{i}\frac{\Omega}{V}\int_{WS} u_{n'0}^{*}\, g(r)\, u_{n0}\, d\tau \;\; U(R_i)\, e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}_i}$$

Let $\sum_i U(R_i)\, e^{-i(\vec{k}'-\vec{k})\cdot R_i} \longrightarrow \int U(r)\, e^{-i(\vec{k}'-\vec{k})\cdot\vec{r}}\, \frac{d\tau}{\Omega}$

Using this theorem we have:

$$\sum_{nk} A_n(\vec{k})\Big[\frac{1}{2m}P^2_{kk'}\,\delta_{nn'} + \vec{P}_{k'k}\cdot\vec{\Pi}_{n'n} - eV'_{k'k}\,\delta_{nn'}$$

$$+ 2\mu_0\,\vec{S}_{nn'}\cdot\vec{H}\,\delta_{k'k} + \frac{\Omega}{V}\left(\mathcal{H}^{a}_{HFS}\right)_{n'n} e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}_a}$$

$$+ \frac{\Omega}{V}\left(\mathcal{H}^{a}_{Q}\right)_{n'n} e^{-i(\vec{k}'-\vec{k})\cdot\vec{R}_a} + \mathcal{H}^{a}_{NZ}\,\delta_{n'n}\,\delta_{k'k}$$

$$- (\mathcal{E}-\mathcal{E}^{0}_{n}).\,\delta_{n'n}\,\delta_{k'k}\Big] = 0$$

There are now two approaches, one is to use BWPT in k-space and the other is BWPT in real space. We will use real space. We take the "Fourier transformation" by operating with $\sum_{k'} e^{i\vec{k}'\cdot\vec{r}'}$. Since we have few Fourier components outside the first Brillouin zone, we can assume closure on:

$$\frac{1}{V}\sum_{k'} e^{i\vec{k}'\cdot(\vec{r}'-\vec{r})} = \delta(\vec{r}'-\vec{r})$$

and get:

$$\sum_{k'}\sum_{nk} A_n(\vec{k})\, e^{i\vec{k}'\cdot\vec{r}'}\,\frac{1}{V}\int e^{-i\vec{k}'\cdot\vec{r}}\,\frac{p^2}{2m}\,e^{i\vec{k}\cdot\vec{r}}\,d\tau\,\delta_{nn'}$$

$$\longrightarrow \sum_{n}\sum_{k}\frac{p^2}{2m}\,A_n(\vec{k})\,e^{i\vec{k}\cdot\vec{r}'}\,\delta_{n'n}$$

Define: $f_n(\vec{r}') = \sum_{k} A_n(\vec{k})\, e^{i\vec{k}\cdot\vec{r}'}$

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Transforming to real space gives:

$$\sum_{n} \Big[\frac{1}{2m} \vec{P}^2 \delta_{n'n} + \vec{P} \cdot \vec{\Pi}_{n'n} - e V'(r) \delta_{n'n} + 2\mu_0 \vec{S}_{n'n} \cdot \vec{H} + \Omega \left(\mathcal{H}^a_{HFS} \right)_{n'n} \delta(\vec{r} - \vec{R}_a) + \Omega \left(\mathcal{H}^a_{Q} \right)_{n'n} \delta(\vec{r} - \vec{R}_a) + \mathcal{H}_{NZ} \delta_{n'n} - (\mathcal{E} - \mathcal{E}^0_n) \Big] f_n(\vec{r}) = 0$$

where $\vec{P} = \left(\vec{p} + \frac{e}{c} \vec{A} \right)$; $\vec{\Pi} = \left(\frac{\vec{p}}{m} - \frac{\mu_0}{mc} \nabla V \times \vec{s} \right)$

$f_n(\vec{r})$ is called the envelope function:

$$\psi = \sum_n f_n(\vec{r}) \, u_{n0}(\vec{r})$$

Consider the decoupling of the interband terms:

Let $n' = \gamma$ and neglect $V'(\vec{r})$, $\mathcal{H}_{NZ}$, $\mathcal{H}_{HFS}$

Also let $n = l$.

$$\sum_{l} \Big[\frac{1}{2m} \vec{P}^2 \delta_{\gamma l} + \vec{P} \cdot \vec{\Pi}_{\gamma l} + 2\mu_0 \vec{S}_{\gamma l} \cdot \vec{H} - (\mathcal{E} - \mathcal{E}^0_l) \delta_{\gamma l} \Big] f_l(\vec{r}) + \sum_{\mu} \Big[\vec{P} \cdot \vec{\Pi}_{\gamma \mu} + 2\mu_0 \vec{S}_{\gamma \mu} \cdot \vec{H} \Big] f_\mu(\vec{r}) = 0$$

Now let $n' = \nu$:

$$\sum_{l} \Big[\vec{P} \cdot \vec{\Pi}_{\nu l} + 2\mu_0 \vec{S}_{\nu l} \cdot \vec{H} \Big] f_l(\vec{r}) + \sum_{\mu} \Big[\frac{1}{2m} \vec{P}^2 \delta_{\nu\mu} + \vec{P} \cdot \vec{\Pi}_{\nu\mu} - (\mathcal{E} - \mathcal{E}^0_\nu) \delta_{\nu\mu} + 2\mu_0 \vec{S}_{\nu\mu} \cdot \vec{H} \Big] f_\mu(\vec{r}) = 0$$

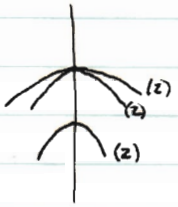
Now approximately:

$$f_\nu(\vec{r}) \, (\mathcal{E} - \mathcal{E}^0_\nu) \approx \sum_{l} \Big[\vec{P} \cdot \vec{\Pi}_{\nu l} + 2\mu_0 \vec{S}_{\nu l} \cdot \vec{H} \Big] f_l(\vec{r})$$

Then we have approximately:

$$\sum_l \left[\frac{1}{2m} \vec{P}^2 \delta_{jl} + \vec{P} \cdot \vec{\pi}_{jl} + 2\mu_0 \vec{S}_{jl} \cdot \vec{H} - (\varepsilon - \varepsilon_l^0)\delta_{jl} + \vec{P} \cdot \sum_\mu \frac{\vec{\pi}_{j\mu} \vec{\pi}_{\mu l}}{\varepsilon - \varepsilon_\mu^0} \cdot \vec{P} \right] f_l(\vec{r}) = 0$$

The dyad is related to the effective mass and band curvature. The above equation can be applied to Ge and Si:



Here l, j run from $1 \to 4$.

Form:

$$\vec{P} \cdot \sum_\mu \frac{\vec{\pi}_{j\mu} \vec{\pi}_{\mu l}}{\varepsilon - \varepsilon_\mu^0} \cdot \vec{P} = \frac{1}{2} \vec{P} \cdot \sum_\mu \frac{(\vec{\pi}_{j\mu} \vec{\pi}_{\mu l} + \vec{\pi}_{\mu l} \vec{\pi}_{j\mu})}{\varepsilon - \varepsilon_\mu^0} \cdot \vec{P} + \frac{1}{2} \vec{P} \cdot \sum_\mu \frac{(\vec{\pi}_{j\mu} \vec{\pi}_{\mu l} - \vec{\pi}_{\mu l} \vec{\pi}_{j\mu})}{\varepsilon - \varepsilon_\mu^0} \cdot \vec{P}$$

Consider a component of the antisymmetric term:

$$\frac{\frac{1}{2} P_x P_y (\pi_{j\mu}^x \pi_{\mu l}^y - \pi_{\mu l}^x \pi_{j\mu}^y) + \frac{1}{2} P_y P_x (\pi_{j\mu}^y \pi_{\mu l}^x - \pi_{\mu l}^y \pi_{j\mu}^x)}{\varepsilon - \varepsilon_\mu^0}$$

$$= \frac{1}{2} \frac{(\pi_{j\mu}^x \pi_{\mu l}^y - \pi_{\mu l}^x \pi_{j\mu}^y)}{\varepsilon - \varepsilon_\mu^0} (P_x P_y - P_y P_x)$$

Now: $P_x P_y - P_y P_x = \frac{\hbar e}{ic} H_z$ from: $\vec{P} \times \vec{P} = \frac{\hbar e}{ic} \vec{H}$

Then the antisymmetric part gives:

$$\frac{1}{2} \sum_\mu \frac{(\vec{\pi}_{j\mu} \times \vec{\pi}_{\mu l})}{\varepsilon - \varepsilon_\mu^0} \cdot \frac{\hbar e}{ic} \vec{H}$$

We can use an approach involving the method of the spin Hamiltonian. For Ge and Si we get a 4×4 matrix for the valence band.

From Kohn and Luttinger, we have for Si and Ge (valence band):

$$\mathcal{H} = -\frac{1}{m}\left[\left(\gamma_1 + \frac{5}{2}\gamma_2\right)\frac{\vec{P}^2}{2} - \gamma_2\left(J_x^2 P_x^2 + J_y^2 P_y^2 + J_z^2 P_z^2\right)\right.$$

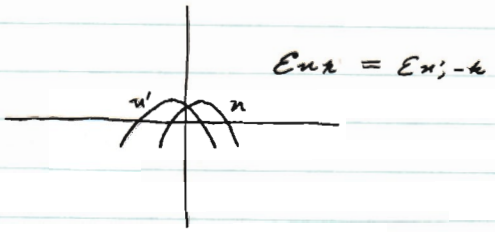
$$- 2\gamma_3\left[\{J_x J_y\}\{P_x P_y\} + \{J_y J_z\}\{P_y P_z\} + \{J_z J_x\}\{P_z P_x\}\right]$$

$$\left. + \frac{e\hbar}{c}\kappa\,\vec{J}\cdot\vec{H} + \frac{e\hbar}{c}q\left(J_x^3 H_x + J_y^3 H_y + J_z^3 H_z\right)\right]$$

The last two terms are not very large. $\{\ \}$ means symmeterized product.

Kramer's Theorem for Bands with Inversion Asymmetry

With non-inversion symmetry, we no longer have two fold degeneracy:



The degeneracy is not at the same point in k-space.

$$\mathcal{H} = \frac{\vec{p}^2}{2m} - eV(\vec{r}) - \frac{\mu_0}{mc}\nabla V \times \vec{p}\cdot\vec{s}$$

Now: $\psi'_{n\vec{k}} = \left[u^a_{n\vec{k}}(\vec{r})\,\alpha + u^b_{n\vec{k}}(\vec{r})\,\beta\right] e^{i\vec{k}\cdot\vec{r}}$

with: $\mathcal{H}\,\psi'_{n\vec{k}} = \mathcal{E}_{n\vec{k}}\,\psi'_{n\vec{k}}$

It may be that there is another $\psi^z_{n\vec{k}}$ such that:

Inversion symmetry: $\psi^z_{n\vec{k}} = \left[-u^{b*}_{n\vec{k}}(-\vec{r})\,\alpha + u^{a*}_{n\vec{k}}(-\vec{r})\,\beta\right] e^{i\vec{k}\cdot\vec{r}}$

Non-inversion symmetry: $\psi^z_{n\vec{k}} = \left[-u^{b*}_{n\vec{k}}(\vec{r})\,\alpha + u^{a*}_{n\vec{k}}(\vec{r})\,\beta\right] e^{-i\vec{k}\cdot\vec{r}}$

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Recall:

$$\psi^1_{nk}(\vec{r}) = (u^a_{no}\,\alpha + u^b_{no}\,\beta)\,e^{i\vec{k}\cdot\vec{r}} = \begin{pmatrix} u^a_{no}(\vec{r}) \\ u^b_{no}(\vec{r}) \end{pmatrix} e^{i\vec{k}\cdot\vec{r}}$$

$$\psi^2_{nk}(\vec{r}) = (-i\sigma_y C R_s)\,\psi^1_{nk}(\vec{r}) = \begin{pmatrix} -u^{b*}_{no}(\vec{r}) \\ u^{a*}_{no}(\vec{r}) \end{pmatrix} e^{i\vec{k}\cdot\vec{r}}$$

R_s is a space inversion operator. Form:

$$-i\sigma_y\,\mathcal{H}^*(-\vec{r})\,\psi^{1*}_{nk}(-\vec{r}) = \mathcal{E}_{nk}\,\psi^2_{nk}(\vec{r})$$

or $$\sigma_y\,\mathcal{H}^*(-\vec{r})\,\sigma_y\,\psi^2_{nk}(\vec{r}) = \mathcal{E}_{nk}\,\psi^2_{nk}(\vec{r})$$

We want to show $\sigma_y\,\mathcal{H}^*(-\vec{r})\,\sigma_y$ is the same as $\mathcal{H}$. Consider the term:

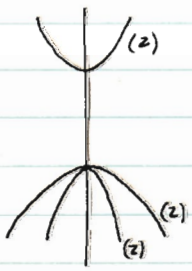
$$\frac{-\mu_o}{mc}\,\underbrace{\sigma_y\,\vec{S}^*\,\sigma_y}_{-\vec{S}}\,R_s\,(\nabla V)\times\vec{p}$$

Now if $V(\vec{r}) = V(-\vec{r})$; $R_s\,\nabla V = -\nabla V$ because the slopes have reversed sign at $\pm r$. Hence:

$$\sigma_y\,\mathcal{H}^*(-\vec{r})\,\sigma_y = \mathcal{H}(\vec{r})$$

and $\mathcal{H}\,\psi^2_{nk}(\vec{r}) = \mathcal{E}_{nk}\,\psi^2_{nk}(\vec{r})$. Hence every point in k space is two-fold degenerate, regardless of SO coupling.

Consider a two fold degenerate valence band: The decoupled effective mass Hamiltonian is:



$$\left[\frac{1}{2m^*}\,\vec{P}^2\,I + \vec{P}\cdot\sum_{\mu}\frac{\vec{\Pi}_{j\mu}\,\vec{\Pi}_{\mu j}}{\mathcal{E}-\mathcal{E}^o_\mu}\cdot\vec{P} + 2\mu_o\,\vec{S}_{jj}\cdot\vec{H}\right.$$

($\mathcal{E}^o_\mu$?)

$$\left. -(\mathcal{E}-\mathcal{E}^o_j)\,I\right]\,\phi_j(\vec{r}) = 0$$

where:

$$\vec{\pi}_{j\mu} = \begin{pmatrix} \vec{\pi}^{11}_{j\mu} & \vec{\pi}^{12}_{j\mu} \\ \vec{\pi}^{21}_{j\mu} & \vec{\pi}^{22}_{j\mu} \end{pmatrix}$$

$$f\!f_j(\vec{r}) = \begin{pmatrix} f^1_j(\vec{r}) \\ f^2_j(\vec{r}) \end{pmatrix}$$ Each component behaves as a spin up and spin down.

$$\vec{S}_{jj} = \begin{pmatrix} \vec{S}^{11}_{jj} & \vec{S}^{12}_{jj} \\ \vec{S}^{21}_{jj} & \vec{S}^{22}_{jj} \end{pmatrix}$$

$$\mathcal{U}^1_{\mu o} = \mathcal{U}^a_{\mu o}\,\alpha + \mathcal{U}^b_{\mu o}\,\beta$$
$$\mathcal{U}^2_{\mu o} = -\mathcal{U}^{b*}_{\mu o}(-\vec{r})\,\alpha + \mathcal{U}^{a*}_{\mu o}(-\vec{r})\,\beta$$

Since $\vec{\pi}_{\mu j}$ is Hermitean:

$$\vec{\pi}_{\mu j} = \begin{pmatrix} \vec{\pi}^{*}_{j\mu}{}^{11} & \vec{\pi}^{*}_{j\mu}{}^{21} \\ \vec{\pi}^{*}_{j\mu}{}^{12} & \vec{\pi}^{*}_{j\mu}{}^{22} \end{pmatrix}$$

Also we have: $\vec{\pi}^{22}_{j\mu} = \vec{\pi}^{*}_{j\mu}$; $\vec{\pi}^{21}_{j\mu} = -\vec{\pi}^{*}_{j\mu}{}^{12}$.
This can be shown from the definition for $\vec{\pi}$. Also:

$\vec{S}^{22}_{jj} = -\vec{S}^{11}_{jj}$ and is real.

$\vec{S}^{21}_{jj} = \vec{S}^{*}_{jj}{}^{12}$

Check the calculation of $\vec{\pi}^{22}_{jj} = \vec{\pi}^{*}_{jj}$. Neglect the so part, $\vec{\pi} \to \vec{p}/m$.

$$\vec{\pi}^{22}_{j\mu} = \int_{WS} \left(-\mathcal{U}^b_{jo}(-\vec{r})\right) \vec{\pi} \left(-\mathcal{U}^{b*}_{\mu o}(-\vec{r})\right) d\tau + \int_{WS} \left(\mathcal{U}^a_{jo}(-\vec{r})\right) \vec{\pi} \left(\mathcal{U}^{a*}_{\mu o}(-\vec{r})\right) d\tau$$

$$= \left[\int_{WS} \left(-\mathcal{U}^{b*}_{jo}(-\vec{r})\right)(-\vec{\pi})\left(-\mathcal{U}^{b}_{\mu o}(-\vec{r})\right) d\tau - \int_{WS} \left(\mathcal{U}^{a*}_{jo}(-\vec{r})\right) \vec{\pi} \left(\mathcal{U}^{a}_{\mu o}(-\vec{r})\right) d\tau \right]^*$$

Now reverse: $\vec{r} \to -\vec{r}$

$$\vec{\Pi}^{22}_{\gamma\mu} = \left[\int_{WS} \mathcal{U}^{b*}_{\gamma 0}(\vec{r})\, \vec{\Pi}\, \mathcal{U}^{b}_{\mu 0}(\vec{r})\, d\tau + \int_{WS} \mathcal{U}^{a*}_{\gamma 0}(\vec{r})\, \vec{\Pi}\, \mathcal{U}^{a}_{\mu 0}(\vec{r})\, d\tau \right]^*$$

$$= \vec{\Pi}^{11}_{\gamma\mu}$$

$$\vec{S}^{22}_{\gamma\gamma} = \int_{WS} \left[-\mathcal{U}^{b*}_{\gamma 0}(-\vec{r})\,\alpha + \mathcal{U}^{a*}_{\gamma 0}\,\beta \right]^* \vec{S} \left[-\mathcal{U}^{b*}_{\gamma 0}(-\vec{r})\,\alpha + \mathcal{U}^{a*}_{\gamma 0}(-\vec{r})\,\beta \right] d\tau$$

$$= \frac{1}{2}\hat{z}\left[\int_{WS} \mathcal{U}^{b}_{\gamma 0}\mathcal{U}^{b*}_{\gamma 0}\, d\tau - \int_{WS} \mathcal{U}^{a}_{\gamma 0}\mathcal{U}^{a*}_{\gamma 0}\, d\tau \right]$$

$$+ \frac{1}{2}\hat{x}\left[-\int_{WS} \mathcal{U}^{b}_{\gamma 0}\mathcal{U}^{a*}_{\gamma 0}\, d\tau - \int_{WS} \mathcal{U}^{a}_{\gamma 0}\mathcal{U}^{b*}_{\gamma 0}\, d\tau \right]$$

$$+ \frac{1}{2i}\hat{y}\left[\int_{WS} \mathcal{U}^{a*}_{\gamma 0}\mathcal{U}_{\gamma 0}\, d\tau - \int_{WS} \mathcal{U}^{b*}_{\gamma 0}\mathcal{U}^{a}_{\gamma 0}\, d\tau \right] = \vec{S}^{11}_{\gamma\gamma}$$

The above symmetry relations allow us to define for $\vec{\Pi}_{\gamma\mu}$:

$$\vec{\Pi}_{\gamma\mu} = \begin{pmatrix} \vec{t}_{\gamma\mu} + i\,\vec{\omega}_{\gamma\mu} & \vec{v}_{\gamma\mu} + i\,\vec{u}_{\gamma\mu} \\ -\vec{v}_{\gamma\mu} + i\,\vec{u}_{\gamma\mu} & \vec{t}_{\gamma\mu} - i\,\vec{\omega}_{\gamma\mu} \end{pmatrix}$$

and:

$$\vec{S}_{\gamma\gamma} = \frac{1}{2}\begin{pmatrix} \vec{c}_{\gamma\gamma} & \vec{a}_{\gamma\gamma} - i\,\vec{b}_{\gamma\gamma} \\ \vec{a}_{\gamma\gamma} + i\,\vec{b}_{\gamma\gamma} & -\vec{c}_{\gamma\gamma} \end{pmatrix}$$

We can use the Pauli matrices to express $\vec{\Pi}_{\gamma\mu}$ and $\vec{S}_{\gamma\gamma}$:

$$\vec{\Pi}_{\gamma\mu} = \vec{t}_{\gamma\mu}\, I + i\,\sigma_z\,\vec{\omega}_{\gamma\mu} + i\,\sigma_y\,\vec{v}_{\gamma\mu} + i\,\sigma_x\,\vec{u}_{\gamma\mu}$$

$$\vec{S}_{\gamma\gamma} = \frac{1}{2}\left(\vec{a}_{\gamma\gamma}\,\sigma_x + \vec{b}_{\gamma\gamma}\,\sigma_y + \vec{c}_{\gamma\gamma}\,\sigma_z \right)$$

Now let $\mathcal{E} \rightarrow \mathcal{E} - \mathcal{E}_j^\circ$. We can now make use of all of our previous relations and use the algebraic properties of the Pauli matrices, we can write the decoupled effective mass equations as:

$$\left[\frac{1}{2m} \vec{P} \cdot \vec{\vec{\alpha}} \cdot \vec{P} + \mu_0 \vec{S} \cdot \vec{\vec{g}} \cdot \vec{H} - \mathcal{E} \right] \mathcal{F}_j(\vec{r}) = 0$$

where:

$$\vec{\vec{\alpha}} = I + 2m \sum_\mu \frac{(\vec{t}_{j\mu}\vec{t}_{j\mu} + \vec{u}_{j\mu}\vec{u}_{j\mu} + \vec{v}_{j\mu}\vec{v}_{j\mu} + \vec{\omega}_{j\mu}\vec{\omega}_{j\mu})}{\mathcal{E} - \mathcal{E}_\mu^\circ}$$

$$\vec{\vec{g}} = 2\left[\hat{x}\vec{a}_{jj} + \hat{y}\vec{b}_{jj} + \hat{z}\vec{c}_{jj} + 2m \sum_\mu \hat{x}(\vec{v}_{j\mu} \times \vec{\omega}_{j\mu} + \vec{u}_{j\mu} \times \vec{t}_{j\mu}) \right.$$

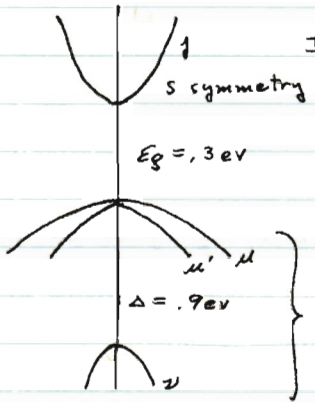
$$\left. \cdot \frac{\hat{y}(\vec{\omega}_{j\mu} \times \vec{u}_{j\mu} + \vec{v}_{j\mu} \times \vec{t}_{j\mu}) + \hat{z}(\vec{u}_{j\mu} \times \vec{v}_{j\mu} + \vec{\omega}_{j\mu} \times \vec{t}_{j\mu})}{\mathcal{E} - \mathcal{E}_\mu^\circ} \right]$$

4
?
0

LECTURE 33 : 5-2-62

Valence Bands of Ge, Si and InSb

The following developments are not exactly applicable to InSb because the ZnS structure does not have inversion symmetry. However, the valence band splitting is very small and has not be measured.



InSb: each band is two-fold degenerate.

u: $J = 3/2$; $M_J = \pm 3/2$
u': $J = 3/2$; $M_J = \pm 1/2$
v: $J = 1/2$; $M_J = \pm 1/2$

Because SO coupling does not affect s symmetry, the conduction band remains:

$$u'_{j0} = u_{s0}(\vec{r})\,\alpha \quad : \quad M_J = 1/2$$
$$u^2_{j0} = u_{s0}(\vec{r})\,\beta \quad : \quad M_J = -1/2$$

For the valence band:

$$u'_{u0} = \frac{1}{\sqrt{2}}(X + iY)\alpha \quad : \quad J = 3/2 \; ; \; M_J = 3/2$$
$$u^2_{u0} = \frac{1}{\sqrt{2}}(X - iY)\beta \quad : \quad J = 3/2 \; ; \; M_J = -3/2$$

$$u'_{u'0} = \frac{1}{\sqrt{6}}\left[-(X - iY)\beta + 2Z\alpha\right] \quad : \quad J = 3/2 \; ; \; M_J = 1/2$$
$$u^2_{u'0} = \frac{1}{\sqrt{6}}\left[(X + iY)\alpha + 2Z\beta\right] \quad : \quad J = 3/2 \; ; \; M_J = -1/2$$

$$u'_{v0} = \frac{1}{\sqrt{3}}\left[(X + iY)\beta + Z\alpha\right] \quad : \quad J = 1/2 \; ; \; M_J = 1/2$$
$$u^2_{v0} = \frac{1}{\sqrt{3}}\left[-(X - iY)\alpha + Z\beta\right] \quad : \quad J = 1/2 \; ; \; M_J = -1/2$$

We now evaluate the π's:

$$(\pi^x)_{sx} = (\pi^y)_{sy} = (\pi^z)_{sz} \Rightarrow i\pi$$

These are the only non-zero π's and they are imaginary.

We find:

$$\vec{\Pi}_{j\mu} = \frac{\imath\pi}{\sqrt{2}} \begin{pmatrix} \hat{x}+\imath\hat{y} & 0 \\ 0 & \hat{x}-\imath\hat{y} \end{pmatrix}$$

$$\vec{\Pi}_{j\mu'} = \frac{\imath\pi}{\sqrt{2}\sqrt{3}} \begin{pmatrix} 2\hat{z} & \hat{x}-\imath\hat{y} \\ -\hat{x}-\imath\hat{y} & 2\hat{z} \end{pmatrix}$$

$$\vec{\Pi}_{j\nu} = \frac{\imath\pi}{\sqrt{3}} \begin{pmatrix} \hat{z} & -\hat{x}+\imath\hat{y} \\ \hat{x}+\imath\hat{y} & \hat{z} \end{pmatrix}$$

The results for the effective mass and the g factor under these conditions is:

$$\alpha = \left[1 + 2m\pi^2\left(\frac{2}{3}\frac{1}{\varepsilon_g} + \frac{1}{3}\frac{1}{\varepsilon_g+\Delta}\right)\right]$$

$$g = 2\left[1 + 2m\pi^2\left(-\frac{1}{3}\frac{1}{\varepsilon_g} + \frac{1}{3}\frac{1}{\varepsilon_g+\Delta}\right)\right]$$

These quantities are accessible to experimental measurement. In fact g can be found in terms of α by eliminating π^2. We find:

$$\frac{\alpha-1}{g-2} = \frac{\left(\frac{2}{3}\frac{1}{\varepsilon_g} + \frac{1}{3}\frac{1}{\varepsilon_g+\Delta}\right)}{\left(-\frac{2}{3}\frac{1}{\varepsilon_g} + \frac{2}{3}\frac{1}{\varepsilon_g+\Delta}\right)} = -\left(\frac{3}{2}\frac{\varepsilon_g}{\Delta} + 1\right)$$

Now, for InSb: $\frac{\varepsilon_g}{\Delta} = \frac{1}{3}$; $\alpha - 1 = -\frac{3}{2}(g-2)$.
Also, $m^* = .013$, so that $\alpha \approx 75$, hence $g \approx -50$

LECTURE 34 : 5-4-62

Consider the effective mass equation :

$$\left[\frac{1}{2m} \vec{P} \cdot \overleftrightarrow{\alpha} \cdot \vec{P} + \mu_0 \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H} - \mathcal{E} \right] \psi = 0$$

We now consider the <u>Effective Mass and Magnetic Moment</u>. Take ψ to be a product of "orbital" and spin: $\psi = \psi_{orb}\, \psi_{spin}$. We can immediately effect the separation into :

$$\left.\begin{aligned} \left[\frac{1}{2m} \vec{P} \cdot \overleftrightarrow{\alpha} \cdot \vec{P} \right] \psi_{orb} &= \mathcal{E}_{orb}\, \psi_{orb} \\ \left[\mu_0 \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H} \right] \psi_s &= \mathcal{E}_s\, \psi_s \end{aligned}\right\} \quad \mathcal{E} = \mathcal{E}_{orb} + \mathcal{E}_s$$

If the band is spherical or elliptical, the solution of the effective mass equation gives :

$$\mathcal{E} = (n + 1/2)\, \hbar\, \frac{eH}{m_c^* c}$$

where :

$$m_c^* = m \left\{ \frac{\frac{1}{\alpha_{11}\, \alpha_{22}\, \alpha_{33}}}{\frac{1}{\alpha_{11}} \alpha^2 + \frac{1}{\alpha_{22}} \beta^2 + \frac{1}{\alpha_{33}} \gamma^2} \right\}^{1/2}$$

as previously found by applying $\frac{1}{2\pi} \frac{\partial A}{\partial \mathcal{E}}$ to the energy ellipsoid. We can also write the above as :

$$\frac{m}{m_c^*} = \left\{ \hat{H} \cdot \overleftrightarrow{\alpha}^{-1} \cdot \hat{H}\ |\overleftrightarrow{\alpha}| \right\}^{1/2}$$

For the spin problem; $\left[\mu_0 \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H} \right] \psi_s = \mathcal{E}_s\, \psi_s$, form:

$$\left(\mu_0 \vec{H} \cdot \tilde{\overleftrightarrow{g}} \cdot \vec{S} \right) \left(\mu_0 \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H} \right) \psi_s = \mathcal{E}_s^2\, \psi_s$$

Then: $$\frac{1}{4} \mu_0^2\, \vec{H} \cdot \left(\tilde{\overleftrightarrow{g}}\, \overleftrightarrow{g} \right) \cdot \vec{H}\, \psi_s = \mathcal{E}_s^2\, \psi_s$$

and:

$$\mathcal{E}_s = \pm \frac{\mu_0}{2} \left\{ \hat{H} \cdot \left(\tilde{\overleftrightarrow{g}}\, \overleftrightarrow{g} \right) \cdot \hat{H} \right\}^{1/2} H = \pm \mu_0 H \left(\frac{m}{m_s^*} \right)$$

This defines the spin resonance mass:

$$\frac{m}{m_s^*} = \frac{1}{2}\left\{ \hat{H}\cdot(\overleftrightarrow{g}\,\vec{g})\cdot\hat{H} \right\}^{1/2}$$

We can show that for simple band problems: $m_c^* = m_s^*$.

We can see now that our assumption of:

$$\mathcal{H} = \mathcal{H}_n^{\text{symmeterized}}\left(\vec{p} + \frac{e}{c}\vec{A}\right) + \mu_0 \vec{s}\cdot\overleftrightarrow{g}\cdot\vec{H}$$

for Landau - Peierls diamagnetism is justified by the form of the effective mass Hamiltonian.

Non - Parabolic Bands

We have succeeded in showing to second order in $\vec{p}$:

$$\left[\frac{1}{2m}\vec{p}\cdot\overleftrightarrow{\alpha}\cdot\vec{p} + \mu_0\vec{s}\cdot\overleftrightarrow{g}\cdot\vec{H}\right]\psi_j(\vec{r}) = \varepsilon\,\psi_j(\vec{r})$$

Does this form hold to higher orders in $\vec{p}$? No, because we get correction terms of the form:

$$\frac{\vec{p}\cdot\vec{\Pi}_{j\mu}\vec{\Pi}_{\mu\nu}\cdot\vec{p}\,\vec{\Pi}_{\nu\rho}\cdot\vec{p}\,\vec{\Pi}_{\rho j}\cdot\vec{p}}{(\varepsilon-\varepsilon_i^\circ)(\varepsilon-\varepsilon_j^\circ)(\varepsilon-\varepsilon_\rho^\circ)}$$

This treatment gives rise to terms (in cubic symmetry) like:

$$\frac{1}{2m}\vec{p}^2 I + D_{xx}\left(p_x^2+p_y^2+p_z^2\right) + \mathbb{D}_{xy}\,p_x p_y + D_{yx}\,p_y p_x + \cdots$$

$$+ D_{x^2y^2}\left(p_x^2 p_y^2 + p_y^2 p_x^2\right) + \mathbb{D}_{xyxy}\left(p_x p_y p_x p_y + p_y p_x p_y p_x\right) + \cdots$$

$\mathbb{D}_{x^2y^2}$ and $\mathbb{D}_{xyxy}$ are not necessarily equal under symmeterization. Symmeterize:

$$D_{x^2y^2}\left(p_x^2 p_y^2 + p_y^2 p_x^2\right) = \frac{1}{3}\mathbb{D}_{x^2y^2}\left(p_x^2 p_y^2 + p_y^2 p_x^2\right)$$

$$+ \frac{2}{3}D_{x^2y^2}\Big(p_x p_y p_x p_y + p_y p_x p_y p_x + p_x\{p_x p_y - p_y p_x\}p_y$$

$$+ p_y\{p_y p_x - p_x p_y\}p_x \Big)$$

Use $P_x P_y - P_y P_x = \frac{\hbar e}{ic} H_z$

Also consider:

$$\frac{1}{3} \mathbb{D}_{x^2y^2} \left[P_x P_y P_y P_x + P_y P_x P_x P_y + P_x P_y \{P_x P_y - P_y P_x\} + P_y P_x \{P_y P_x - P_x P_y\} \right]$$

Finally we obtain the structure:

? what is point of this?

$$\mathbb{D}_{x^2y^2} \{P_x^2 P_y^2\} - \mathbb{D}_{x^2y^2} \left(\frac{\hbar e}{c}\right)^2 H_z^2$$

We then get second order field corrections to both orbital and spin parts and a structure like:

$$\mathcal{E}(\vec{k}) - D(P) H^2 + \mu_0 \vec{S} \cdot \vec{\vec{g}}(P) \cdot \vec{H}$$

The effective mass theory can be applied to cyclotron resonance:

$$\left[\frac{1}{2m} \vec{P} \cdot \vec{\vec{\alpha}} \cdot \vec{P} + \mu_0 \vec{S} \cdot \vec{\vec{g}} \cdot \vec{H} \right] \psi = \mathcal{E} \psi$$

The band edge will split up into Landau levels:

In an RF field the kinetic momentum appears as:

$$\vec{P} = \vec{p} + \frac{e}{c} \vec{A} + \frac{e}{c} \vec{A}'$$

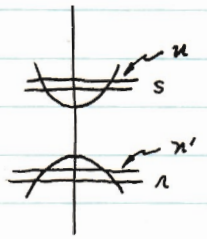
where $\vec{A}'$ is the RF field. The Hamiltonian then has as the cyclotron resonance interaction terms:

$$\frac{1}{2m} \left(\vec{p} \cdot \vec{\vec{\alpha}} \cdot \frac{e}{c} \vec{A}' + \frac{e}{c} \vec{A}' \cdot \vec{\vec{\alpha}} \cdot \vec{p} \right)$$

LECTURE 35 : 5-7-62

Interband Magneto-Spectroscopy

Consider a two band problem at $k=0$



We have:

$$\mathcal{H} = \frac{1}{2m}\vec{P}\cdot\overleftrightarrow{\alpha}\cdot\vec{P} + \mu_0\,\vec{S}\cdot\overleftrightarrow{g}\cdot\vec{H}$$

With an applied RF electric field, the interaction term is:

$$\frac{1}{2m}\left(\vec{p}\cdot\overleftrightarrow{\alpha}\cdot\frac{e}{c}\vec{A}' + \frac{e}{c}\vec{A}'\cdot\overleftrightarrow{\alpha}\cdot\vec{p}\right) \quad ; \quad \vec{A}' = \frac{c}{i\omega}\vec{E}$$

For interband transitions, we have to deal with matrix elements like:

$$\langle \psi_{n'}^{(r)} \mid \frac{1}{m}\frac{e}{c}\vec{p}\cdot\vec{A}' \mid \psi_n^{(s)} \rangle$$

where r, s are bands and n, n' denote Landau levels. Also:

$$\psi_{n'}^{(r)} = f_{n'}^{(r)}(\vec{r})\,u_{n'0}^{(r)}(\vec{r}) + \sum_{\mu} f_{n'}^{(\mu)}(\vec{r})\,u_{\mu 0}^{(\mu)}(\vec{r})$$

We cut off the $\sum_{\mu}$ terms for a two band problem. Then:

$$\langle \psi_{n'}^{(r)} \mid \vec{p}\cdot\vec{E} \mid \psi_n^{(s)} \rangle = \int f_{n'}^{(r)*}\,u_0^{(r)*}\,\vec{p}\cdot\vec{E}\,f_n^{(s)}\,u_0^{(s)}\,d\tau$$

$$= \int \left\{ f_{n'}^{(r)*}\vec{E}\,f_n^{(s)} \right\}\cdot\left\{ u_0^{(r)*}\,\vec{p}\,u_0^{(s)} \right\} d\tau$$

$$+ \int \left\{ f_{n'}^{(r)*}\vec{E}\cdot\vec{p}\,f_n^{(s)} \right\}\left\{ u_0^{(r)*}\,u_0^{(s)} \right\} d\tau$$

Now, by virtue of the effective mass derivation, the f's are slowly varying functions of the lattice parameter while the u's vary rapidly. Thus we can split up into two integrals and the last term will vanish by orthogonality giving:

$$\langle \psi_{n'}^{(r)} \mid \vec{p}\cdot\vec{E} \mid \psi_n^{(s)} \rangle = \frac{1}{\Omega}\int f_{n'}^{(r)*}\vec{E}\,f_n^{(s)}\,d\tau \cdot \int_{WS} u_0^{(r)*}\,\vec{p}\,u_0^{(s)}\,d\tau$$

We have assumed that the so coupling is weak and we neglect it. In the presence of so coupling, we would have to write:

$$\psi_{n'}^{(n)} = f_{n'}^{(n)1} u'_{k_0} + f_{n'}^{(n)2} u''_{k_0} + \cdots$$

We now determine the selection rules for the interband transition. First of all the band to band selection rule must be satisfied:

$$\int u_0^{(n)*} \vec{p}\, u_0^{(s)}\, d\tau$$

and then the one for the Landau levels:

$$\int f_{n'}^{(n)*} \vec{E}\, f_n^{(s)}\, d\tau$$

For spherical energy surfaces:

$$f_{n'}^{(n)} = u_{n'}\left(\left\{x + \hbar k'_y \frac{c}{eH}\right\}\left\{\frac{\hbar c}{eH}\right\}\right) e^{\imath k'_y y}\, e^{\imath k'_z z}$$

$$f_n^{(s)} = u_n\left(\left\{x + \hbar k_y \frac{c}{eH}\right\}\left\{\frac{\hbar c}{eH}\right\}\right) e^{\imath k_y y}\, e^{\imath k_z z}$$

These functions are orthogonal in n, k_y and k_z. Note that as they are independent of the effective mass, they are hence independent of the band. Now take for the interaction:

$$\vec{E} = \vec{E}_0\, e^{\imath k''_z z + \imath \omega t}$$

Immediately we have $k'_y = k_y$, $n' = n$, and $k_z - k'_z = k''_z$ as the selection rules. However, $\hbar k''_z$ is usually very small compared to the band $\hbar k_z$, $\hbar k'_z$, so that we can take as a selection rule $k_z = k'_z$, thus all transitions are vertical.

The interband magneto-optic transitions have been measured by reflectivity and absorption.

Non-Parabolic Bands

Consider the two band problem:

For the j band:

$$\left[\frac{1}{2m}\vec{P}^2 I + 2\mu_0 \vec{S}_{jj}\cdot\vec{H} + (\mathcal{E}_j^\circ - \mathcal{E})I\right] ff_j(\vec{r}) + \left[\vec{P}\cdot\vec{\Pi}_{jl} + 2\mu_0 \vec{S}_{jl}\cdot\vec{H}\right] ff_l(\vec{r}) = 0$$

For the l band:

$$\left[\frac{1}{2m}\vec{P}^2 I + 2\mu_0 \vec{S}_{ll}\cdot\vec{H} + (\mathcal{E}_l^\circ - \mathcal{E})I\right] ff_l(\vec{r}) + \left[\vec{P}\cdot\vec{\Pi}_{lj} + 2\mu_0 \vec{S}_{lj}\cdot\vec{H}\right] ff_j(\vec{r}) = 0$$

Neglect the spin Zeeman terms and assume that the band curvature is sharp, that is $|\mathcal{E}_l^\circ - \mathcal{E}| \gg \frac{P^2}{2m}$.

Decoupling gives: $ff_l(\vec{r}) = \dfrac{\vec{P}\cdot\vec{\Pi}_{lj}}{\mathcal{E}-\mathcal{E}_l^\circ} ff_j(\vec{r})$.

Thus, the effective mass equation becomes, with respect to BWPT:

$$\left[\frac{1}{2m}\vec{P}^2 I + (\mathcal{E}_j^\circ - \mathcal{E})I + \frac{\vec{P}\cdot\vec{\Pi}_{jl}\vec{\Pi}_{lj}\cdot\vec{P}}{\mathcal{E}-\mathcal{E}_l^\circ}\right] ff_j(\vec{r}) = 0$$

If we write $\dfrac{1}{\mathcal{E}-\mathcal{E}_l^\circ} = \dfrac{1}{\mathcal{E}_j^\circ - \mathcal{E}_l^\circ}\left(\dfrac{\mathcal{E}_j^\circ - \mathcal{E}_l^\circ}{\mathcal{E}-\mathcal{E}_l^\circ}\right)$

and if we take $\mathcal{E} \gg \mathcal{E}_j^\circ$, we have:

$$\frac{\mathcal{E}_j^\circ - \mathcal{E}_l^\circ}{\mathcal{E}-\mathcal{E}_l^\circ} \approx \frac{\mathcal{E}_g}{\mathcal{E}+\mathcal{E}_g} \approx 1$$

This motivates writing the effective mass equation as:

$$\left[\left\{ \frac{1}{2m} \vec{P} \cdot \vec{\vec{\alpha}}(0) \cdot \vec{P} + \mu_0 \vec{S} \cdot \vec{\vec{g}}(0) \cdot \vec{H} \right\} \left(\frac{\mathcal{E}_g}{\mathcal{E} + \mathcal{E}_g} \right) - \mathcal{E} I \right] \mathcal{F}_j(\vec{r}) = 0$$

The solution without $\frac{\mathcal{E}_g}{\mathcal{E}+\mathcal{E}_g}$ is:

$$\mathcal{E} = (n + 1/2)\hbar \frac{eH}{m_c^* c} \pm \frac{\mu_0}{2} g^*(0) H$$

where g^* is for $\mathcal{E} = 0$. Now, if we scale all terms in the Hamiltonian by $\frac{\mathcal{E}_g}{n+\mathcal{E}_g}$, then $\mathcal{E}$ is scaled by the same factor. Then we set $n = \mathcal{E}$ and solve for the final energy $\mathcal{E}$:

$$\mathcal{E} = -\frac{\mathcal{E}_g}{2} \pm \left\{ \left(\frac{\mathcal{E}_g}{2}\right)^2 + \mathcal{E}_g \left[\frac{\hbar e H}{m_c^*(0) c} (n + 1/2) \pm \frac{\mu_0}{2} g^*(0) H \right] \right\}^{1/2}$$

For a simple spin problem: $\mathcal{E} = \left\{ \left(\frac{\mathcal{E}_g}{2}\right)^2 + \mathcal{E}_g \left[\frac{\hbar e H}{m_c^*(0) c} (n + \frac{1}{2} \pm 1/2) \right] \right\}^{1/2}$

Nuclear Interactions in Semiconductors

Recall the types: $\vec{I} \cdot \vec{\vec{A}} \cdot \vec{S} \sim (\vec{I} \cdot \vec{L}_{ja})(\vec{L}_{ag} \cdot \vec{S})$

$\vec{I} \cdot \vec{\vec{\gamma}} \cdot \vec{H} \sim \vec{I} \cdot \left(\frac{\Gamma}{\Lambda^3}\right)_{ja} (\vec{L}_{ag} \cdot \vec{H})$

This assumes we can write: $\mu_0 \vec{S} \cdot \vec{\vec{g}} \cdot \vec{H} \sim \frac{\vec{S} \cdot \vec{L}_{ja} \vec{L}_{ag} \cdot \vec{H}}{\mathcal{E}_j^0 - \mathcal{E}_a^0}$

However, here we have: $\vec{\vec{g}} \sim \frac{\vec{\pi}_{ja} \vec{\pi}_{ag}}{\mathcal{E}_j^0 - \mathcal{E}_a^0}$ which has a physically different origin than it does in crystal field theory.

Impurities and Excitons in Magnetic Fields

The impurity or exciton Hamiltonian is:

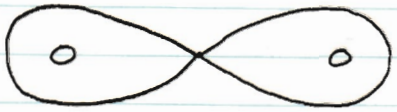
$$\left[\frac{1}{2m} \vec{P} \cdot \vec{\vec{\alpha}} \cdot \vec{P} + \mu_0 \vec{S} \cdot \vec{\vec{g}} \cdot \vec{H} + \frac{eZ}{\kappa r} \right]$$

The dielectric approximation may be shown to hold outside the impurity center. This description gives good results for p states. The Zeeman spectrum of these p-type states has been observed, as has exciton structure splitting.

LECTURE 36 : 5-9-62

V. Ferromagnetism and Antiferromagnetism

Origins : consider a two atom system.



We stipulate that the wave functions involved are orthogonal. The total wave function is a determinant:

$$D = \frac{1}{\sqrt{2!}} A \left\{ \mu_a(1)\, \chi_a(1)\, \mu_b(2)\, \chi_b(2) \right\}$$

where A is an antisymmetrizing operator. Recall the coulomb interaction from earlier work :

$$\langle D' | \sum_{i<j} \frac{e^2}{r_{ij}} | D \rangle = \langle \pi' | \sum_{i<j} \frac{e^2}{r_{ij}} \left[1 - P_{ij}^{q} \tfrac{1}{2} (1 + 4\, \vec{S}_i \cdot \vec{S}_j) \right] | \pi \rangle$$

Here: $\pi = \mu_a(1)\, \chi_a(1)\, \mu_b(2)\, \chi_b(2)$

Recall the effective interaction for the coulomb interaction:

$$\mathcal{H}_{eff} = K_{12} - \tfrac{1}{2} J_{12} \left(1 + 4 \vec{S}_1 \cdot \vec{S}_2 \right)$$

where $K_{12} = \int \mu_1^*(1)\, \mu_1(1)\, \frac{e^2}{r_{12}}\, \mu_2^*(2)\, \mu_2(2)\, d\tau$

$$J_{12} = \int \mu_1^*(1)\, \mu_2(1)\, \frac{e^2}{r_{12}}\, \mu_2^*(2)\, \mu_1(2)\, d\tau > 0$$

We can form: $\langle D' | \frac{e^2}{r_{12}} | D \rangle = \langle \pi' | \mathcal{H}_{eff} | \pi \rangle$
where π', π differ by spin but not space.

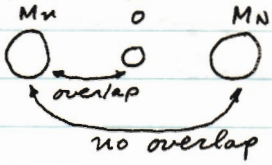
The lowest energy arises for parallel spins because of $-2 J_{12} \vec{S}_1 \cdot \vec{S}_2$. For interactions among all levels of each atom, we cannot tell whether J_{12} is + or −, however, we still have the form: $-2 \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$ for the exchange interaction.

With this kind of interaction, we can get either ferromagnetic ($J>0$) or antiferromagnetic ($J<0$) interaction. This form for the exchange is called the Heisenberg model but it rarely fits any known magnetic material, that is, a model of localized spins with overlap.

Classification of Magnetic Origins:

(1) Direct exchange between magnetic ions (ground and excited states) for $J>0$ or $J<0$. This is observed in $CrBr_3$ where Cr has an integral number of Bohr magnetons and they interact directly (weakly ferromagnetic). This is possibly the mechanism in ferromagnetic metals (Fe, Ni, Co), but not completely because of the conduction electrons and the non-integral number of Bohr magnetons. This is still in question.

(2) Superexchange between magnetic ions with no direct overlap of atomic orbitals, for example, MnO:



The Mn's interact through excited states of O so it is hard to tell if the interaction is ferromagnetic or antiferromagnetic. There is is an integral number of Bohr magnetons and may be a good model for insulators or semiconductors. Examples are the ferrites, garnets, and MnF_2.

(3) Indirect exchange via the conduction electrons as in the rare earth metals. Non-integral μ_B. The coupling is thru the polarization of the conduction electrons, or is a Yoshida type interaction:

$$J\,\vec{S}_i\cdot\vec{S}_j\;\frac{\{\cos(kR)\,(kR)-\sin(kR)\}}{(kR)^4}\rightarrow \text{spiral structures}$$

Also in Cu Mn alloys (dilute amount of Mn in Cu).

(4) Other mechanisms:
   a. Stoner theory of metallic ferromagnetism
   b. Overhauser skin-density wave

LECTURE 37 : 5-11-62

Weiss Molecular Field Theory

Recall the effective exchange Hamiltonian:

$$\mathcal{H}_{eff} = -2 \sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

We do not specify the sign of J, thus not specifying ferromagnetic (F) or antiferromagnetic (AF) coupling. We now single out a particular spin, interacting with the rest of the spins. Weiss maintained that the effect of the other spins could be replaced by an effective field for the ith spin:

$$\mathcal{H}_{eff\,i} = -z J z \langle \vec{S} \rangle \cdot \vec{S}_i$$

This is suggestive of an effective field obtained by a self-consistent calculation. Now, for an assembly of spins in an external magnetic field:

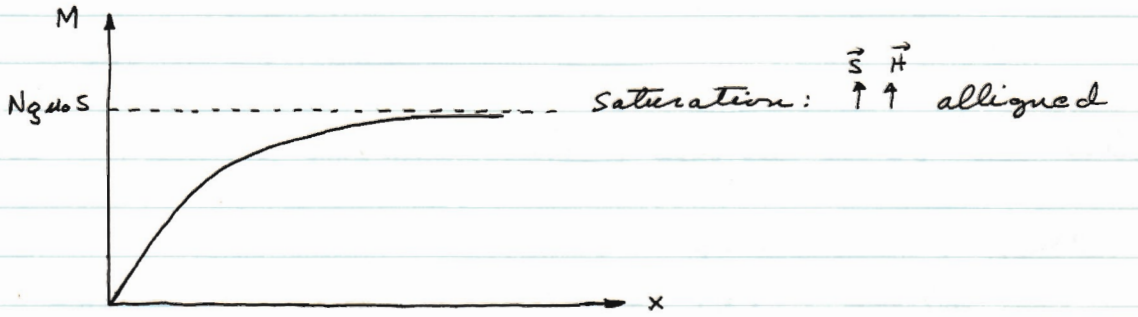
$$M = N g \mu_0 S B_S(x)$$

$$B_S(x) = \frac{2S+1}{2S} \coth\left\{\frac{2S+1}{2S} x\right\} - \frac{1}{2S} \coth\left\{\frac{x}{2S}\right\}$$

$$x = \frac{g \mu_0 S H}{kT}$$

The high temperature limit is:

$$M = \frac{N g^2 \mu_0^2 S(S+1) H}{3kT} = N g \mu_0 \frac{S+1}{3} x \quad \text{(Weiss' Law)}$$



Now we can write: $\mathcal{H}_{eff_i} = g\mu_0 \vec{H}_{eff} \cdot \vec{S}_i$

where:

$$\vec{H}_{eff} = \frac{-2Jz\langle \vec{S} \rangle}{g\mu_0} \quad ; \quad M = -g\mu_0 \langle S \rangle N$$

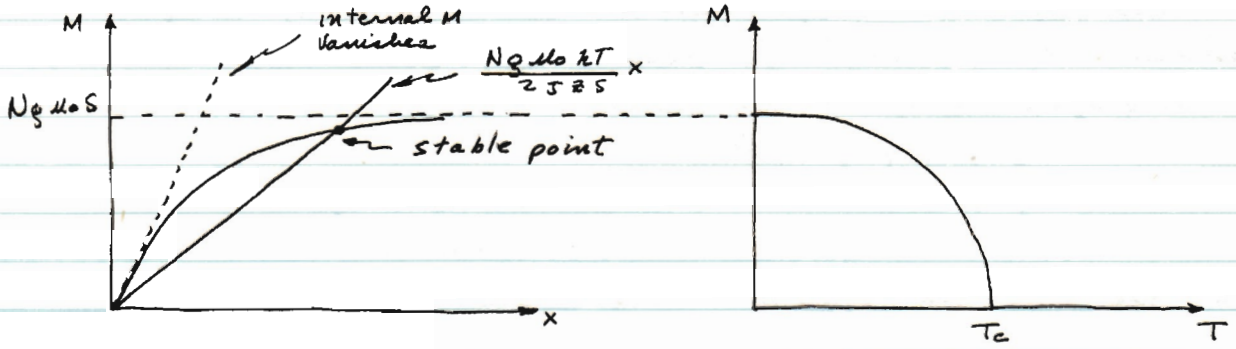
Now take:

$$x = \frac{g\mu_0 S H_{eff}}{kT}$$

Use $H_{eff} = \frac{2JzM}{Ng^2\mu_0^2}$ in order to get:

$$M = \frac{Ng\mu_0 kT}{2Jzs} x$$

This gives us two relations for M, the linear one due to the internal field above and the $B_S(x)$ relation in an external field, caused by the net internal field.



One can see that there is a given temperature at which M vanishes. This is T_c, where the slopes of the two curves for M will be equal. This, of course, occurs in the high temperature limit:

$$\frac{Ng\mu_0 kT_c}{2Jzs} = \frac{Ng\mu_0 (s+1)}{3}$$

or: $kT_c = \frac{2Jzs(s+1)}{3}$ (curie temperature)

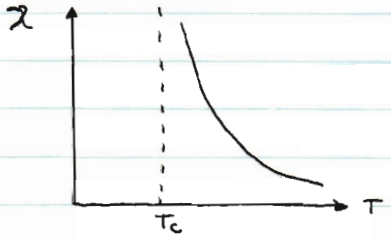
This relation is not to be taken too literally in its quantitative value, although the relationships among the variables is qualitatively correct. What happens in an external field above T_c? Consider F case.

$$M = \frac{Ng^2\mu_0^2 S(s+1)}{3kT} \left\{ H + \frac{2JzM}{Ng^2\mu_0^2} \right\}$$

Solving for M we find:

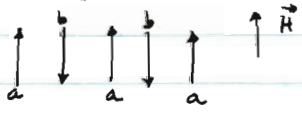
$$M = \frac{N g^2 \mu_0^2 S(S+1)}{3k} \frac{H}{T - \frac{2 J z S(S+1)}{3k}}$$

$$= \frac{C H}{T - T_c} \quad \text{(Curie's Law)}$$



We see that we have the usual paramagnetic behaviour above T_c.

Antiferromagnetic Molecular Field: The physical situation is that of two sublattices of oppositely aligned spins. This could be caused by anisotropy fields in a crystallographic direction.



Assume the spins a and b are identical.

Now we have the effective interactions:

$$\mathcal{H}^a_{eff_a} = -2 J_{aa} z_{aa} \langle \vec{S}_a \rangle \cdot \vec{S}_a + 2 J_{ab} z_{ab} \langle \vec{S}_b \rangle \cdot \vec{S}_a + g \mu_0 \vec{H} \cdot \vec{S}_a$$

$$\mathcal{H}^b_{eff_a} = \underbrace{-2 J_{aa} z_{aa} \langle \vec{S}_b \rangle \cdot \vec{S}_b}_{\text{F part}} + \underbrace{J_{ab} z_{ab} \langle \vec{S}_a \rangle \cdot \vec{S}_b}_{\text{AF part}} + \underbrace{g \mu_0 \vec{H} \cdot \vec{S}_b}_{\text{External field}}$$

Consider the AF substance in an external field above some critical temperature. This means writing Curie's Law for each sublattice:

$$M_a = \frac{C}{T}(H + \lambda_{aa} M_a - \lambda_{ab} M_b)$$

$$M_b = \frac{C}{T}(H + \lambda_{aa} M_b - \lambda_{ab} M_a)$$

where: $\lambda_{aa} = \frac{2 J_{aa} z_{aa}}{\frac{N}{2} g^2 \mu_0^2}$; $\lambda_{ab} = \frac{2 J_{ab} z_{ab}}{\frac{N}{2} g^2 \mu_0^2}$

Put the equations in the form:

$$M_a (T - C\lambda_{aa}) + M_b (C\lambda_{ab}) = cH$$
$$M_a (C\lambda_{ab}) + M_b (T - C\lambda_{aa}) = cH$$

A critical temperature will be obtained by the Homogeneous solution of the above. We get:

$$(T - C\lambda_{aa})^2 - (C\lambda_{ab})^2 = 0$$
$$T = C\lambda_{aa} \pm C\lambda_{ab}$$

The proper critical temperature is the higher root as this produces the first anomaly on decreasing the temperature. This critical point is called the Neél temperature T_N:

$$T_N = C(\lambda_{aa} + \lambda_{ab})$$

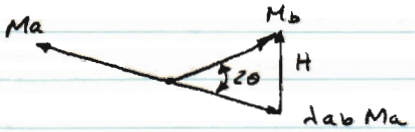
If we resubstitute T_N, we find $M_a = M_b$ so this is the onset of the ordered state. We now solve for χ and M for $T > T_N$. We obtain immediately:

$$M_a = M_b = \frac{CH}{T - C(\lambda_{aa} - \lambda_{ab})} = \frac{CH}{T - \theta} \quad \text{(paramagnetic behaviour)}$$

Now θ is lower than T_N, so that we have ordering before reaching θ.

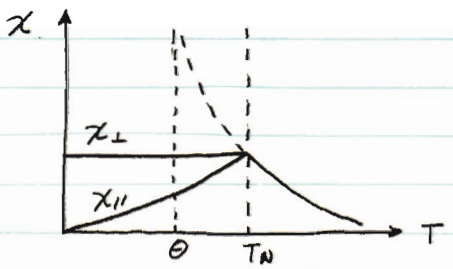
Now consider $T < T_N$. We have two cases, $H \parallel M_a, M_b$ and $H \perp M_a, M_b$. We can easily see that $\chi_\parallel = 0$ at $T = 0$ because the ordering is complete. For $H \perp M_a, M_b$, we have the following situation:

$$\sin 2\theta = \frac{H}{M_b}$$



$$\tan 2\theta = \frac{H}{\lambda_{ab} M_a} \; ; \quad M_\perp = M_a \sin 2\theta$$

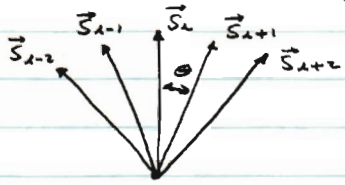
For small angles, $\tan 2\theta \simeq \sin 2\theta$, and: $M_\perp = \frac{H}{\lambda_{ab}}$ so that $\chi_\perp = 1/\lambda_{ab}$. Check at T_N: $\chi_N = \frac{2C}{T_N - \theta} = \frac{1}{\lambda_{ab}}$



For more details, see Kittel.

LECTURE 38: 5-14-62

We have been discussing simple uniaxial models of ferromagnets and antiferromagnets. We now consider spiral models. Take ferromagnetic coupling between nearest neighbors and antiferromagnetic coupling between next nearest neighbors. This causes the nearest neighbors to be canted slightly with respect to each other at equal angles. Consider the plane projection of a symmetry direction.



The energy is: $\mathcal{E}_i = \underbrace{-2 J_n \vec{S}_i \cdot (\vec{S}_{i+1} + \vec{S}_{i-1})}_{F} + \underbrace{2 J_{nn} \vec{S}_i \cdot (\vec{S}_{i+2} - \vec{S}_{i-2})}_{AF}$

since all spins are of the same magnitude:

$$\mathcal{E}_i = -4 J_n S^2 \cos\theta + 4 J_{nn} S^2 \cos(2\theta)$$

The equilibrium angle is given by:

$$\frac{\partial \mathcal{E}_i}{\partial \theta} = 0 = 4 J_n S^2 \sin\theta - 2 \cdot 4 J_{nn} S^2 \sin 2\theta$$

or: $\sin\theta (J_n - 4 J_{nn} \cos\theta) = 0$: $\sin\theta = 0$

$$\cos\theta = \frac{J_n}{4 J_{nn}}$$

Note that if $J_{nn} = 0$, $\sin\theta = 0$ and we have an ferromagnet. For $4 J_{nn} > J_n$, the root is $\cos\theta = \frac{J_n}{4 J_{nn}}$ we have a spiral whose equation is this root. If we have anisotropy along the symmetry axis, we have tilting along this "easy" direction. We can measure spirals by neutron diffraction and find in the rare earths periods for the spirals of about 20 lattice constants.

more generally in the rare earth metals, we have a Yoshida type interaction that will give oscillations:

$$J \vec{S}_i \cdot \vec{S}_{i+n} \qquad \frac{k_F \cdot a_n \cos k_F \cdot a_n - \sin k_F \cdot a_n}{(k_F \cdot a_n)^4}$$

Suppose we have such a simple spherical energy surface that k_F is: $k_F = (3\pi^2 n)^{1/3}$. Also assume simple cubic symmetry. Then $k_F \simeq \pi/a$ and $k_F \cdot a_n = n\pi$ so the interaction may be written:

$$\frac{\cos n\pi}{(n\pi)^3} - \frac{\sin n\pi}{(n\pi)^4}$$

$n=1$: $J \vec{S}_i \cdot \vec{S}_j \left(-\frac{1}{\pi^3}\right)$
$n=2$: $J \vec{S}_i \cdot \vec{S}_j \left(\frac{1}{8\pi^3}\right)$
$n=3$: $J \vec{S}_i \cdot \vec{S}_j \left(-\frac{1}{27\pi^3}\right)$

We can see the oscillations which will cause the spiraling so that in the rare earth metals, the origin of the spiraling is the Kittel Ruderman Yoshida interaction.

The molecular field approximation does not work at very high or low temperatures or near the critical temperature. This is because we have assumed an interaction $J \vec{S}_i \cdot \langle \vec{S} \rangle$ near T_c where the correlation effects produces more order than the molecular field method.

The Bethe - Peierls - Weiss Method

Suppose we have a cubic array:

$$\mathcal{H} = -2J \vec{S}_0 \cdot \sum_i \vec{S}_i - 2J \sum_i \vec{S}_i \cdot \sum_j \vec{S}_j - 2J \sum \vec{S}_i \cdot \vec{S}_j$$

We reduce this to a "cluster" problem:

$$\mathcal{H}_{cl} = -2J \vec{S}_0 \cdot \vec{S}_a - 2J \sum_a \vec{S}_a \cdot \vec{H}_{eff}$$

$$= -2J \vec{S}_0 \cdot \vec{S}_a - 2J \vec{S}_a \cdot \vec{H}_{eff}$$

This interaction can be treated exactly quantum mechanically and use is made of the resulting levels to compute the free energy and get $\langle \vec{S}_a \rangle$ which must match H_{eff} self-consistently. This gives good results around T_c and for some short range order.

Neither the molecular field or Bethe-Peierls-Weiss methods are very good at low temperatures. However, we can get an exact solution at $T=0$ for a ferromagnet. Consider:

$$\mathcal{H} = -2J \sum_{i<j} \vec{S}_i \cdot \vec{S}_j$$

operating on the spin ground state of maximum alignment at $T=0$: $\alpha\alpha\alpha\cdots$. Rewrite $\mathcal{H}$:

$$\mathcal{H} = -2J \left\{ \sum_{i<j} \frac{S_i^+ S_j^-}{2} + \sum_{i<j} \frac{S_i^- S_j^+}{2} + \sum_{i<j} S_i^z S_j^z \right\}$$

Now raising operators cannot operate on a maximum aligned ground state, so only the S^z term works. The lowest eigenstate is:

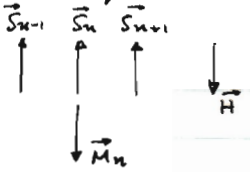
$$\mathcal{E} = -2JN\tfrac{1}{4} = -\frac{JN}{2}$$

LECTURE 39 : 5-16-62

Spin Waves in a Ferromagnet

Semiclassical

Consider the following ferromagnetic ordering of the spins:



It is conventional to take the spins opposite to the field and the magnetization. The nearest neighbor exchange Hamiltonian is:

$$\mathcal{H} = \sum_n g\mu_0 \vec{S}_n \cdot \vec{H} - 2J \sum_n \vec{S}_n \cdot \vec{S}_{n-1}$$

The equation of motion for a spin is:

$$\frac{d\vec{S}_n}{dt} = \frac{1}{i\hbar}\left[\mathcal{H}, \vec{S}_n\right] = \frac{1}{i\hbar}\left[g\mu_0 \vec{H} - 2J\vec{S}_{n+1} - 2J\vec{S}_{n-1}\right] \times \vec{S}_n$$

Define the following quantities:

$$\vec{M}_N = -g\mu_0 \vec{S}_n \; ; \quad \gamma = \frac{g\mu_0}{\hbar} \; ; \quad \frac{1}{2} = \frac{2J}{(g\mu_0)^2}$$

Then:

$$\frac{d\vec{M}_n}{dt} = -\gamma \vec{M}_n \times \left[\vec{H} + \frac{1}{2}\vec{M}_{n+1} + \frac{1}{2}\vec{M}_{n-1}\right]$$

Take a classical solution: $\vec{M}_N = \vec{M}_0 + \vec{M}_1 e^{i(kna+\omega t)}$
where $\vec{M}_1$ is small and we will work only to order $\vec{M}_1$.

$$i\omega \vec{M}_1 e^{i(kna+\omega t)} = -\gamma \vec{M}_0 \times \left[\frac{1}{2}\vec{M}_1 e^{i(kna+\omega t)} e^{ika}\right.$$

$$\left. + \frac{1}{2}\vec{M}_1 e^{i(kna+\omega t)} e^{-ika}\right] - \gamma \vec{M}_1 e^{i(kna+\omega t)} \times \left[\vec{H} + \frac{1}{2}\vec{M}_0\right]$$

or:

$$i\omega \vec{M}_1 = -\gamma \vec{M}_1 \times \left[\vec{H} + \frac{1}{2}\vec{M}_0\right] + \gamma \vec{M}_1 \times \frac{1}{2}\vec{M}_0 \cos ka$$

Now take $\vec{H}$, $\vec{M_0}$ in the z direction:

$$i\omega M_{ix} = -\gamma M_{iy}\left[H + \lambda M_0 (1 - \cos ka)\right]$$

$$i\omega M_{iy} = \gamma M_{ix}\left[H + \lambda M_0 (1 - \cos ka)\right]$$

Define M_i^+ and M_i^-, then:

$$i\omega M_i^+ = i\gamma M_i^+\left[H + \lambda M_0 (1 - \cos ka)\right]$$

and the dispersion relation is:

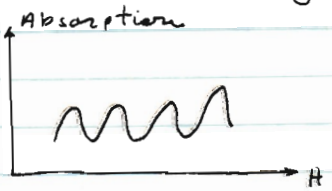
$$\omega = \gamma H + \gamma \lambda M_0 \left[1 - \cos ka\right]$$

For low k vectors we have a quadratic form:

$$\omega = \gamma H + \frac{\gamma \lambda M_0 k^2 a^2}{2} = \gamma H + D k^2$$

This simple spin wave relation actually describes some observations as obtained by neutron diffraction. It is also observed in the ferromagnetic resonance of thin ferromagnetic films:

The magnetic moment of the film is forced parallel to the surface by demagnetization. We can apply an RF field and actually measure the k^2 dependence. Because of the thinness of the film, we can get mode generation and the curve looks something like:



We now consider the quantum theory of spin waves:

$$\mathcal{H} = g\mu_0 \sum_n \vec{S}_n \cdot \vec{H} - \sum_{nn'} 2 J_{nn'} \vec{S}_n \cdot \vec{S}_{n'}$$

Use the "Fourier properties" of the lattice in order to form:

$$\vec{S}(\vec{k}) = \sum_n \vec{S}_n e^{i\vec{k}\cdot\vec{R}_n}$$

Using BVK boundary conditions, there will be as many $\vec{S}(\vec{k})$ as there are spins. Recall the closure relations:

$$\sum_n e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_n} = N\delta_{\vec{k},\vec{k}'} \quad ; \quad \sum_k e^{i\vec{k}\cdot(\vec{R}_n - \vec{R}_{n'})} = N\delta_{nn'}$$

We now transform the entire Hamiltonian into $\vec{k}$ space. Operate with $\sum_k e^{-i\vec{k}\cdot\vec{R}_{n'}}$ and get:

$$\mathcal{H} = g\mu_0 \frac{1}{N} \sum_{nk} e^{-i\vec{k}\cdot\vec{R}_n} \vec{S}(\vec{k})\cdot\vec{H} - \frac{2}{N^2} \sum_{nn'} \sum_{kk'} J_{nn'} \vec{S}(\vec{k}) e^{-i\vec{k}'\cdot\vec{R}_{n'}} \cdot \vec{S}(\vec{k}') e^{-i\vec{k}'\cdot\vec{R}_n}$$

or: $$\mathcal{H} = g\mu_0 \vec{S}(0)\cdot\vec{H} - \frac{1}{2}\frac{2}{N^2} \sum_n \sum_\ell{}' \sum_{kk'} J_\ell \vec{S}(\vec{k}) e^{i\vec{k}\cdot\vec{R}_n} \cdot \vec{S}(\vec{k}') \cdot e^{-i\vec{k}'\cdot\vec{R}_n} e^{-i\vec{k}'\cdot\vec{R}_\ell}$$

$$\mathcal{H} = g\mu_0 \vec{S}(0)\cdot\vec{H} - \frac{1}{N^2} \sum_\ell{}' \sum_{kk'} J_\ell \vec{S}(\vec{k})\cdot\vec{S}(\vec{k}') N\delta_{k,-k'} e^{-i\vec{k}'\cdot\vec{R}_\ell}$$

Now define: $J(\vec{k}) = \sum_\ell{}' J_\ell e^{i\vec{k}\cdot\vec{R}_\ell}$. Then:

$$\mathcal{H} = g\mu_0 \vec{S}(0)\cdot\vec{H} - \frac{1}{N}\sum_k J(\vec{k})\,\vec{S}(\vec{k})\cdot\vec{S}(-\vec{k})$$

LECTURE 40: 5-18-62

Suppose we can find an operator O such that:

$$[\mathcal{H}, O] = \Omega O$$

Assume that $\mathcal{H}$ satisfies an eigenvalue equations: $\mathcal{H}\phi_n = E_n \phi_n$ and let the commutator act on ϕ_n:

$$\mathcal{H}(O\phi_n) - O\mathcal{H}\phi_n = \Omega O \phi_n$$

Then: $\mathcal{H}(O\phi_n) = [E_n + \Omega](O\phi_n)$, so that $E_n + \Omega$ is an eigenvalue of $O\phi_n$.

Now define the operators $S^+(\vec{k})$, $S^-(\vec{k})$. $S^+(\vec{k})$ will satisfy the requirements for O at least for the ground state:

$$[\mathcal{H}, S^+(\vec{k})]\,\phi_0 = C\, S^+(\vec{k})\phi_0$$

where $S^+(\vec{k})\phi_0$ is an eigenstate of $\mathcal{H}$ with $E_0 + C$ as its eigenvalue. To show this, we must investigate the commutation rules among the $S^\pm(\vec{k})$. Obviously:

$$[S^-(\vec{k}), S^-(\vec{k}')] = [S^+(\vec{k}), S^+(\vec{k}')] = 0$$

$$[S^-(\vec{k}), S^+(\vec{k}')] = -2\, S_z(\vec{k}+\vec{k}')$$

$$[S^+(\vec{k}), S_z(\vec{k}')] = -S^+(\vec{k}+\vec{k}')$$

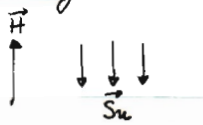
$$[S^-(\vec{k}), S_z(\vec{k}')] = S^-(\vec{k}+\vec{k}')$$

With $\vec{H}$ in the $\hat{z}$ direction, we have:

$$[\mathcal{H}, S^+(\vec{k})] = g\mu_0 S^+(\vec{k}) H - \frac{1}{N}\sum_{k'} J(\vec{k}')\Big[-S^+(-\vec{k}')\, S_z(\vec{k}+\vec{k}')$$

$$- S^+(\vec{k}')\, S_z(\vec{k}-\vec{k}') + S^+(\vec{k}-\vec{k}')\, S_z(\vec{k}') + S^+(\vec{k}+\vec{k}')\, S_z(-\vec{k}')\Big]$$

The ground state is:



$$: \quad \phi_0 = \phi^1(M_s = -s)\ \phi^2(M_s = -s) \ldots$$

On the Fourier expansion of the ground state, we have only $\vec{k} = 0$ components so we set $\vec{k} + \vec{k}' = 0$. Now we know:

$$S_z(0)\,\phi_0 = -NS\,\phi_0$$
$$S_z(\vec{k})\,\phi_0 = 0, \quad \vec{k} \neq 0$$

and hence:

$$\left[\mathcal{H}, S^+(\vec{k})\right]\phi_0 = g\mu_0 H\, S^+(\vec{k})\phi_0 + s\left[-J(-\vec{k}) - J(\vec{k}) + J(0) + J(0)\right] \cdot S^+(\vec{k})\,\phi_0$$

This shows that $S^+(\vec{k})\,\phi_0$ is an eigenstate, and we have the eigenvalue:

$$\mathcal{E} = \mathcal{E}_0 + g\mu_0 H + s\underbrace{\left[-\sum_\ell \left\{ J_\ell \left(e^{i\vec{k}\cdot\vec{R}_\ell} + e^{-i\vec{k}\cdot\vec{R}_\ell} \right) - 2J_\ell \right\}\right]}_{-2s\sum_\ell J_\ell(\cos\vec{k}\cdot\vec{R}_\ell - 1)}$$

or:

$$\mathcal{E} = \mathcal{E}_0 + g\mu_0 H - 2s\sum_\ell J_\ell(\cos\vec{k}\cdot\vec{R}_\ell - 1)$$

For nearest neighbor interactions:

$$\mathcal{E} = \mathcal{E}_0 + g\mu_0 H - 2sJ_1\sum_m (\cos\vec{k}\cdot\vec{R}_1^m - 1)$$

Or, for small $\vec{k}$:

$$\mathcal{E} = \mathcal{E}_0 + g\mu_0 H + 2sJk^2a^2$$

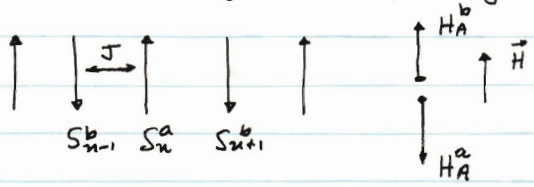
The state $S^+(\vec{k})\,\phi_0$ describes a spin wave. In the right approximation (small number of spin waves) operating successively with $S^+(\vec{k})$ generates another spin wave each time so that we can write the energy as:

$$\mathcal{E} = \mathcal{E}_0 + \sum_{\vec{k}} n(\vec{k})\,(g\mu_0 H + 2sJ_1 k^2 a^2)$$

where $n(\vec{k})$ is the number of quasi-particles (magnons).

Classical Spin Waves in an Antiferromagnet

We will work with a one dimensional model with an anisotropy field present and with nearest neighbor exchange coupling:



We have from inspection:

$$\frac{d\vec{S}^a_n}{dt} = \frac{1}{\hbar}\left[\mathcal{H}, \vec{S}^a_n\right] \quad ; \quad \frac{d\vec{S}^b_m}{dt} = \frac{1}{\hbar}\left[\mathcal{H}, \vec{S}^b_m\right]$$

where:

$$\mathcal{H} = \sum_n g\mu_0 \vec{S}^a_n \cdot (\vec{H} + \vec{H}^a_A) + \sum_m g\mu_0 \vec{S}^b_m \cdot (\vec{H} + \vec{H}^b_A)$$

$$+ 2J \sum_{nm} \vec{S}^a_n \cdot \vec{S}^b_m$$

The equations of motion are:

$$\frac{d\vec{S}^a_n}{dt} = -\frac{g\mu_0}{\hbar} \vec{S}^a_n \times \left[\vec{H} + \vec{H}^a_A + \frac{2J}{g\mu_0}\vec{S}^b_{n+1} + \frac{2J}{g\mu_0}\vec{S}^b_{n-1}\right]$$

$$\frac{d\vec{S}^b_m}{dt} = -\frac{g\mu_0}{\hbar} \vec{S}^b_m \times \left[\vec{H} + \vec{H}^b_A + \frac{2J}{g\mu_0}\vec{S}^a_{m+1} + \frac{2J}{g\mu_0}\vec{S}^a_{m-1}\right]$$

Linearize by taking the solutions:

$$\vec{S}^a_n = \vec{S}^a_0 + \vec{S}^a_1 e^{i(kna + \omega t)}$$

$$\vec{S}^b_m = \vec{S}^b_0 + \vec{S}^b_1 e^{i(kma + \omega t)}$$

where $\vec{S}^a_1$, $\vec{S}^b_1$ are small quantities.

Define: $\gamma \equiv \frac{g\mu_0}{\hbar}$; $\frac{1}{z} \equiv \frac{2J}{(g\mu_0)^2}$; $\vec{\mu}_n \equiv -g\mu_0 \vec{S}_n$

We have the equations: ($M_0^a = M_0^b = M$, $H, H_A^a = H_A^b$, in the $\hat{z}$ direction)

$$i\omega M_{ix}^a = -\gamma M\left[-\lambda M_{iy}^b \cos ka\right] - \gamma M_{iy}^a\left[H - H_A - \lambda M\right]$$

$$i\omega M_{iy}^a = \gamma M\left[-\lambda M_{ix}^b \cos ka\right] + \gamma M_{ix}^a\left[H - H_A - \lambda M\right]$$

$$i\omega M_{ix}^b = \gamma M\left[-\lambda M_{iy}^a \cos ka\right] - \gamma M_{iy}^b\left[H + H_A + \lambda M\right]$$

$$i\omega M_{iy}^b = -\gamma M\left[-\lambda M_{ix}^a \cos ka\right] + \gamma M_{ix}^b\left[H + H_A + \lambda M\right]$$

Defining M_{ia}^+ and M_{ib}^+ gives:

$$\left\{\omega - \gamma\left[H - H_A - \lambda M\right]\right\} M_{ia}^+ + \left(\gamma\lambda M\cos ka\right) M_{ib}^+ = 0$$

$$\left(-\gamma\lambda M\cos ka\right) M_{ia}^+ + \left\{\omega - \gamma\left[H + H_A + \lambda M\right]\right\} M_{ib}^+ = 0$$

which yields the secular equation:

$$(\omega - \gamma H)^2 - \gamma^2 (H_A + \lambda M)^2 + \gamma^2\lambda^2 M^2 \cos^2 ka = 0$$

or: $$\omega = \gamma H \pm \left\{(H_A + \lambda M)^2 - \lambda^2 M^2 \cos^2 ka\right\}^{1/2}$$

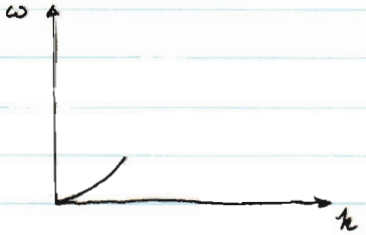
Recall the ferromagnetic dispersion relation:

$$\omega = \gamma H + \gamma\lambda M \cos ka$$

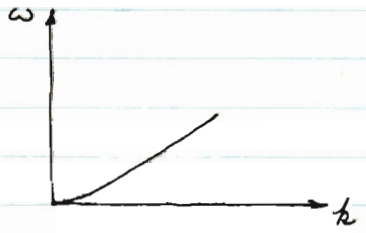
Take the long wavelength limit; $\cos^2 ka \approx 1 - \frac{k^2a^2}{2}$. Then:

$$\omega = \gamma H \pm \gamma\left\{H_A^2 + 2H_A\lambda M + \frac{\lambda^2 M^2}{2} k^2 a^2\right\}^{1/2}$$

We see that for weak anisotropy fields, ω is linear in k.



Ferromagnet



Anti-ferromagnet

LECTURE 41 : 5-21-62

Low Temperature Magnetization : Bloch $T^{3/2}$ Law

We can write the total energy of a ferromagnet as:

$$\mathcal{E} = \mathcal{E}_0 + \sum_{k} \sum_{n(k)} n(k)\ \hbar\omega(k)$$

where $\omega(k)$ is given by the dispersion relation, $n(\vec{k})$ denotes the number of magnons in k.

——— $n(k) = 4$
——— $n(k) = 3$
——— $n(k) = 2$
——— $n(k) = 1$

This is rigourous for only one spin wave, approximate for $n(k) > 1$.

Now the ground state magnetic moment is:

$$M = \frac{N}{V} g \mu_0 S \quad \text{(All spins alligned at } T = 0\text{)}$$

For each $n(\vec{k})$ we get a unit of spin reversal. We ask for the average value of $n(\vec{k})$:

$$\overline{n(\vec{k})} = \frac{\sum_{n(k)} n(k)\ e^{-\beta n(k) \hbar\omega(k)}}{\sum_{n(k)} e^{-\beta n(k) \hbar\omega(k)}}$$

Generally, at any temperature:

$$M = \frac{1}{V} g \mu_0 \left[NS - \sum_{k} \overline{n(k)} \right]$$

Motivation: One magnon state : $S^+(\vec{k})\phi_0$, let $S_z(0) = \sum_n S_{zn}$, then:

$$S_z(0)\ S^+(\vec{k})\phi_0 = -(NS-1)\ S^+(\vec{k})\phi_0$$

and one can see the extension to more than one excited state.

Now:

$$\overline{n(\vec{k})} = -\frac{1}{\hbar\omega(\vec{k})}\frac{\partial}{\partial\beta}\ln\left[\sum_{n(\vec{k})} e^{-\beta n(\vec{k})\hbar\omega(\vec{k})}\right]$$

$$= \frac{1}{e^{\beta\hbar\omega(\vec{k})} - 1}$$

and:

$$M = \frac{1}{V}g\mu_0\left[NS - \sum_{\vec{k}}\frac{1}{e^{\beta\hbar\omega(\vec{k})} - 1}\right]$$

Let: $\sum_{\vec{k}} \rightarrow \int \frac{4\pi k^2 dk\, V}{(2\pi)^3}$ and then:

$$M = \frac{1}{V}g\mu_0\left[NS - \frac{1}{2\pi^2}\int_0^\infty \frac{k^2 dk\, V}{e^{\beta D k^2} - 1}\right]$$

since $\hbar\omega(\vec{k}) = \gamma H + Dk^2$. Ignore γH or put into ε_0.

Let: $x^2 = \beta D k^2$, then:

$$M = g\mu_0\left[nS - \frac{1}{2\pi^2}(\beta D)^{-3/2}\int_0^\infty \frac{x^2 dx}{e^{x^2} - 1}\right]$$

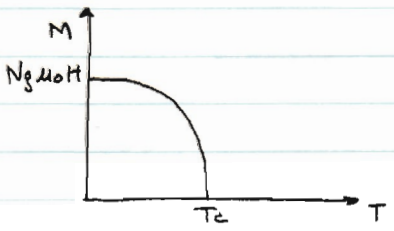
Now: $\frac{1}{2\pi^2}\int_0^\infty \frac{x^2 dx}{e^{x^2} - 1} = .0587$

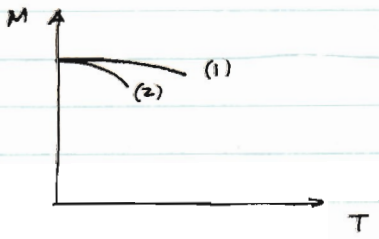
Then:

$$\frac{\Delta M}{M} = \frac{.0587}{nS}\left(\frac{kT}{2SJ}\right)^{3/2}$$

This is the Bloch $T^{3/2}$ law, where ΔM is taken from the $T=0$ value M.

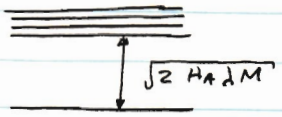
Recall:





(1) is for the molecular field approximation and has an exponential behaviour and drops off too slow. (2) is the Bloch $T^{3/2}$ law and gives the observed drop off.

Let us qualitatively consider the low temperature behaviour of a ferromagnet (anti). Now for ferromagnets, we had excited states near the ground state. However, in an antiferromagnet, the anisotropy energy separates the excited states from the ground state:



$$\omega = \gamma H \pm \{ 2 H_A \lambda M + \lambda M^2 k^2 a^2 \}^{1/2}$$

At low temperatures, there should be a sudden collapse in M. This is thought to have been observed in MnF_2.

Origins of Anisotropy in Ferromagnets and Antiferromagnets

(1) Anisotropic exchange: $\dfrac{(\lambda \vec{L}_a \cdot \vec{S}_a)(\vec{S}_a \cdot \vec{S}_b)(\lambda \vec{L}_b \cdot \vec{S}_b)}{(\epsilon_a - \epsilon_b)(\epsilon_b - \epsilon_a)}$

This goes to 0 for $L = 0$, so it is not good for S states.

(2) Dipolar anisotropy: alligned spins which vanish with high temperature, approach zero for cubic arrays (MnF_2)

(3) Crystal Field splitting: $D S_z^2$ type, important in the magnetic oxides, small for $L = 0$. This comes from the $\lambda \vec{L} \cdot \vec{S}$ second order term.

Van Vleck thinks that (1) is important for ferro-metals.

Nuclear Resonance and Mossbauer Effect

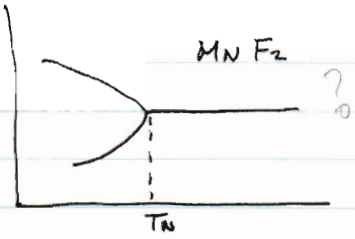
It is possible to have interaction between nuclei via spin waves:

$$\underbrace{\vec{I}_a \cdot \vec{S}_a}_{\vec{I}_a \cdot \sum e^{i k \cdot \lambda a} S(k)} \qquad \underbrace{\vec{I}_b \cdot \vec{S}_b}_{\vec{I}_b \cdot \sum e^{i k \cdot \lambda b} S(k)}$$

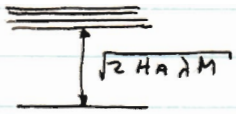
couple together in the second order.

Thus we can have an interaction between nuclei.

Nuclear resonance in Fe, Co, MnF_2 :

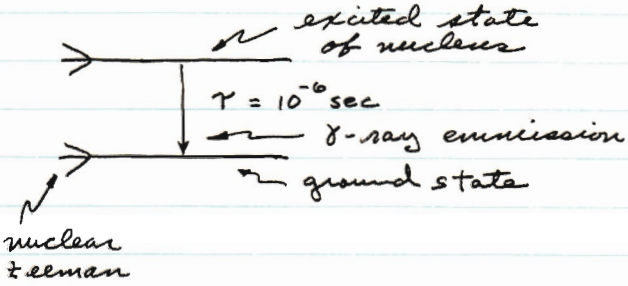


This behaviour can be explained by:



We can find the sublattice magnetizations as a function of temperature.

Mossbauer Effect :



Momentum is conserved by the nucleus as part of the lattice. A very narrow linewidth is obtained because of the long lifetime. We can get very sharp lines from stainless steel.

END OF COURSE

Applied Physics 296

Problem Set I

Due: March 12, 1962

1. (See Condon and Shortley, p. 125)

Start with Dirac equation,

$$\left[-c\,\vec{\alpha} \cdot \left(\vec{p} + \frac{e}{c}\vec{A}\right) - \beta m c^2 - ev \right] \psi = \epsilon\psi$$

ψ is four component wave function, $\vec{\alpha}$ is a 4 x 4 matrix vector, and β is a 4 x 4 matrix.

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix},$$

and $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

(Pauli matrices - $\vec{S} = \frac{1}{2}\vec{\sigma}$)

Write $\psi = \begin{pmatrix} \psi^- \\ \psi^+ \end{pmatrix}$,

where ψ^- is small (negative energy) part of wave function, ψ^+ is large part of wave function (ψ^- and ψ^+ are two component column wave functions). Eliminate ψ^-, to obtain,

$$\left[mc^2 - ev + \frac{1}{2m}\,\vec{\sigma} \cdot \left(\vec{p} + \frac{e}{c}\vec{A}\right) f(\vec{r})\, \vec{\sigma} \cdot \left(\vec{p} + \frac{e}{c}\vec{A}\right) \right] \psi^+ = \epsilon\psi^+,$$

where $f(\vec{r}) = \dfrac{1}{1 + \dfrac{(\epsilon - mc^2 + ev)}{2mc^2}}$

Expand out last term in $[\ ]$, and obtain,

$$\left[mc^2 - ev + \frac{f(\vec{r})}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2 + \frac{\hbar}{m}\vec{S} \cdot \nabla f \times \left(\vec{p} + \frac{e}{c}\vec{A}\right) \right.$$
$$\left. - i\frac{\hbar}{2m}\nabla f \cdot \left(\vec{p} + \frac{e}{c}\vec{A}\right) + f(\vec{r})\ \frac{e\hbar}{mc}\ \vec{S} \cdot \nabla \times \vec{A} \right] \psi^+ = \epsilon\psi^+$$

For the electron far from a nucleus, show that the interaction $\frac{1}{2m}(\vec{p} + \frac{e}{c}\vec{A})^2$, the spin-orbit interaction, and the electron spin Zeeman interaction appear as given in class.

Show that near a nucleus, the contact hyperfine interaction energy inside a sphere of radius R about the nucleus is,

$$\epsilon_c = -\vec{\mu}_s \cdot \int_{Vol} \nabla \times \left[f(\vec{r})\, \vec{A}_n\right] |\psi(\vec{r})|^2 \, dt ,$$

where $\psi(\vec{r})$ is now the spin independent function ψ^+. If $|\psi(\vec{r})|^2 = |\psi(o)|^2$, and if $\vec{A}_n = \vec{\mu}_n \times \frac{\vec{r}}{r^3}$ outside the nucleus, then the contact interaction energy is again,

$$\epsilon_c = \frac{8\pi}{3} \vec{\mu}_s \cdot \vec{\mu}_n \, |\psi(o)|^2$$

2. Consider a uniform spherical shell of volume $d\tau'$, charge $\rho\, d\tau'$, and radius r', rotating with angular frequency $\vec{\omega}$. Using,

$$\vec{A}(\vec{r}) = \int \frac{\rho(\vec{r}')\, \vec{v}(\vec{r}')\, d\tau'}{|\vec{r}-\vec{r}'|} ,$$

show that the vector potential at a point $\vec{r}$ due to this shell is,

$$d\vec{A}(\vec{r}) = d\vec{\mu} \times \frac{\vec{r}}{r^3} \qquad r > r'$$

$$= d\vec{\mu} \times \frac{\vec{r}}{r'^3} \qquad r < r'$$

where $d\vec{\mu} = \frac{1}{3} \frac{\rho}{c} \, d\tau' \, r'^2 \, \vec{\omega}$

3. Using the result that the vector potential due to a magnetic moment is,

$$\vec{A} = \vec{\mu} \times \frac{\vec{r}}{r^3} ,$$

show that the vector potential due to a uniformly magnetized spherical shell of total magnetic moment $d\vec{\mu}$ and radius r' is,

$$d\vec{A}(\vec{r}) = d\vec{\mu} \times \frac{\vec{r}}{r^3} \qquad r > r'$$

$$= 0 \qquad r < r'$$

4. As a simplified model of the nucleus, take a spherically symmetric distribution of charge and intrinsic magnetic moment of radius r_o, rotating with angular frequency $\vec{\omega}$. The rotating charge produces a total magnetic moment $\vec{\mu}_{nL}$, and the total intrinsic spin moment is $\vec{\mu}_{ns}$. $\vec{\mu}_{nL} + \vec{\mu}_{ns}$ are parallel, and the total nuclear moment is $\vec{\mu}_n = \vec{\mu}_{ns} + \vec{\mu}_{nL}$. The element of charge is $\rho(\vec{r}')\, d\tau'$, and the element of intrinsic spin moment is $\rho s(\vec{r}')\vec{\mu}_{ns}\, d\tau'$.

Using the results of problem 2 and 3, show that the vector potential at a point outside the nucleus is, $\vec{A}_n = \vec{\mu}_n \times \frac{\vec{r}}{r^3}$.

The contact interaction energy can be obtained from the result of problem 1,

$$\epsilon_c = -\vec{\mu}_s \cdot \int_{Vol} \nabla \times \left[f(\vec{r})\, \vec{An} \right] |\psi(\vec{r})|^2 \, d\tau .$$

The radius of the sphere of integration can be taken as $R = r_o$ for $\psi(\vec{r})$ spherically symmetric. (This follows, since the interaction outside the nucleus then gives a vanishing angular average.) Using the results of problems 2 and 3, show that the contact interaction is then,

$$\epsilon_c = -\frac{8}{3}\,\pi \vec{\mu}_s \cdot \vec{\mu}_n \,|\psi_p(o)|^2 \left[f(r_o)\,\frac{|\psi(r_o)|^2}{|\psi_p(o)|^2} \right.$$

$$\left. - \int_o^{r_o} \frac{f(r)}{|\psi_p(o)|^2}\,\frac{\partial |\psi(r)|^2}{\partial r} \left\{ \frac{\mu_{nL}}{\mu_n} K_L(r) + \frac{\mu_{ns}}{\mu_n} K_s(r) \right\} dr \right] ,$$

where

$$K_s(r) = \frac{\int_o^r \rho_s(r')\, r'^2\, d\, r'}{\int_o^{r_o} \rho_s(r')\, r'^2\, dr'}$$

$$K_L(r) = \frac{\int_o^r \rho(r')\, r'^4\, dr' + r^3 \int_r^{r_o} \rho(r')\, r'\, dr'}{\int_o^{r_o} \rho(r')\, r'^4\, dr'} ,$$

and $\psi_p(o)$ is the wave function at the origin for a point nucleus. (We have introduced $\psi_p(o)$, since the real $\psi(r)$ may differ slightly for 2 isotopes with different distributions of nuclear change.)

For $f(r_o) \sim 1$, and $\psi(r) \sim \psi_p(o)$, the bracketed term approaches 1.

AP 296

Assignment Number 1

Paul M. Grant

Problem ①

$$\left\{ -c\vec{\alpha}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) - \beta mc^2 - eV \right\}\psi = \epsilon\psi$$

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad ; \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Take: $\psi = \begin{pmatrix} \psi^- \\ \psi^+ \end{pmatrix}$

$$\left\{ -c\begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 - eV \right\}\begin{pmatrix} \psi^- \\ \psi^+ \end{pmatrix} = \epsilon\begin{pmatrix} \psi^- \\ \psi^+ \end{pmatrix}$$

$$-c\,\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi^+ - mc^2\psi^- - eV\psi^- = \epsilon\psi^-$$

$$-c\,\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi^- + mc^2\psi^+ - eV\psi^+ = \epsilon\psi^+$$

$$\psi^- = \frac{-c\,\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi^+}{\epsilon + mc^2 + eV}$$

$$\left\{ mc^2 - eV + c^2\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\frac{\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)}{\epsilon + mc^2 + eV} \right\}\psi^+ = \epsilon\psi^+$$

or: $$\left\{ mc^2 - eV + \frac{1}{2m}\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\frac{\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)}{\frac{\epsilon + mc^2 + eV}{2mc^2}} \right\}\psi^+ = \epsilon\psi^+$$

However: $$\frac{\epsilon + mc^2 + eV}{2mc^2} = \frac{\epsilon + eV}{2mc^2} + \frac{1}{2} = 1 + \frac{(\epsilon - mc^2 + eV)}{2mc^2} = \left\{ f(\vec{r}) \right\}^{-1}$$

Then we can write directly:

$$\boxed{\left\{ mc^2 - eV + \frac{1}{2m}\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) f(\vec{r})\,\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) \right\}\psi^+ = \epsilon\psi^+}$$

$$\boxed{f(\vec{r}) = \left\{ 1 + \frac{(\epsilon - mc^2 + eV)}{2mc^2} \right\}^{-1}}$$

We have to form the quantity: $(\vec{\sigma}\cdot\vec{a})(\vec{\sigma}\cdot\vec{b})$

$$(\vec{\sigma}\cdot\vec{a})(\vec{\sigma}\cdot\vec{b}) = \sigma_x a_x \sigma_y b_y = \sigma_x \sigma_y a_x b_y$$

From the properties of the Pauli matrices, we may write:

$$\sigma_x \sigma_y = \delta_{xy} + i \epsilon_{xyk} \sigma_k$$

Then:

$$(\vec{\sigma}\cdot\vec{a})(\vec{\sigma}\cdot\vec{b}) = a_x b_x + i \epsilon_{xyk} \sigma_k a_x b_y = \vec{a}\cdot\vec{b} + i\vec{\sigma}\cdot(\vec{a}\times\vec{b})$$

We then form:

$$\left\{\vec{\sigma}\cdot\left(\vec{p}+\tfrac{e}{c}\vec{A}\right) f(\vec{x})\right\}\left\{\vec{\sigma}\cdot\left(\vec{p}+\tfrac{e}{c}\vec{A}\right)\right\}$$

$$= \vec{\pi} f(x)\cdot\vec{\pi} + i\vec{\sigma}\cdot(\vec{\pi} f(x)\times\vec{\pi}) \quad ; \text{ setting } \vec{\pi} = \vec{p} + \tfrac{e}{c}\vec{A}$$

$$\vec{\pi} f(\vec{x}) = \vec{\pi}[f(x)] + f(x)\vec{\pi}$$

$$\vec{\pi} f(\vec{x}) = \left(\vec{p} + \tfrac{e}{c}\vec{A}\right) f(x) = \vec{p}[f(x)] + f(x)\vec{\pi}$$

$$\{\ \}\{\ \} = \left[\vec{p}[f(x)]\cdot\vec{\pi}\right] + f(x)\pi^2 + i\vec{\sigma}\cdot f(x)(\vec{\pi}\times\vec{\pi}) + i\vec{\sigma}\cdot\left[\vec{p}[f(x)]\times\vec{\pi}\right]$$

$$\vec{p}[f(x)]\cdot\vec{\pi} = -i\hbar\nabla f\cdot\vec{\pi}$$

$$\vec{\pi}\times\vec{\pi} = \epsilon_{xyk}\pi_y\pi_k = \epsilon_{xyk}\left(p_y + \tfrac{e}{c}A_y\right)\left(p_k + \tfrac{e}{c}A_k\right)$$

$$= \epsilon_{xyk}\left\{p_y p_k + \tfrac{e}{c}p_y A_k + \tfrac{e}{c}A_y p_k + \tfrac{e}{c}A_y A_k\right\}$$

$$= \epsilon_{xyk}\tfrac{e}{c}\left(p_y A_k + A_y p_k\right) = -\tfrac{i\hbar e}{c}\epsilon_{xyk}\left(\partial_y A_k + A_y\partial_k\right)$$

$$= -\tfrac{i\hbar e}{c}\epsilon_{xyk}\left(\partial_y[A_k] + A_k\partial_y + A_y\partial_k\right) = -\tfrac{i\hbar c}{c}\nabla\times\vec{A}$$

$\vec{p}\,\{f(r)\} \times \vec{\Pi} = -i\hbar\,\nabla f \times \vec{\Pi}$; Now $\vec{S} = \frac{1}{2}\vec{\sigma}$; $\vec{\sigma} = 2\vec{S}$

Then: $\{\,\}\{\,\} = f(r)\,(\vec{p} + \frac{e}{c}\vec{A})^2 + 2\hbar\,\vec{S}\cdot\nabla f \times (\vec{p} + \frac{e}{c}\vec{A})$

$-i\hbar\,\nabla f \cdot (\vec{p} + \frac{e}{c}\vec{A}) + 2f\,\frac{e\hbar}{c}\,\vec{S}\cdot\nabla\times\vec{A}$

Resubstituting the $\{\,\}\{\,\}$ we obtain the desired expression:

$$\left\{ mc^2 - eV + \frac{f}{2m}\,(\vec{p} + \tfrac{e}{c}\vec{A})^2 + \frac{\hbar}{m}\,\vec{S}\cdot\nabla f \times (\vec{p} + \tfrac{e}{c}\vec{A}) - i\,\frac{\hbar}{2m}\,\nabla f \cdot (\vec{p} + \tfrac{e}{c}\vec{A}) + f\,\frac{e\hbar}{mc}\,\vec{S}\cdot\nabla\times\vec{A} \right\}\psi^+ = \epsilon\,\psi^+$$

We now wish to extract out the kinetic energy, spin-orbit, Darwin, and Zeeman terms in the non-relativistic limit, that is, when the electron is far from the nucleus. Recall:

$$f(r) = \frac{2}{1 + \frac{\epsilon + eV}{mc^2}} = \frac{1}{1 + \frac{(\epsilon - mc^2 + eV)}{2mc^2}}$$

In the non-relativistic limit, $|\epsilon + eV - mc^2| << 2mc^2$ so that we may expand $f(r)$ to first order in $\frac{\epsilon + eV - mc^2}{2mc^2}$

$$f(r) \approx 1 - \frac{(\epsilon - mc^2 + eV)}{2mc^2}$$

From $\frac{f}{2m}\,(\vec{p} + \frac{e}{c}\vec{A})^2$ we immediately extract the "kinetic energy" terms:

$$H_{KE} = \frac{1}{2m}\,(\vec{p} + \tfrac{e}{c}\vec{A})^2$$

Now: $\nabla f = \frac{-e}{2mc^2}\nabla V$ and from $\frac{\hbar}{m}\vec{s}\cdot\nabla f \times (\vec{p}+\frac{e}{c}\vec{A})$

we find:

$$\mathcal{H}_{so} = \frac{-e\hbar}{2m^2c^2}\vec{s}\cdot\nabla V\times(\vec{p}+\tfrac{e}{c}\vec{A}) = \frac{\vec{\mu}_s}{2mc}\cdot\nabla V\times(\vec{p}+\tfrac{e}{c}\vec{A})$$

where $\vec{\mu}_s = -\frac{e\hbar\vec{s}}{mc}$,

To find the Darwin term, we put ∇f into $-i\frac{\hbar}{2m}\nabla f\cdot(\vec{p}+\frac{e}{c}\vec{A})$ and get:

$$\mathcal{H}_{Darwin} = i\frac{e\hbar}{4m^2c^2}\nabla V\cdot(\vec{p}+\tfrac{e}{c}\vec{A})$$

To find the Zeeman Term, we use $f\frac{e\hbar}{mc}\vec{s}\cdot\nabla\times\vec{A}$

where we have $\vec{H}=\nabla\times\vec{A}$ subject to the gauge $\vec{A}=\frac{1}{2}\vec{H}\times\vec{r}$

or: $A_i = \frac{1}{2}\epsilon_{ijk}H_j x_k$

$$(\nabla\times\vec{A})_l = \epsilon_{lmi}\partial_m A_i = \frac{1}{2}\epsilon_{lmi}\epsilon_{ijk}\partial_m H_j x_k$$

$$\epsilon_{lmi}\epsilon_{ijk} = \epsilon_{ilm}\epsilon_{ijk} = \delta_{lj}\delta_{mk} - \delta_{lk}\delta_{mj}$$

$$(\nabla\times\vec{A})_l = \frac{1}{2}\{\partial_k H_l x_k - \partial_m H_m x_l\}$$

$$= \frac{1}{2}\{x_m\partial_m H_l + 3H_l - x_l\partial_m H_m - H_m\delta_{ml}\}$$

$$= H_l + \frac{1}{2}\{x_m\partial_m H_l - x_l\partial_m H_m\}$$

If we take $\vec{H}$ to be a constant external field, $\nabla\times\vec{A}=\vec{H}$, and we find for the spin Zeeman Term to the zeroth order:

$$\mathcal{H}_{spin\text{-}zeeman} = \frac{e\hbar}{mc}\vec{s}\cdot\vec{H} = -\vec{\mu}_s\cdot\vec{H}$$

where $\vec{\mu}_s$ is the same as above.

We now go to find the contact hyperfine interaction between the electron spin and the vector field due to the nuclear magnetic moment. A glance at the total Hamiltonian makes clear that the interaction terms will come from $\mathcal{H}_{SO}$ and $\mathcal{H}_{Z(spin)}$. We thus see:

$$\mathcal{H}_C = \frac{\hbar}{m}\vec{s}\cdot\left(\nabla f \times \frac{e}{c}\vec{A}_n\right) + f\,\frac{e\hbar}{mc}\vec{s}\cdot\left(\nabla\times\vec{A}_n\right)$$

when $\vec{A}_n$ is the nuclear field and we recall that the ∇ operator operates only on its immediate operand, that is, it does not now also operate on ψ^*. Regrouping:

$$\mathcal{H}_C = -\vec{\mu}_s\cdot\left(\nabla f\times\vec{A}_n + f\left[\nabla\times\vec{A}_n\right]\right) \quad ; \quad \vec{\mu}_s = -\frac{e\hbar}{mc}\vec{s}$$

We now use the vector identity:

$$\nabla\times f\vec{A}_n = \nabla f\times\vec{A}_n + f\left\{\nabla\times\vec{A}_n\right\}$$

Hence:

$$\mathcal{H}_C = -\vec{\mu}_s\cdot\nabla\times f\vec{A}_n$$

The contact interaction is, as defined in lecture, the expectation value of $\mathcal{H}_C$ with respect to spin-independent wave functions taken over a volume contained in a sphere about the nucleus, hence:

$$\boxed{\epsilon_C = -\vec{\mu}_s\cdot\int_{Vol}\nabla\times\left[f(r)\vec{A}_n\right]\,|\psi(\vec{r})|^2\,d\tau}$$

If we have: $f(\vec{r}) \sim 1$; $|\psi(\vec{r})|^2 \sim |\psi(0)|^2$, we can write:

$$\epsilon_c = -|\psi(0)|^2 \vec{\mu}_s \cdot \int_{vol} \nabla \times \vec{A}_n \, d\tau$$

We change to a surface integral:

$$\int_{vol} \nabla \times \vec{A}_n \, d\tau \rightarrow \int_S d\hat{n} \times \vec{A}_n \, dS$$

For a more careful derivation of this result and these operations, see problem 4.

Taking a spherical surface of radius R and $\vec{A}_n = \vec{\mu}_n \times \frac{\vec{r}}{r^3}$:

$$\int d\hat{n} \times \vec{A}_n \, dS = \int \hat{r} \times \vec{\mu}_n \times \hat{r} \, d\Omega$$

$$\hat{r} \times \vec{\mu}_n \times \hat{r} = \vec{\mu}_n - \hat{r}(\vec{\mu}_n \cdot \hat{r})$$

$$\int (\hat{r} \times \vec{\mu}_n \times \hat{r}) = 4\pi \vec{\mu}_n - \int \frac{x}{R} \mu_{nx} \left(\frac{x}{R}\hat{i} + \frac{y}{R}\hat{j} + \frac{z}{R}\hat{k} \right) + \cdots d\Omega$$

$$= \left(4\pi - \frac{4\pi}{3}\right) \vec{\mu}_n = \frac{8\pi}{3} \vec{\mu}_n$$

Hence:

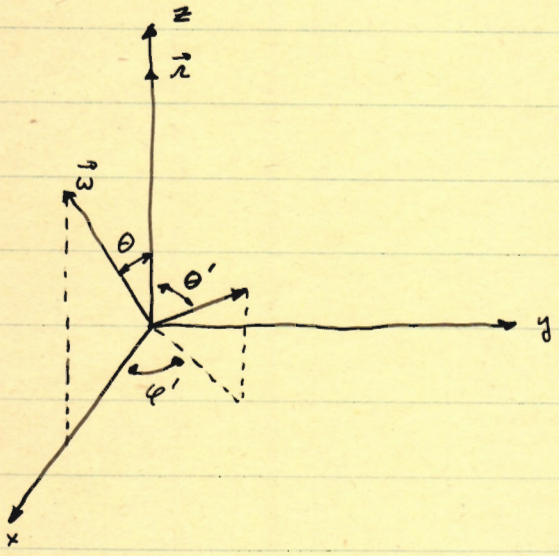
$$\boxed{\epsilon_c = -|\psi(0)|^2 \vec{\mu}_s \cdot \vec{\mu}_n \frac{8\pi}{3}}$$

Problem 2

The vector field is given by:

$$\vec{A}(\vec{r}) = \int \frac{\rho(\vec{r}')\,\vec{V}(\vec{r}')\,d\tau'}{c\,|\vec{r}-\vec{r}'|} = \frac{1}{c}\int \frac{\rho(\vec{r}')\,\vec{\omega}\times\vec{r}'\,d\tau'}{|\vec{r}-\vec{r}'|}$$

Here we have $\vec{V}(\vec{r}') = \vec{\omega}\times\vec{r}$. Choose the coordinate system as follows:



$$\vec{\omega}\times\vec{r}' = \omega r' \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \sin\theta & 0 & \cos\theta \\ \sin\theta\cos\varphi' & \sin\theta\sin\varphi' & \cos\theta' \end{vmatrix}$$

$$= \omega r' \{ -\hat{i}\cos\theta\sin\theta'\sin\varphi' - \hat{j}(\sin\theta\cos\theta' - \cos\theta\sin\theta'\cos\varphi') + \hat{k}\sin\theta\sin\theta'\sin\varphi' \}$$

$$|\vec{r}-\vec{r}'| = (r^2 + r'^2 - 2rr'\cos\theta')^{1/2}$$

The only terms that are kept in $\vec{\omega}\times\vec{r}'$ is $-\hat{j}\,\omega\sin\theta\cos\theta'$ and the others drop out because of integration over a periodic function over its period. Note: $-\hat{j}\,\omega\sin\theta = \frac{\vec{\omega}\times\vec{r}}{r}$. Then:

$$\vec{A}(\vec{r}) = \frac{2\pi}{c}\int \rho(\vec{r}')\,r'^3\,dr'\,\frac{\vec{\omega}\times\vec{r}}{r}\int_{-1}^{1}\frac{u\,du}{(r^2+r'^2-2rr'u)^{1/2}}$$

The generating functions of the Legendre polynomials are:

$$\sum_{l=0}^{\infty} x^l P_l(\mu) = \frac{1}{(1 - 2x\mu + x^2)^{1/2}} \quad ; \quad x \leq 1$$

$$\sum_{l=0}^{\infty} \frac{P_l(\mu)}{x^{l+1}} = \frac{1}{(1 - 2x\mu + x^2)^{1/2}} \quad ; \quad x \geq 1$$

with the orthogonality condition: $\int_{-1}^{1} P_l(\mu) P_{l'}(\mu) \, d\mu = \frac{2}{2l+1} \delta_{ll'}$

$$(r^2 + r'^2 - 2rr'\mu)^{-1/2} = \frac{1}{|\vec{r} - \vec{r}'|}$$

$$(r^2 + r'^2 - 2rr'\mu)^{-1/2} = r' \left(1 - 2\frac{r}{r'}\mu + \frac{r^2}{r'^2}\right)^{-1/2}$$

Therefore:

$$\frac{1}{|\vec{r} - \vec{r}'|} = \begin{cases} \frac{1}{r'} \sum_{l=0}^{\infty} \left(\frac{r}{r'}\right)^l P_l(\mu) & ; \quad r < r' \\ \frac{1}{r'} \sum_{l=0}^{\infty} \left(\frac{r'}{r}\right)^{l+1} P_l(\mu) & ; \quad r > r' \end{cases}$$

For $r > r'$: and $\mu = P_1(\mu)$:

$$\vec{A}(\vec{r}) = \frac{2\pi}{c} \int \rho(\vec{r}') r_1^2 \, dr' \, \frac{\vec{\omega} \times \vec{r}}{r} \sum_{l=0}^{\infty} \left(\frac{r'}{r}\right)^{l+1} \int_{-1}^{1} P_1(\mu) P_l(\mu) \, d\mu$$

$$= \frac{2\pi}{c} \int \rho(\vec{r}') r_1^2 dr' \, \frac{\vec{\omega} \times \vec{r}}{r^3} \, r'^2 \, \frac{2}{3}$$

$$= \frac{1}{3c} \int \rho(\vec{r}) r'^2 \, d\tau' \, \vec{\omega} \times \frac{\vec{r}}{r^3} \quad , \text{ where } d\tau' = 4\pi r'^2 dr'$$

Finally:

$$d\vec{A}(\vec{r}) = d\vec{u} \times \frac{\vec{r}}{r^3} \quad ; \; r > r'$$

where $d\vec{u} = \frac{\rho(\vec{r}')}{3c} r'^2 \, dr' \, \vec{\omega}$

For $r < r'$:

$$\vec{A}(\vec{r}) = \frac{2\pi}{c} \int \rho(\vec{r}') r'^2 \, dr' \, \frac{\vec{\omega} \times \vec{r}}{r} \sum_{\ell=0}^{\infty} \left(\frac{r}{r'}\right)^{\ell} \int_{-1}^{1} P_\ell(u) P_1(u) \, du$$

$$= \frac{4\pi}{3c} \int \rho(\vec{r}') r'^4 \, dr' \, \frac{\vec{\omega} \times \vec{r}}{r'^3} = \frac{1}{3c} \int \rho(\vec{r}') r'^2 \, dr' \, \frac{\vec{\omega} \times \vec{r}}{r'^3}$$

Finally:

$$d\vec{A}(\vec{r}) = d\vec{u} \times \frac{\vec{r}}{r'^3} \quad ; \; r < r'$$

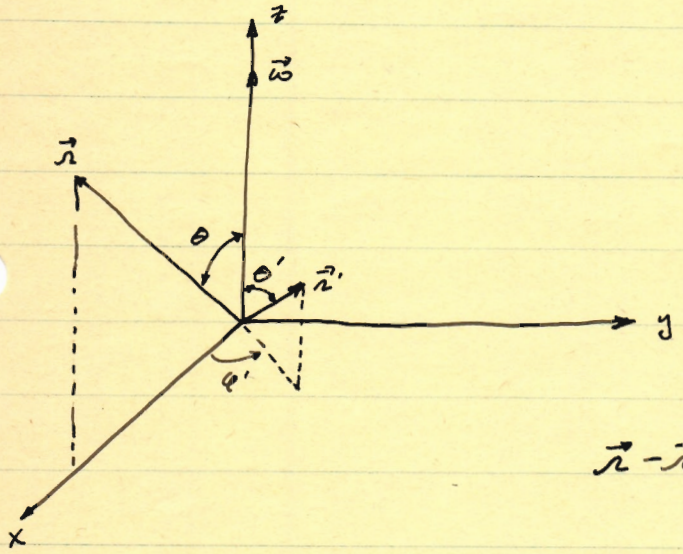
where $d\vec{u} = \frac{\rho(\vec{r}')}{3c} r'^2 \, dr' \, \vec{\omega}$

Problem 2

The vector field is given by:

$$\vec{A}(\vec{r}) = \int \frac{\rho(\vec{r}')\,\vec{v}(\vec{r}')\,d\tau'}{c\,|\vec{r}-\vec{r}'|} = \frac{1}{c}\int \frac{\rho(\vec{r}')\,\vec{\omega}\times\vec{r}'\,d\tau'}{|\vec{r}-\vec{r}'|}$$

Here we have $\vec{v}(\vec{r}') = \vec{\omega}\times\vec{r}'$. Choose the coordinates system as follows:



$$\vec{\omega}\times\vec{r}' = \omega r' \sin\theta' (\hat{j}\cos\varphi' - \hat{i}\sin\varphi')$$

$$\vec{r}-\vec{r}' = \hat{i}(r\sin\theta - r'\sin\theta'\cos\varphi') + \hat{j}(-r'\sin\theta'\sin\varphi') + \hat{k}(r\cos\theta - r'\cos\theta')$$

$$|\vec{r}-\vec{r}'|^2 = r^2\sin^2\theta - 2rr'\sin\theta\sin\theta'\cos\varphi' + r'^2\sin^2\theta'\cos^2\varphi' + r'^2\sin^2\theta'\sin^2\varphi' + r^2\cos^2\theta - 2rr'\cos\theta\cos\theta' + r'^2\cos^2\theta$$

$$= r^2 + r'^2 - 2rr'\cos\theta\cos\theta' - 2rr'\sin\theta\sin\theta'\cos\varphi'$$

Then:

$$\vec{A}(\vec{r}) = \frac{1}{c}\int \frac{\rho(\vec{r}')\,\omega r'\sin\theta'(\hat{j}\cos\varphi' - \hat{i}\sin\varphi')\,r'^2\,dr'\sin\theta'\,d\theta'\,d\varphi'}{\{r^2 + r'^2 - 2rr'\cos\theta\cos\theta' - 2rr'\sin\theta\sin\theta'\cos\varphi'\}^{1/2}}$$

We see immediately that integrals of the type:

$$\int_0^{2\pi} \frac{\sin\varphi'\, d\varphi'}{[a - b\cos\varphi']^{1/2}} = 0$$ because the integrant is odd in φ'.

$$\vec{A}(\vec{r}) = \frac{1}{c}\hat{1}\int\int_{\mathcal{V}'} \rho(\vec{r}')\,\omega r' \sin\theta'\, r'^2\, dr' \sin\theta' d\theta' \int_0^{2\pi} \frac{\cos\varphi'\, d\varphi'}{\{r^2 + r'^2 - 2rr'\cos\theta\cos\theta' - 2rr'\sin\theta\sin\theta'\cos\varphi'\}^{1/2}}$$

The last term above can be expressed in terms of the complete elliptic integrals K and E as follows:

$$\int_0^{2\pi} \cdots d\varphi' = \frac{4}{\{r^2 + r'^2 - 2rr'\cos\theta\cos\theta' + 2rr'\sin\theta\sin\theta'\}^{1/2}} \left[\frac{(2-k^2)K(k) - 2E(k)}{k^2}\right]$$

where: $$k^2 = \frac{4rr'\sin\theta\sin\theta'}{r^2 + r'^2 - 2rr'\cos\theta\cos\theta' + 2rr'\sin\theta\sin\theta'}$$

For small k^2, corresponding to $r' >> r$; $r' << r$, or $\theta << 1$, we have:

$$\left[\quad\right] \approx \frac{\pi k^2}{16}$$

Then:

$$\int_0^{2\pi} \cdots d\varphi' = \frac{\pi rr'\sin\theta\sin\theta'}{\{r^2 + r'^2 - 2rr'\cos\theta\cos\theta' + 2rr'\sin\theta\sin\theta'\}^{3/2}}$$

Let us now consider the case $r >> r'$ explicitly, then:

$$\int_0^{2\pi} \cdots d\varphi' \approx \frac{\pi r'\sin\theta\sin\theta'}{r^2}$$

$$\vec{A}(\vec{r}) = \frac{\pi}{c}\hat{j}\int\int_0^{\pi}\rho(\vec{r}')\,\omega r'\sin\theta'\,r'^2\,dr'\,\frac{r'\sin\theta\sin\theta'}{r^2}\sin\theta'\,d\theta'$$

$$= \frac{\pi}{c}\hat{j}\int\rho(\vec{r}')\,\frac{\omega r\sin\theta}{r^3}\,r'^4\,dr'\int_0^{\pi}\sin^2\theta'\sin\theta'\,d\theta'$$

$$\int_0^{\pi}\sin^2\theta'\sin\theta'\,d\theta' = \int_{-1}^{1}(1-u^2)\,du = u-\frac{u^3}{3}\Big]_{-1}^{1} = 2-\frac{2}{3} = \frac{4}{3}$$

Now $\hat{j}\,\omega r\sin\theta \equiv \vec{\omega}\times\vec{r}$ as can be seen from the diagram. Since our element of volume is a spherical shell, we can take $d\tau' = 4\pi r'^2 dr'$. We form $d\vec{A}(\vec{r})$ meaning that we take the differential to be with respect to r' and get:

$$\boxed{d\vec{A}(\vec{r}) = \frac{\rho(\vec{r}')}{3c}\,d\tau'\,r'^2\,\vec{\omega}\times\frac{\vec{r}}{r^3} = d\vec{u}\times\frac{\vec{r}}{r^3}} \qquad r > r'$$

if we define $d\vec{u} = \frac{\rho(\vec{r}')}{3c}\,d\tau'\,r'^2\,\vec{\omega}$.

Now for $r << r'$, we immediately see:

$$\int_0^{2\pi}\cdots d\varphi' = \frac{\pi r\sin\theta\sin\theta'}{r'^2}$$

$$\vec{A}(\vec{r}) = \frac{\pi}{c}\hat{j}\int\rho(\vec{r}')\int_0^{\pi}\omega r'\sin\theta'\,r'^2\,dr'\,\frac{r\sin\theta\sin\theta'}{r'^2}\sin\theta'\,d\theta'$$

$$= \frac{4\pi}{3c}\hat{j}\int\rho(\vec{r}')\,\omega r\sin\theta\,r'\,dr'$$

$$= \frac{4\pi}{3c}\hat{j}\int\rho(\vec{r}')\,\omega r\sin\theta\,\frac{r'^4}{r'^3}\,dr'$$

then:

$$d\vec{A}(\vec{r}) = \frac{\rho(\vec{r}')}{3c}\, d\tau'\, r'^2\, \vec{\omega} \times \frac{\vec{r}}{r^3} = d\vec{m} \times \frac{\vec{r}}{r'^2} \; ; \; r < r'$$

Hence we have the required results in the two regions.

Problem 3

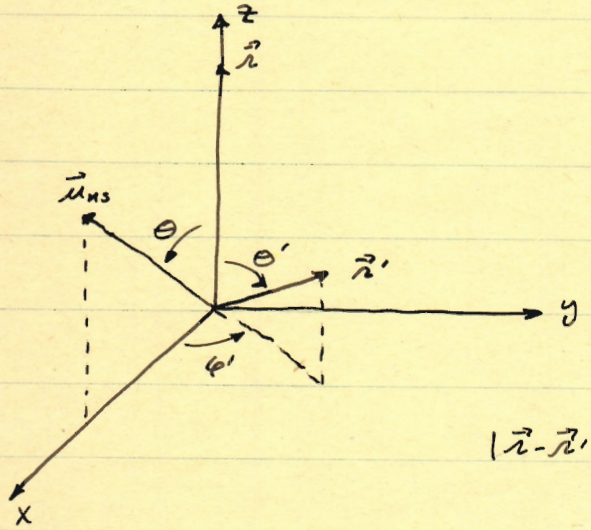
We take as the potential due to a magnetic moment:

$$\vec{A} = \vec{m} \times \frac{\vec{r}}{r^3}$$

We have a uniformly magnetized spherical shell composed of infinitesimal moments $\vec{m}_{ms}$, placed by a density function $\rho_s(\vec{r}')$ and all pointing in the same direction. If we consider a source point $\vec{r}'$ and an observing point $\vec{r}$, the potential at $\vec{r}$ is, by the above definition:

$$\vec{A} = \int \frac{\vec{m}_{ms} \times (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} \rho_s(\vec{r}')\, d\tau'$$

Choose the coordinate system as follows:



$$\vec{m}_{ms} \times (\vec{r} - \vec{r}') = -\hat{j}\, m_{ms} \sin\theta\, r$$
$$- m_{ms} r' \{ -\hat{i} \cos\theta \sin\theta' \sin\varphi'$$
$$- \hat{j} (\sin\theta \cos\theta' - \cos\theta \sin\theta' \cos\varphi')$$
$$+ \hat{k} \sin\theta \sin\theta' \sin\varphi' \}$$

$$|\vec{r} - \vec{r}'|^3 = (r^2 + r'^2 - 2rr' \cos\theta')^{3/2}$$

All terms with $\cos\varphi'$ or $\sin\varphi'$ vanish because of the integration of these functions over an interval of 2π.

$$\vec{A} = -\hat{\jmath}\, 2\pi \int \mu_{ms} \sin\theta\, \rho_s(\vec{r}')\, r'^2\, dr' \int_{-1}^{1} \frac{(r - r'\mu)\, d\mu}{(r^2 + r'^2 - 2rr'\mu)^{3/2}}$$

$$= 2\pi \int \rho_s(\vec{r}')\, r'^2\, dr'\, \frac{\vec{\mu}_{ms} \times \vec{r}}{r} \int_{-1}^{1} \frac{(r - r'\mu)\, d\mu}{(r^2 + r'^2 - 2rr'\mu)^{3/2}}$$

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{1}{r'} \begin{cases} \sum_{\ell=0}^{\infty} \left(\frac{r}{r'}\right)^{\ell} P_\ell(\mu) ; & r < r' \\ \sum_{\ell=0}^{\infty} \left(\frac{r'}{r}\right)^{\ell+1} P_\ell(\mu) ; & r > r' \end{cases} = \frac{1}{(r^2 + r'^2 - 2rr'\mu)^{1/2}}$$

Take $\frac{\partial}{\partial r}$ of above:

$$\frac{-\frac{1}{2} \cdot 2\,(r - r'\mu)}{(r^2 + r'^2 - 2rr'\mu)^{3/2}} = \frac{1}{r'} \begin{cases} \sum_{\ell=0}^{\infty} \frac{\ell r^{\ell-1}}{r'^{\ell}} P_\ell(\mu) ; & r < r' \\ \sum_{\ell=0}^{\infty} -\frac{(\ell+1)\, r'^{\ell+1}}{r^{\ell+2}} P_\ell(\mu) ; & r > r' \end{cases}$$

or:

$$\frac{r - r'\mu}{(r^2 + r'^2 - 2rr'\mu)^{3/2}} = \frac{1}{r'} \begin{cases} \frac{(\ell+1)\, r'^{\ell+1}}{r^{\ell+2}} P_\ell(\mu) ; & r > r' \\ -\frac{\ell\, r^{\ell-1}}{r'^{\ell}} P_\ell(\mu) ; & r < r' \end{cases}$$

For $r > r'$; using $1 = P_0(\mu)$

$$\vec{A}(\vec{r}) = 2\pi \int \rho_s(\vec{r}')\, r'^2 dr'\, \frac{\vec{\mu}_{ms} \times \vec{r}}{r}\, \frac{1}{r'} \sum_{\ell=0}^{\infty} \frac{(\ell+1)\, r'^{\ell+1}}{r^{\ell+2}} \int_{-1}^{1} P_\ell(\mu)\, P_0(\mu)\, d\mu$$

$$= 4\pi \int \rho_s(\vec{r}')\, r'^2 dr'\, \vec{\mu}_{ms} \times \frac{\vec{r}}{r^3}$$

or:

$$\boxed{d\vec{A}(\vec{r}) = d\vec{\mu}_{ms} \times \frac{\vec{r}}{r^3} \quad ; \quad r > r'}$$

where $d\vec{\mu}_{ms} = 4\pi \rho_s(\vec{r}')\, r'^2 dr'\, \vec{\mu}_{ms}$

For $r < r'$:

$$\vec{A}(\vec{r}) = 2\pi \int \rho_s(\vec{r}') r'^2 dr' \frac{\vec{M}_{NS} \times \vec{r}}{r} \frac{1}{r'} \sum_{l=0}^{\infty} \frac{-l r^{l-1}}{r'^l} \int_{-1}^{1} P_l(u) P_0(u) du$$

$$= 0$$

or:

$$\boxed{\vec{A}(\vec{r}) = 0 \; ; \; r < r'}$$

Problem 4

Recapitulation of the results of problems 2 and 3:

Rotation: $$d\vec{A}(\vec{r}) = \frac{4\pi\vec{\omega}}{3c}\,\rho(\vec{r}')\,r'^4\,dr' \times \begin{cases} \frac{\vec{r}}{r^3} & r > r' \\ \frac{r^3}{r'^3}\,\frac{\vec{r}}{r^3} & r < r' \end{cases}$$

Intrinsic: $$d\vec{A}(\vec{r}) = 4\pi\vec{\mu}_{ns}\,\rho_s(\vec{r}')\,r'^2\,dr' \times \begin{cases} \frac{\vec{r}}{r^3} & r > r' \\ 0 & r < r' \end{cases}$$

Redefine: $\vec{\mu}_{nl} \equiv \frac{4\pi\vec{\omega}}{3c}$; $\vec{\mu}_{ns} \langle\equiv\rangle 4\pi\vec{\mu}_{ns}$

Given a nucleus of radius r_0, we have:

For $r < r_0$:

$$\vec{A}_n(\vec{r}) = \vec{\mu}_{nl}\left[\int_0^r \rho(\vec{r}')\,r'^4\,dr' + r^3\int_r^{r_0}\rho(\vec{r}')\,r'\,dr'\right] \times \frac{\vec{r}}{r^3}$$

$$+ \vec{\mu}_{ns}\left[\int_0^r \rho_s(\vec{r}')\,r'^2\,dr'\right] \times \frac{\vec{r}}{r^3}$$

For $r > r_0$:

$$\vec{A}_n = \left\{\vec{\mu}_{nl}\int_0^{r_0}\rho(r')\,r'^4\,dr' + \vec{\mu}_{ns}\int_0^{r_0}\rho(r')\,r'^2\,dr'\right\} \times \frac{\vec{r}}{r^3}$$

We now note that the total rotational magnetic moment of the nucleus is given by:

$$\vec{\mu}_{NL} = \vec{\mu}_{Ne} \int_0^{r_0} \rho(\vec{r}\,') r'^4 \, dr'$$

and the total intrinsic magnetic moment is given by:

$$\vec{\mu}_{NS} = \vec{\mu}_{Ns} \int_0^{r_0} \rho_s(\vec{r}\,') r'^2 \, dr'$$

Hence the total nuclear magnetic moment is:

$$\vec{\mu}_N = \vec{\mu}_{NL} + \vec{\mu}_{NS}$$

and we have for $r > r_0$, the simple relation:

$$\boxed{\vec{A}_N = \vec{\mu}_N \times \frac{\vec{r}}{r^3}}$$

The same sort of relation holds for $r < r_0$, except that the moment is now a function of r: $\mu_N(r)$. However, functionally $\vec{A}_N$ is the same structure in both regions and we treat it thus as far as we can.

The following vector identities are used in this problem:

$$\int (\nabla \times \vec{F}) \, d\tau = -\int_S \vec{F} \times d\vec{S}$$

$$(\vec{A} \times \vec{B}) \times \vec{C} = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{B} \cdot \vec{C})\vec{A}$$

$$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C}$$

$$\nabla(\psi)(u\vec{A}) = (\nabla u)(\psi)\vec{A} + u\nabla(\psi)\vec{A}$$

Consider the contact interaction:

$$\epsilon_c = -\vec{\mu}_S \cdot \int_V \nabla \times \left[f(\vec{r}) \vec{A}_N \right] |\psi(\vec{r})|^2 \, d\tau$$

Consider: $\nabla \times \left[f(\vec{r}) \, |\psi(\vec{r})|^2 \vec{A}_n \right] = \left\{ \nabla |\psi(\vec{r})|^2 \right\} \times f(\vec{r}) \vec{A}_n + |\psi(\vec{r})|^2 \nabla \times f(\vec{r}) \vec{A}_n$

Then: $\int_V \nabla \times \left[f \vec{A}_n \right] |\psi|^2 \, d\tau = \int_V \nabla \times \left[f |\psi|^2 \vec{A}_n \right] d\tau - \int_V \left\{ \nabla |\psi|^2 \right\} \times f \vec{A}_n \, d\tau$

Convert $\int_V \nabla \times \left[f |\psi|^2 \vec{A}_n \right] d\tau$ into a surface integral and evaluate at $r = r_0$; assuming a spherical nucleus:

$$\int_V \nabla \times \left[f |\psi|^2 \vec{A}_n \right] d\tau = - \int_S f |\psi|^2 \vec{A}_n \times d\vec{S}$$

$$= - \int_\Omega f(r_0) \, |\psi(r_0)|^2 \left\{ \vec{\mu}_n \times \frac{\hat{r}}{r_0^2} \right\} \times \hat{r} \, r_0^2 \, d\Omega \quad ; \quad \psi(\vec{r}) \text{ spherically symmetric}$$

$$= - f(r_0) \, |\psi(r_0)|^2 \int_\Omega (\vec{\mu}_n \times \hat{r}) \times \hat{r} \, d\Omega$$

Now: $(\vec{\mu}_n \times \hat{r}) \times \hat{r} = (\vec{\mu}_n \cdot \hat{r}) \hat{r} - \vec{\mu}_n \quad ; \quad \hat{r} = \hat{i} \sin\theta \cos\varphi + \hat{j} \sin\theta \sin\varphi + \hat{k} \cos\theta$

$$\vec{\mu}_n \cdot \hat{r} = \hat{i} \mu_{nx} \sin\theta \cos\varphi + \hat{j} \mu_{ny} \sin\theta \sin\varphi + \hat{k} \mu_{nz} \cos\theta$$

$$(\vec{\mu}_n \cdot \hat{r}) \hat{r} = \left(\hat{i} \mu_{nx} \sin^2\theta \cos^2\varphi + \hat{j} \mu_{nx} \sin^2\theta \sin\varphi \cos\varphi + \hat{k} \mu_{nx} \cos\theta \sin\theta \cos\varphi \right)$$
$$+ \left(\hat{i} \mu_{ny} \sin^2\theta \sin\varphi \cos\varphi + \hat{j} \mu_{ny} \sin^2\theta \sin^2\varphi + \hat{k} \mu_{ny} \cos\theta \sin\theta \sin\varphi \right)$$
$$+ \left(\hat{i} \mu_{nz} \cos\theta \sin\theta \cos\varphi + \hat{j} \mu_{nz} \cos\theta \sin\theta \sin\varphi + \hat{k} \mu_{nz} \cos^2\theta \right)$$

Upon taking $\int_{-\pi}^{\pi} \cdots d\varphi \quad ; \quad \int_{-\pi}^{\pi} \sin^2\varphi \, d\varphi = \int_{-\pi}^{\pi} \cos^2\varphi \, d\varphi = \pi$, we have left:

$$- \int_\Omega (\vec{\mu}_n \times \hat{r}) \times \hat{r} \, d\Omega = 4\pi \vec{\mu}_n - \int_{-1}^{1} \left(\hat{i} \pi \mu_{nx} (1-\mu^2) + \hat{j} \pi \mu_{ny} (1-\mu^2) + \hat{k} 2\pi \mu^2 \right) d\mu$$

$$\left\{ \int_{-1}^{1} (1-\mu^2) \, d\mu = \mu - \frac{\mu^3}{3} \Big]_{-1}^{1} = \left(1 - \tfrac{1}{3}\right) - \left(-1 + \tfrac{1}{3}\right) = \frac{4}{3} \; ; \; \int_{-1}^{1} \mu^3 \, d\mu = \frac{2}{3} \right\}$$

$$= 4\pi \vec{\mu}_n - \frac{4\pi}{3} \vec{\mu}_n = \frac{8\pi}{3} \vec{\mu}_n$$

Hence: $\int_V \nabla \times \left[f |\psi|^2 \vec{A}_n \right] d\tau = \frac{8\pi}{3} \vec{\mu}_n \, f(r_0) |\psi(r_0)|^2$

Now consider: $\int_V \{ \nabla |\psi|^2 \} \times f \vec{A}_n \, d\tau$.

It is given as part of the problem that $\psi(\vec{r})$ be spherically symmetric, hence:

$$\{ \nabla |\psi|^2 \} \times f \vec{A}_n = \frac{\partial |\psi|^2}{\partial r} \hat{r} \times f \vec{A}_n$$

Now; we use $\vec{A}_n = \vec{\mu}_n(r) \times \frac{\vec{r}}{r^3}$, where $\vec{\mu}_n(r)$ is found in the expression for $\vec{A}_n$ with $r < r_0$ as it will be in this part of the problem. Now; from $\{ \nabla |\psi|^2 \} \times f \vec{A}_n = \frac{f(r)}{r^2} \frac{\partial |\psi|^2}{\partial r} \hat{r} \times (\vec{\mu}_n(r) \times \hat{r})$ we look at:

$$\hat{r} \times (\vec{\mu}_n(r) \times \hat{r}) = \vec{\mu}_n(r) - (\vec{\mu}_n(r) \cdot \hat{r}) \hat{r}$$

But this is of the same form for the angular integrations that we had before, hence:

$$\int_V \{ \nabla |\psi|^2 \} \times f A_n \, d\tau = \frac{8\pi}{3} \int_0^{r_0} \frac{f(r)}{r^2} \frac{\partial |\psi|^2}{\partial r} \vec{\mu}_n(r) \, r^2 \, dr$$

$$= \frac{8\pi}{3} \int_0^{r_0} f(r) \frac{\partial |\psi|^2}{\partial r} \vec{\mu}_n(r) \, dr$$

Now; $\vec{\mu}_n(r) = \vec{\mu}_{nL} \left[\int_0^r \rho(\vec{r}') \, r'^4 \, dr' + r^3 \int_r^{r_0} \rho(\vec{r}') \, r' \, dr' \right] + \vec{\mu}_{nS} \left[\int_0^r \rho_S(\vec{r}') \, r'^2 \, dr' \right]$

To eliminate $\vec{\mu}_{nL}$ and $\vec{\mu}_{nS}$, use the definitions of $\vec{\mu}_{nL}$, $\vec{\mu}_{nS}$ and set:

$$\vec{\mu}_n(r) = \vec{\mu}_{nL} \left[\frac{\int_0^r \rho(\vec{r}') \, r'^4 \, dr' + r^3 \int_r^{r_0} \rho(\vec{r}') \, r' \, dr'}{\int_0^{r_0} \rho(\vec{r}') \, r'^4 \, dr'} \right] + \vec{\mu}_{nS} \left[\frac{\int_0^r \rho_S(\vec{r}') \, r'^2 \, dr'}{\int_0^{r_0} \rho_S(\vec{r}') \, r'^2 \, dr'} \right]$$

Define:
$$K_L(r) = \frac{\int_0^r \rho(\vec{r}')\, r'^4\, dr' + r^3 \int_r^{r_0} \rho(\vec{r}')\, r'\, dr'}{\int_0^{r_0} \rho(\vec{r})\, r'^4\, dr'}$$

$$K_S(r) = \frac{\int_0^r \rho_S(\vec{r}')\, r'^2\, dr'}{\int_0^{r_0} \rho_S(\vec{r}')\, r'^2\, dr'}$$

Then: $\vec{\mu}_n(r) = \vec{\mu}_{nL}\, K_L(r) + \vec{\mu}_{nS}\, K_S(r)$

Now, it is stated in the problem that $\vec{\mu}_{nL}$, $\vec{\mu}_{nS}$, $\vec{\mu}_n$ are all in the same direction, hence:

$$\vec{\mu}_{nL} = \mu_{nL}\, \hat{\mu}_n = \mu_{nL} \frac{\vec{\mu}_n}{\mu_n} \;;\; \vec{\mu}_{nS} = \mu_{nS} \frac{\vec{\mu}_n}{\mu_n}$$

$$\therefore \quad \vec{\mu}_n(r) = \vec{\mu}_n \left(\frac{\mu_{nL}}{\mu_n} K_L(r) + \frac{\mu_{nS}}{\mu_n} K_S(r) \right)$$

Threading all our relations together and multiplying and dividing by $|\psi_p(0)|^2 = \text{constant}$, we obtain the final desired relation:

$$\epsilon_c = -\frac{8\pi}{3} \vec{\mu}_S \cdot \vec{\mu}_n |\psi_p(0)|^2 \left\{ f(r_0) \frac{|\psi(r_0)|^2}{|\psi_p(0)|^2} - \int_0^{r_0} \frac{f(r)}{|\psi_p(0)|^2} \frac{\partial |\psi(r)|^2}{\partial r} \left[\frac{\mu_{nL}}{\mu_n} K_L(r) + \frac{\mu_{nS}}{\mu_n} K_S(r) \right] dr \right\}$$

It is easy to see that as $f(r_0) \to 1$ and $\psi(r) \to \psi_0(0)$, $\{\ \} \to 1$ and we obtain the same result as in problem 1.

Applied Physics 296

Problem Set II

Due: March 21, 1962

1. The Hund's rule ground term for an atom or ion is the term of maximum multiplicity (or maximum S); and for that S, the term of maximum L consistent with the Pauli principle.

A state $\Psi(L\ M_L\ S\ M_S)$ of the ion is a linear combination of determinants of the form, $\Psi(L\ M_L\ S\ M_S) = \sum_i a_i D_i(M_L, M_S)$.

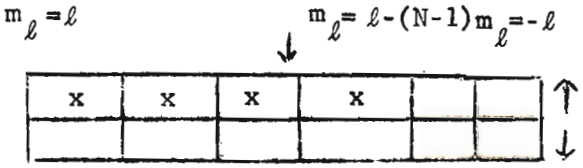
Therefore, the state

$$\Psi(L, M_L = L, S, M_S = S) \tag{1}$$

of the Hund's rule ground term for an ion with N electrons in a single unfulled shell less than half full, is the single determinant formed from the product function,

$$\pi_{<1/2} = u^{(1)}_{m_\ell = \ell}\chi^{\uparrow}(1)\ u^{(2)}_{m_\ell = \ell-1}\chi^{\uparrow}(2)\cdots u^{(N)}_{m_\ell = \ell-(N-1)}\chi^{\uparrow}(N) \tag{2}$$

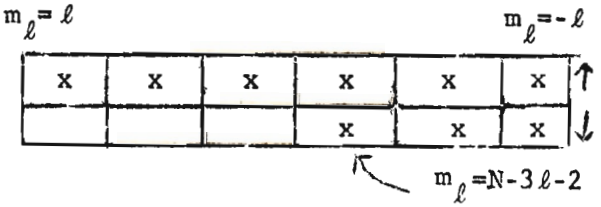
Here ℓ is the angular momentum of the unfilled shell, and χ is a spin function of spin up.



This is the only determinant having the maximum M_L and M_S, and therefore must itself be the state (1).

Similarly, the state (1) for N electrons in a shell more than 1/2 full is,

$$\pi_{>1/2} = u^{(1)}_{m_\ell = \ell}\chi^{\uparrow}(1)\cdots u^{(2\ell+1)}_{m_\ell = -\ell}\chi^{\uparrow}(2\ell+1)\ u^{(2\ell+2)}_{m_\ell = -\ell}\chi^{\downarrow}(2\ell+2)\cdots u^{(N)}_{m_\ell = N-3\ell-2}\chi^{\downarrow}(N) \tag{3}$$



Now, for an ionic state L, S, the Wigner - Eckart theorem says that we may write

$$(4) \quad \left\langle LSM_L',M_S' \left| \sum_i -\frac{\mu_o}{mc} \frac{1}{r_i} \frac{\partial v}{\partial r_i} \, L_i \cdot S_i \right| LSM_L M_S \right\rangle$$

$$= \lambda \left\langle LSM_L',M_S' \left| L \cdot S \right| LSM_L M_S \right\rangle .$$

By evaluating both sides of (4) for the case of the Hund's rule ground term of an ion, with $M_L' = M_L = L$, $M_S' = M_S = S$, show that

$$(5) \quad \begin{cases} \lambda = \dfrac{+\left\langle n\,\ell \left| -\frac{\mu_o}{mc} \frac{1}{r} \frac{\partial v}{\partial r} \right| n\ell \right\rangle}{2S} & \text{for shell less than half full,} \\ \lambda = \dfrac{-\left\langle n\,\ell \left| -\frac{\mu_o}{mc} \frac{1}{r} \frac{\partial v}{\partial r} \right| n\ell \right\rangle}{2S} & \text{for shell more than half full.} \end{cases}$$

2. Consider the Hamiltonian,

$$\mathcal{H} = \lambda \vec{L} \cdot \vec{S} + \mu_o (L_z + 2S_z) H$$

Find the energy levels of this Hamiltonian for S = 1/2 and arbitrary orbital angular momentum L. This result is known as the Breit-Rabi formula.

Show that, for small H, the energies become,

$$(1) \quad \mathcal{E} = \frac{\lambda}{2} \left[J(J+1) - L(L+1) - S(S+1) \right]$$

$$+ g(LSJ) \mu_o M_J H,$$

where $g(LSJ) = \left[\dfrac{2[J(J+1)+S(S+1)-L(L+1)]}{2J(J+1)} \right.$

$$\left. + \frac{J(J+1)+L(L+1)-S(S+1)}{s\,J(J+1)} \right],$$

and $\begin{cases} J = (L \pm 1/2), & S = 1/2 \\ M_J = J, \ldots -J. \end{cases}$

This verifies Landé g-factor result for S = 1/2.

AP 296

Assignment Number 2

Paul M. Grant

Problem 1:

We have from the Wigner-Eckart theorem for an ionic state L, S:

$$\langle L S M_L' M_S' | \sum_i -\frac{\mu_0}{mc} \frac{1}{r_i} \frac{\partial V}{\partial r_i} \vec{l}_i \cdot \vec{s}_i | L S M_L M_S \rangle$$

$$= \lambda \langle L S M_L' M_S' | \vec{L} \cdot \vec{S} | L S M_L M_S \rangle \qquad (1)$$

We are interested in the matrix elements of the Hund's rule ground state, $M_L = L$, $M_S = S$.
For a shell less than half full, we have:

$$\pi_{<1/2} = u_l(1)\chi^{\uparrow}(1)\, u_{l-1}(2)\chi^{\uparrow}(2) \cdots u_{l-(N-1)}^{(N)}\chi^{\uparrow}(N)$$

and for a shell more than half full:

$$\pi_{>1/2} = u_l(1)\chi^{\uparrow}(1) \cdots u_{-l}(2l+1)\chi^{\uparrow}(2l+1)\, u_{-l}(2l+2)\chi^{\downarrow}(2l+2) \cdots u_{N-3l-2}^{(N)}\chi^{\downarrow}(N)$$

Generally, we will have..

$$\Psi(LS, M_L = L, M_S = S) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P\pi$$

We ask for the diagonal of (1) with $M_L = L$ and $M_S = S$.

Consider:

$$\vec{L}\cdot\vec{S} = L_x S_x + L_y S_y + L_z S_z$$

$$L_+ = L_x + i L_y \quad ; \quad S_+ = S_x + i S_y$$

$$L_- = L_x - i L_y \quad ; \quad S_- = S_x - i S_y$$

$$L_+ S_- = L_x S_x + i L_y S_x + (-i) L_x S_y + L_y S_y$$

$$L_- S_+ = L_x S_x - i L_y S_x + i L_x S_y + L_y S_y$$

Then: $$L_x S_x + L_y S_y = \frac{1}{2}\{L_+ S_- + L_- S_+\}$$

and:

$$\boxed{\vec{L}\cdot\vec{S} = L_z S_z + \frac{1}{2}\{L_+ S_- + L_- S_+\}}$$

Because of the well known properties of the ladder operators, we immediately see:

$$\langle LS, M_L = L, M_S = S \mid \vec{L}\cdot\vec{S} \mid LS, M_L = L, M_S = S\rangle = \langle LS, M_L = L, M_S = S \mid L_z S_z \mid LS, M_L = L, M_S = S\rangle$$

$$= L S$$

We also see, following the outline above:

$$\vec{l}_i \cdot \vec{s}_i = l_{iz} s_{iz} + \frac{1}{2}\{l_{i+} s_{i-} + l_{i-} s_{i+}\}$$

In what follows, we will consider the radial parts to be split off from the u's in the product wave functions π. The radial wave functions are to be labelled with the quantum numbers n and l as usual. We then readily see that:

$$\langle LS, M_L=L, M_S=S | \sum_i -\frac{\mu_0}{mc} \frac{1}{r_i} \frac{\partial V}{\partial r_i} \vec{l}_i \cdot \vec{s}_i | LS, M_L=L, M_S=S \rangle$$

$$= \langle nl | -\frac{\mu_0}{mc} \frac{1}{r} \frac{\partial V}{\partial r} | nl \rangle \langle \psi(LS, M_L=L, M_S=S) | \sum_i \vec{l}_i \cdot \vec{s}_i | \psi(LS, M_L=L, M_S=S) \rangle$$

where $$\psi(LS, M_L=L, M_S=S) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \pi$$

What allows us to take $\langle nl | \cdots | nl \rangle$ out of $\sum_i$ is the fact that it is the same for every electron and is left invariant under permutations.

Now obviously, $\vec{l}_i \cdot \vec{s}_i$ being a single electron operator, can only connect states of the same electron. Also, we assume that the u's and the χ's are orthonormal among themselves. If this is true, then it is easily seen that the only non-vanishing matrix elements of the one-electron operator $\vec{l}_i \cdot \vec{s}_i$ occur when π is the same on both sides of the matrix element.

Now consider the shell less than half full: Because of the nature of s_{i+} and s_{i-} as ladder operators and the fact that all χ's are $+\frac{1}{2}$ states, we see we need only consider $\vec{l}_i \cdot \vec{s}_i \to l_{iz} s_{iz}$:

$$\langle \pi_{\ell 1/2} | \sum_i l_{iz} s_{iz} | \pi_{\ell 1/2} \rangle = \frac{1}{2} \left\langle \prod_{j=1}^{N} u_{\ell - (j-1)}^{(j)} \middle| \sum_{i=1}^{N} l_{iz} \middle| \prod_{j=1}^{N} u_{\ell-(j-1)}^{(j)} \right\rangle$$

$$= \frac{1}{2} \sum_{i=1}^{N} (\ell - (i-1))$$

However, $\sum_{i=1}^{N} (\ell-(i-1))$ is just the total M_L of the shell and we have stipulated that $M_L = L$. Also, we must remember that there are $N!$ ways of arranging the electrons among the orbitals in an independent manner, each of which gives a result indistinguishable from the above. Hence we have for the less than half filled shell:

$$\langle \psi(LS, M_L = L, M_S = S) | \sum_i \vec{l}_i \cdot \vec{s}_i | \psi(LS, M_L = L, M_S = S) \rangle = \frac{1}{2} L$$

and:

$$\lambda = \frac{\langle u l | -\frac{\mu_0}{mc} \frac{1}{r} \frac{\partial V}{\partial r} | u l \rangle}{2S}$$

For the case of the more than half filled shell, we still connect to states of the same π because of the orthonormality of the u's and χ's. And again because of the non-diagonal nature of s_{i+}, s_{i-} we need only take $\vec{l}_i \cdot \vec{s}_i \rightarrow l_{iz} s_{iz}$. Hence, we form:

$$\langle \pi_{>1/2} | \sum_{i=1}^{N} l_{iz} s_{iz} | \pi_{>1/2} \rangle = \langle \pi_{>1/2} | \sum_{i=1}^{2l+1} l_{iz} s_{iz} | \pi_{>1/2} \rangle$$

$$+ \langle \pi_{>1/2} | \sum_{i=2l+2}^{N} l_{iz} s_{iz} | \pi_{>1/2} \rangle$$

Consider: $\langle \pi_{>1/2} | \sum_{i=1}^{2l+1} l_{iz} s_{iz} | \pi_{>1/2} \rangle$

$$= \frac{1}{2} \langle \prod_{j=1}^{2l+1} u_{l+(j-1)}(\downarrow) | \sum_{i=1}^{2l+1} l_{iz} | \prod_{j=1}^{2l+1} u_{l-(j-1)}(\downarrow) \rangle$$

$$= \frac{1}{2} \sum_{i=1}^{2l+1} [l-(i-1)] = \frac{1}{2} \sum_{j=-l}^{l} j = 0$$

Now consider: $\langle \pi_{>1/2} | \sum_{i=2l+2}^{N} l_{iz} s_{iz} | \pi_{>1/2} \rangle$

$$= -\frac{1}{2} \langle \prod_{j=2l+2}^{N} u_{j-3l-2}(\downarrow) | \sum_{i=2l+2}^{N} l_{iz} | \prod_{j=2l+2}^{N} u_{j-3l-2}(\downarrow) \rangle$$

$$= -\frac{1}{2} \sum_{i=2l+2}^{N} [i-3l-2]$$

Again, this sum is just the total M_L of the shell which is here L. Also, we once more have $N!$ indistinguishable arrangements that give the same result as above.

Hence, for the more than half filled shell, we have:

$$\langle \psi(LS, M_L = L, M_S = S) | \sum_i \vec{l}_i \cdot \vec{s}_i | \psi(LS, M_L = L, M_S = S) \rangle = -\frac{L}{2}$$

and:

$$\lambda = -\frac{\langle nl | -\frac{\mu_0}{mc} \frac{1}{r} \frac{\partial V}{\partial r} | nl \rangle}{2S}$$

Problem 2

We are given the effective Hamiltonian:

$$\mathcal{H} = \lambda \vec{L}\cdot\vec{S} + \mu_0 (L_z + 2S_z) H$$

In order to gain a suitable matrix representation of this Hamiltonian, we form $\langle LS M_L' M_S' | \mathcal{H} | LS M_L M_S \rangle$. Note that we have not taken the problem diagonal in $\vec{J} = \vec{L} + \vec{S}$ as this is only true for the magnetic field interaction much weaker than the spin-orbit interaction.

Using $\vec{L}\cdot\vec{S} = L_z S_z + \frac{1}{2}\{L_+ S_- + L_- S_+\}$ we obtain:

$$\lambda \langle LS M_L' M_S' | L_z S_z | LS M_L M_S \rangle = \lambda M_L M_S \delta_{M_L M_L'} \delta_{M_S M_S'}$$

$$\mu_0 \langle LS M_L' M_S' | L_z | LS M_L M_S \rangle H = \mu_0 M_L H \delta_{M_L M_L'} \delta_{M_S M_S'}$$

$$2\mu_0 \langle LS M_L' M_S' | S_z | LS M_L M_S \rangle H = 2\mu_0 M_S H \delta_{M_L M_L'} \delta_{M_S M_S'}$$

$$\frac{\lambda}{2} \langle LS M_L' M_S' | L_+ S_- | LS M_L M_S \rangle = \frac{\lambda}{2} \sqrt{(L-M_L)(L+M_L+1)(S+M_S)(S-M_S+1)}\, \delta_{M_L', M_L+1} \delta_{M_S', M_S-1}$$

$$\frac{\lambda}{2} \langle LS M_L' M_S' | L_- S_+ | LS M_L M_S \rangle = \frac{\lambda}{2} \sqrt{(L+M_L)(L-M_L+1)(S-M_S)(S+M_S+1)}\, \delta_{M_L', M_L-1} \delta_{M_S', M_S+1}$$

We are to take $S = 1/2$; $M_S = \pm 1/2$ and L arbitrary.

The appropriate matrix representation of $\mathcal{H}$ is given in terms of a section of the matrix typical of any value of M_L.

M_L / M_L'		M_L		M_L+1	
	M_S / M_S'	$-1/2$	$1/2$	$-1/2$	$1/2$
M_L	$-1/2$	$-\frac{1}{2}M_L + \mu_0(M_L-1)H$			
	$1/2$		$\frac{1}{2}M_L + \mu_0(M_L+1)H$	$\frac{1}{2}\sqrt{(L-M_L)(L+M_L+1)}$	
M_L+1	$-1/2$		$\frac{1}{2}\sqrt{(L-M_L)(L+M_L+1)}$	$-\frac{1}{2}(M_L+1) + \mu_0 M_L H$	
	$1/2$				$\frac{1}{2}(M_L+1) + \mu_0(M_L+2)H$

$$\frac{1}{2}\langle LS, M_L+1, -1/2 \,|\, L_+S_- \,|\, LS\, M_L, 1/2\rangle = \frac{1}{2}\sqrt{(L-M_L)(L+M_L+1)}$$

$$\frac{1}{2}\langle LS, M_L, 1/2 \,|\, L_-S_+ \,|\, LS, M_L+1, -1/2\rangle = \frac{1}{2}\sqrt{(L+M_L+1)(L-M_L)}$$

Hence, we see we have as a matrix representation for $\mathcal{H}$ a series of 2×2 matrices. Focusing our attention on an arbitrary M_L, we immediately arrive at the following secular equation:

$$\mathcal{E}^2 + \left[\frac{\Delta}{2} - \mu_0 H(2M_L+1)\right]\mathcal{E} - \left[\frac{\Delta}{2}\mu_0 H(2M_L+1) - \mu_0^2 H^2 M_L(M_L+1) + \frac{\Delta^2}{4}L(L+1)\right] = 0$$

whose solution is:

$$\mathcal{E} = -\frac{\Delta}{4} + \frac{\mu_0 H}{2}(2M_L+1) \pm \frac{\Delta}{4}\left[(2L+1)^2 + \frac{4\mu_0 H}{\Delta}(2M_L+1) + 4\frac{\mu_0^2 H^2}{\Delta^2}\right]^{1/2}$$

or:

$$\boxed{\mathcal{E} = -\frac{\Delta}{4} + \frac{\mu_0 H}{2}(2M_L+1) \pm \frac{\Delta}{4}(2L+1)\left[1 + \frac{4\mu_0 H}{\Delta}\frac{(2M_L+1)}{(2L+1)^2} + \frac{4}{(2L+1)^2}\frac{\mu_0^2 H^2}{\Delta^2}\right]^{1/2}}$$

If we take $\frac{\mu_0 H}{\Delta} \ll 1$, or the usual Zeeman condition, and expand $[\ ]^{1/2}$ to order $\frac{\mu_0 H}{\Delta}$, we obtain:

$$\mathcal{E} = -\frac{\Delta}{4} + \frac{\mu_0 H}{2}(2M_L+1) \pm \left[\frac{\Delta}{4}(2L+1) + \frac{\mu_0 H}{2}\frac{2M_L+1}{2L+1}\right]$$

or:

$$\boxed{\mathcal{E} = \frac{\Delta}{4}\left[-1 \pm (2L+1)\right] + \mu_0 H \frac{2M_L+1}{2}\left[1 \pm \frac{1}{2L+1}\right]}$$

We could also write:

$$\varepsilon = \frac{\lambda}{2} L + \mu_0 H \frac{2M_L+1}{2}\left[1 + \frac{1}{2L+1}\right]$$

$$\varepsilon = -\frac{\lambda}{2}(L+1) + \mu_0 H \frac{2M_L+1}{2}\left[1 - \frac{1}{2L+1}\right]$$

Now if the Zeeman splitting is much less than the term intervals ($\frac{\mu_0 H}{\lambda} << 1$), we can formulate the problem in terms of R-S coupling where J is the total angular momentum quantum number. If we form $\langle J M_J' | H | J M_J \rangle$ and use the Wigner-Eckhardt Theorem, we will obtain the following:

Identities:

$$J^2 = (\vec{L}+\vec{S})^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$$

$$\vec{L}\cdot\vec{S} = \frac{J^2 - L^2 - S^2}{2}$$

$$S^2 = (\vec{J}-\vec{L})^2 = J^2 + L^2 - 2\vec{J}\cdot\vec{L}$$

$$\vec{J}\cdot\vec{L} = \frac{-S^2 + J^2 + L^2}{2} \quad ; \quad \vec{J}\cdot\vec{S} = \frac{J^2 + S^2 - L^2}{2}$$

Then: $\lambda \langle L S J M_J' | \vec{L}\cdot\vec{S} | L S J M_J \rangle = \frac{\lambda}{2}\left[J(J+1) - L(L+1) - S(S+1)\right] \delta_{M_J' M_J}$

We now make the Wigner-Eckhardt Theorem:

$$\langle LSJM_J' | \mu_0 (\vec{L} + 2\vec{S}) \cdot \vec{H} | LSJM_J \rangle$$

$$= \left[\frac{\langle JLSM_J | \vec{J} \cdot \vec{L} | LSJM_J \rangle}{J(J+1)} + \frac{2 \langle JLSM_J | \vec{J} \cdot \vec{S} | JLSM_J \rangle}{J(J+1)} \right] \mu_0 \langle LSJM_J' | \vec{J} | LSJM_J \rangle \cdot \vec{H}$$

Hence:

$$\langle LSJM_J' | \mu_0 (L_z + 2S_z) H | LSJM_J \rangle$$

$$= \left[\frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + 2 \frac{\{ J(J+1) + S(S+1) - L(L+1) \}}{2J(J+1)} \right] M_J \mu_0 H \delta_{M_J' M_J}$$

$$= g(LSJ) \mu_0 M_J H$$

where: $g(LSJ) = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

and hence:

$$\boxed{E = \frac{d}{2} \left[J(J+1) - L(L+1) - S(S+1) \right] + g(LSJ) \mu_0 M_J H}$$

To establish the connection between our two results, take:

$$J = L \pm 1/2 \; ; \; S = 1/2 \; ; \; M_J = J, \ldots, -J = M_L + 1/2$$

for $J = L + 1/2$;

$$J(J+1) = L^2 + 2L + \frac{3}{4} = (L+1/2)(L+3/2) = \frac{1}{4}(2L+1)(2L+3)$$

$$J(J+1) - L(L+1) - S(S+1) = L^2 + 2L + \frac{3}{4} - L^2 - L - \frac{3}{4} = L$$

$$g(LST) = 1 + 2\left[\frac{L^2+2L+3/4+3/4-L^2-L}{(2L+1)(2L+3)}\right] = 1 + 2\left[\frac{L+3/2}{(2L+1)(2L+3)}\right]$$

$$= 1 + \frac{1}{2L+1}$$

Hence: $$\boxed{\mathcal{E} = \frac{d}{2}L + \mu_0 H \frac{2M_L+1}{2}\left[1 + \frac{1}{2L+1}\right]}$$

for $J = L - 1/2$:

$$J(J+1) = L^2 - 1/4 = (L-1/2)(L+1/2) = \frac{1}{4}(2L+1)(2L-1)$$

$$J(J+1) - L(L+1) - S(S+1) = L^2 - 1/4 - L^2 - L - 3/4 = -(L+1)$$

$$g(LST) = 1 + 2\left[\frac{L^2-1/4+3/4-L^2-L}{(2L+1)(2L-1)}\right] = 1 + 2\left[\frac{-L+1/2}{(2L-1)(2L+1)}\right] = 1 + \frac{-1}{2L+1}$$

Hence: $$\boxed{\mathcal{E} = -\frac{d}{2}(L+1) + \mu_0 H \frac{2M_L+1}{2}\left[1 - \frac{1}{2L+1}\right]}$$

Therefore, we see that our two results correlate.

Applied Physics 296

Problem Set III

Due: April 11, 1962

1. Two 3d electrons couple to give a ground term ^3F.
Suppose a ^3F ion is put in a crystal field of octahedral symmetry, which in operator equivalent form, diagonal in L, is given by,

$$V_c = D_q \left[L_4^{\,o} + \left(\frac{5}{14}\right)^{1/2} \left(L_4^{\,+4} + L_4^{\,-4}\right) \right].$$

Find the matrix of V_c, ignoring the interaction of the ground term with higher terms. From the matrix, find the energy levels in the field V_c. Make use of,

$$\begin{cases} L_4^{\,o} = \frac{1}{8}\left(35\, L_z^{\,4} - 30\left\{\vec{L}^{\,2} L_z^{\,2}\right\} + 3\left\{\vec{L}^{\,4}\right\}\right) \\ L_4^{\,+} = \sqrt{\frac{70}{16}}\,(L^+)^4 \\ L_4^{\,-} = \sqrt{\frac{70}{16}}\,(L^-)^4 \\ \left\{\vec{L}^{\,4}\right\} = \vec{L}^{\,2}\left(\vec{L}^{\,2} - \frac{1}{3}\right) \\ \left\{\vec{L}^{\,2} L_z^{\,2}\right\} = \vec{L}^{\,2} L_z^{\,2} + \frac{1}{6}\vec{L}^{\,2} - \frac{5}{6} L_z^{\,2} \end{cases}$$

2. Consider the Hamiltonian for a nuclear moment in a crystal,

$$(1)\quad \mathcal{H} = g_{I/ON}\, \vec{I} \cdot \vec{H} - \frac{e^2 q Q}{4I(2I-1)}\left[3I_z^{\,2} - \vec{I}^{\,2} \right].$$

For the case $\mathcal{H}_{NZ} \gg \mathcal{H}_Q$, and I = 3/2 compute the energy levels for (1), to first order perturbation theory in $\mathcal{H}_Q$, assuming the field H is applied at some angle θ with respect to the symmetry axis. What transitions due to an R.F. magnetic field h applied at right angles to H, are allowed. Sketch the spectrum you would observe in a resonance experiments.

AP 296

Assignment number 3

Paul M. Grant

Problem 1

Given an ion with a ^3F ground state subject to a crystalline field of octahedral symmetry which in operator equivalent form is:

$$V_c = Dq \left[L_4^0 + \left(\frac{5}{14}\right)^{1/2} \left(L_4^{+4} + L_4^{-4} \right) \right]$$

where:

$$L_4^0 = \frac{1}{8} \left(35 L_z^4 - 30 \left\{ \vec{L}^2 L_z^2 \right\} + 3 \left\{ \vec{L}^4 \right\} \right)$$

$$L_4^{+4} = \sqrt{\frac{70}{16}} \, (L^+)^4$$

$$L_4^{-4} = \sqrt{\frac{70}{16}} \, (L^-)^4$$

$$\left\{ \vec{L}^4 \right\} = \vec{L}^2 \left(\vec{L}^2 - 1/3 \right)$$

$$\left\{ \vec{L}^2 L_z^2 \right\} = \vec{L}^2 L_z^2 + \frac{1}{6} \vec{L}^2 - \frac{5}{6} L_z^2$$

Now consider the matrix elements $\langle L M_L' | V_c | L M_L \rangle$:

$$\langle L M_L' | \left\{ \vec{L}^4 \right\} | L M_L \rangle = L(L+1) \left[L(L+1) - 1/3 \right] \delta_{M_L M_L'}$$

$$\langle L M_L' | \left\{ \vec{L}^2 L_z^2 \right\} | L M_L \rangle = \left\{ M_L^2 L(L+1) + \frac{1}{6} L(L+1) - \frac{5}{6} M_L^2 \right\} \delta_{M_L M_L'}$$

Then:

$$\langle L M_L' | L_4^0 | L M_L \rangle = \frac{1}{8} \left[35 M_L^4 - 30 \left\{ M_L^2 L(L+1) + \frac{1}{6} L(L+1) - \frac{5}{6} M_L^2 \right\} \right.$$

$$\left. + L(L+1) \left\{ 3L(L+1) - 1 \right\} \right] \delta_{M_L M_L'}$$

recall: $\langle L M_L' | L^+ | L M_L \rangle = \sqrt{(L-M_L)(L+M_L+1)}\ \delta_{M_L', M_L+1}$

$\langle L M_L' | L^- | L M_L \rangle = \sqrt{(L+M_L)(L-M_L+1)}\ \delta_{M_L', M_L-1}$

now: $(L^+)^n | L M_L \rangle = (L^+)^{n-1} \sqrt{(L-M_L)(L+M_L+1)}\ | L, M_L+1 \rangle$

$= (L^+)^{n-2} \left[(L-M_L)(L-M_L-1)(L+M_L+1)(L+M_L+2) \right]^{1/2} | L, M_L+2 \rangle$

$= \left[(L-M_L)(L-M_L-1)\cdots(L-M_L-n+1)(L+M_L+1)(L+M_L+2)\cdots(L+M_L+n) \right]^{1/2} | L, M_L+n \rangle$

$(L^-)^n | L M_L \rangle = (L^-)^{n-1} \left[(L+M_L)(L-M_L+1) \right]^{1/2} | L, M_L-1 \rangle$

$= (L^-)^{n-2} \left[(L+M_L)(L+M_L-1)(L-M_L+1)(L-M_L+2) \right]^{1/2} | L, M_L-2 \rangle$

$= \left[(L+M_L)(L+M_L-1)\cdots(L+M_L-n+1)(L-M_L+1)(L-M_L+2)\cdots(L-M_L+n) \right]^{1/2} | L, M_L-n \rangle$

Hence:

$\langle L M_L' | (L^+)^n | L M_L \rangle = \left[(L-M_L)(L-M_L-1)\cdots(L-M_L-n+1)(L+M_L+1)(L+M_L+2)\cdots(L+M_L+n) \right]^{1/2} \delta_{M_L', M_L+n}$

$\langle L M_L' | (L^-)^n | L M_L \rangle = \left[(L+M_L)(L+M_L-1)\cdots(L+M_L-n+1)(L-M_L+1)(L-M_L+2)\cdots(L-M_L+n) \right]^{1/2} \delta_{M_L', M_L-n}$

We are now in position to calculate the secular determinant for the system $L = 3$; $M_L = 0, \pm 1, \pm 2, \pm 3$. We only denote the values of M_L from now on:

$\langle 0 | V_c | 0 \rangle = D_q \langle 0 | C_4^0 | 0 \rangle = \frac{1}{8} \left[-30 \{ 2 \} + 12 \{ 35 \} \right] D_q$

$= \frac{1}{8} \left[420 - 60 \right] D_q = 45\, D_q$

$$\langle \pm 1 | V_c | \pm 1 \rangle = D_q \langle \pm 1 | L_4^0 | \pm 1 \rangle = \frac{1}{8}\left[35 - 30\left\{12 + 2 - \frac{5}{6}\right\} + 420\right] D_q$$

$$= \frac{1}{8}\left[35 - 5\cdot 79 + 420\right] D_q = \frac{15}{2} D_q$$

$$\langle \pm 2 | V_c | \pm 2 \rangle = D_q \langle \pm 2 | L_4^0 | \pm 2 \rangle = \frac{1}{8}\left[140 - 30\left\{48 + 2 - \frac{20}{6}\right\} + 420\right] D_q$$

$$= \frac{1}{8}\left[560 - 10\cdot 140\right] D_q = -105\, D_q$$

$$\langle \pm 3 | V_c | \pm 3 \rangle = D_q \langle \pm 3 | V_c | \pm 3 \rangle = \frac{1}{8}\left[2855 - 30\left\{108 + 2 - \frac{15}{2}\right\} + 420\right] D_q$$

$$= \frac{1}{8}\left[3255 - 15\cdot 205\right] D_q = +\frac{45}{2} D_q$$

Form:

$$\langle M_L + 4 \,|\, (L^+)^4 \,|\, M_L \rangle = \left[(3-M_L)(2-M_L)(1-M_L)(-M_L)(4+M_L)(5+M_L)(6+M_L)(7+M_L)\right]^{1/2}$$

$$\langle M_L - 4 \,|\, (L^-)^4 \,|\, M_L \rangle = \left[(3+M_L)(2+M_L)(1+M_L)(M_L)(4-M_L)(5-M_L)(6-M_L)(7-M_L)\right]^{1/2}$$

$$\langle -1 | V_c | 3 \rangle = \sqrt{\frac{5}{14}}\frac{\sqrt{70}}{16} D_q \langle -1 | (L^-)^4 | 3 \rangle = \left[(6)(5)(4)(3)(1)(2)(3)(4)\right]^{1/2} \frac{\sqrt{70}}{16} D_q \sqrt{\frac{5}{14}}$$

$$= \sqrt{\frac{5}{14}}\frac{3}{4}\sqrt{70}\, D_q \sqrt{60} = \frac{15}{2}\sqrt{42}\, D_q \sqrt{\frac{5}{14}} = \frac{15}{2}\sqrt{15}\, D_q$$

$$\langle 3 | V_c | -1 \rangle = \sqrt{\frac{5}{14}}\frac{\sqrt{70}}{16} D_q \langle 3 | (L^+)^4 | -1 \rangle = \left[(4)(3)(2)(1)(3)(4)(5)(6)\right]^{1/2} \frac{\sqrt{70}}{16} D_q \sqrt{\frac{5}{14}}$$

$$= \frac{15}{2}\sqrt{42}\, D_q \sqrt{\frac{5}{14}}$$

$$= \frac{15}{2}\sqrt{15}\, D_q$$

$\langle \pm 2 | V_c | \mp 2 \rangle = \frac{\sqrt{5}\sqrt{70}}{\sqrt{14}\,16} D_q$ $\langle \pm 2 | (L^{\pm})^4 | \mp 2 \rangle = \left[(5)(4)(3)(2)(2)(3)(4)(5)\right]^{1/2} \frac{\sqrt{70}}{16} D_q \sqrt{\frac{5}{14}}$

$= \sqrt{\frac{5}{14}} \frac{1680}{16} \sqrt{70}\, D_q = \frac{15}{2}\sqrt{70}\, D_q \sqrt{\frac{5}{14}} = \frac{75}{2} D_q$

$\langle {}^{+1}_{-3} | V_c | {}^{-3}_{+1} \rangle = \frac{\sqrt{5}\sqrt{70}}{\sqrt{14}\,16} D_q$ $\langle {}^{+1}_{-3} | (L^{\pm})^4 | {}^{-3}_{+1} \rangle = \left[(4)(3)(2)(1)(3)(4)(5)(6)\right]^{1/2} \frac{\sqrt{70}}{16} D_q \sqrt{\frac{5}{14}}$

$= \frac{15}{2}\sqrt{42}\, D_q \sqrt{\frac{5}{14}} = \frac{15}{2}\sqrt{15}\, D_q$

We can now construct the matrix representation of V_c:

M_L / M_L'	0	+3	−1	−3	+1	+2	−2
0	$45\,D_q$						
+3	~~$\frac{1680}{16} D_q$~~	~~$\frac{45}{2} D_q$~~	$\frac{15}{2}\sqrt{15}\, D_q$				
−1		$\frac{15}{2}\sqrt{15}\, D_q$	$\frac{15}{2} D_q$				
−3				~~$\frac{45}{2} D_q$~~	$\frac{15}{2}\sqrt{15}\, D_q$		
+1				$\frac{15}{2}\sqrt{15}\, D_q$	$\frac{15}{2} D_q$		
+2						$-105\,D_q$	$\frac{75}{2} D_q$
−2						$\frac{75}{2} D_q$	$-105\,D_q$

Note that the crystal field does not completely remove the M_L degeneracy of the ion.

The energy levels, apart from a constant factor, are the following:

$$\varepsilon = \underline{\underline{45\,D_q}}$$

$$(\varepsilon + 105\,D_q)^2 - \frac{75^2}{4} D_q^2 = 0$$

$$\varepsilon^2 + 210\,D_q + \left[\frac{4\cdot 105^2 - 75^2}{4}\right] D_q^2 = 0$$

or: $$\varepsilon^2 + 210\,D_q\varepsilon + \frac{38475}{4} D_q^2 = 0$$

$$\varepsilon = \left[-105 \pm \frac{1}{2}\left\{44100 - 38475\right\}^{1/2}\right] D_q$$

$$= \left[-105 \pm \tfrac{1}{2}\cdot 75\right] D_q = \frac{-210 \pm 75}{2} D_q = \underline{\underline{\frac{-285}{2} D_q \;;\; \frac{-135}{2} D_q}}$$

$$\left(\varepsilon + \frac{-45}{2} D_q\right)\left(\varepsilon - \frac{15}{2} D_q\right) - \frac{225}{4}\cdot 15\, D_q^2 = 0$$

or $$4\varepsilon^2 - 60\, D_q\varepsilon + 15\cdot 45\, D_q^2 - 225\cdot 15\, D_q^2 = 0$$

$$4\varepsilon^2 - 60\, D_q\varepsilon - 2700\, D_q^2 = 0$$

$$2\varepsilon^2 - 30\, D_q\varepsilon - 1350\, D_q^2 = 0$$

$$\varepsilon = \frac{1}{4}\left[-285 \pm \left\{81225 + 48600\right\}^{1/2}\right] D_q$$

$$\varepsilon = \underline{\underline{\frac{-285 + 5\sqrt{5193}}{4} D_q \;,\; \frac{-285 - 5\sqrt{5193}}{4} D_q}}$$

Or: $\varepsilon^2 - 15\varepsilon D_q - 675 D_q^2 = 0$

$$\varepsilon = \frac{1}{2}\left[15 \pm (225 + 2700)^{1/2}\right]$$

$$\varepsilon = \frac{15 + (2925)^{1/2}}{2} \quad ; \quad \frac{15 - (2925)^{1/2}}{2}$$

$\varepsilon = 45 D_q$ (3)

$\varepsilon = -15 D_q$ (3)

$\varepsilon = -90 D_q$ (1)

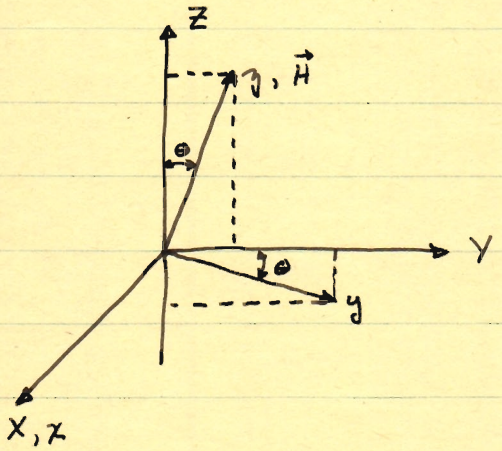
Problem 2:

The Hamiltonian for a nuclear moment in a crystal in a magnetic field is:

$$\mathcal{H} = g_I \mu_N \vec{I}\cdot\vec{H} - \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - \vec{I}^2 + \frac{1}{2}\eta\,(I_+^2 + I_-^2)\right]$$

where $\eta = \dfrac{V_{xx} - V_{yy}}{V_{zz}}$ and x, y, z are the crystal axes. Apparently our problem has cylindrical symmetry about the z axis as $\eta = 0$.

We will find it convenient to quantize the problem along the direction of $\vec{H}$, hence consider the following coordinate transformations. We take $\vec{H}$ to lie in the YZ plane without loss of generality:



$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

In the lattice frame: $\vec{I}^2 = \begin{pmatrix} I_x & I_y & I_z \end{pmatrix}\begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$

Define: $I_+ = I_x + \imath I_y$; $I_- = I_x - \imath I_y$

In the Field frame: $\vec{I}^2 = I_x^2 + I_y^2 + I_z^2 = \frac{1}{2}\left\{I_+ I_- + I_- I_+\right\} + I_z^2$

Also: $I_x = \frac{1}{2}(I_+ + I_-)$; $I_y = \frac{1}{2i}(I_+ - I_-)$

$$\begin{pmatrix} I_x & I_y & I_z \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(I_+ + I_-) & \frac{1}{2i}(I_+ - I_-) & I_3 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

Transposing:

$$\begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(I_+ + I_-) \\ \frac{\cos\theta}{2i}(I_+ - I_-) + I_3 \sin\theta \\ \frac{-\sin\theta}{2i}(I_+ - I_-) + I_3 \cos\theta \end{pmatrix}$$

Then: $\vec{I}^2_{\text{(old frame)}} = \frac{1}{4}(I_+^2 + I_-^2 + I_+I_- + I_-I_+)$

$$- \frac{\cos^2\theta}{4}(I_+^2 + I_-^2 - I_+I_- - I_-I_+) + I_3^2 \sin^2\theta$$
$$+ \left[\frac{I_3 \cos\theta}{2i}(I_+ - I_-) + \frac{\cos\theta}{2i}(I_+ - I_-)I_3\right]\sin\theta$$
$$- \frac{\sin^2\theta}{4}(I_+^2 + I_-^2 - I_+I_- - I_-I_+) + I_3^2\cos^2\theta$$
$$- \frac{\sin\theta}{2i}\{I_3(I_+ - I_-) + (I_+ - I_-)I_3\}\cos\theta$$

$= \vec{I}^2_{\text{(Field Frame)}}$

$$I_z^2 = -\frac{\sin^2\theta}{4}(I_+^2 + I_-^2 - I_+I_- - I_-I_+) + I_3^2\cos^2\theta$$
$$- \frac{\sin\theta\cos\theta}{2i}\left[I_3(I_+ - I_-) + (I_+ - I_-)I_3\right]$$

$$= I_3^2\cos^2\theta + \frac{1}{4}(1 - \cos^2\theta)(I_+I_- + I_-I_+ + 2I_3^2 - 2I_3^2)$$

$$- \frac{\sin\theta\cos\theta}{2i}\left[I_3(I_+ - I_-) + (I_+ - I_-)I_3\right] - \frac{\sin^2\theta}{4}(I_+^2 + I_-^2)$$

Thus, in transferring from the lattice frame to the field frame, we find:

$$3I_z^2 - \vec{I}^2 \longrightarrow 3I_3^2\cos^2\theta + \frac{3}{2}(1-\cos^2\theta)(\vec{I}^2 - I_3^2) - \frac{3}{2}\sin\theta\cos\theta\left\{I_3(I_+ - I_-) + (I_+ - I_-)I_3\right\} - \frac{3}{4}\sin^2\theta(I_+^2 + I_-^2) - I^2$$

Finally, we have for the complete Hamiltonian in the field frame:

$$\mathcal{H} = g_I \mu_N I_3 H - \frac{e^2 q Q}{4I(2I-1)}\left[\begin{array}{l}\frac{1}{2}(3\cos^2\theta - 1)(3I_3^2 - \vec{I}^2) \\ -\frac{3}{2}\sin\theta\cos\theta\left[I_3(I_+ - I_-) + (I_+ - I_-)I_3\right] \\ -\frac{3}{4}\sin^2\theta(I_+^2 + I_-^2)\end{array}\right]$$

We consider $\mathcal{H}_Z >> \mathcal{H}_Q$ and take $\mathcal{H}_Z$ as the unperturbed problem. Hence we have for the unperturbed energy levels:

$$E_{M_I}^{(0)} = g_I \mu_N M_I H$$

Since the magnetic field has removed the degeneracies, we have from ordinary first order perturbation theory, the level shifts due to $\mathcal{H}_Q$ are:

$$E_{M_I}^{(1)} = -\frac{e^2 q Q}{4I(2I-1)}(3\cos^2\theta - 1)(3M_I^2 - I(I+1))$$

Since the orthogonal transformation of coordinates preserved the operator $\vec{I}^2$, a value of $I = 3/2$ will hold in both frames with $M_I = \pm 3/2, \pm 1/2$ in the field frame. Hence:

$$E^{(1)}_{M_I} = -\frac{e^2 q Q}{24}\left(3\cos^2\theta - 1\right)\left(3M_I^2 - \frac{15}{4}\right)$$

$$E^{(0)}_{M_I} = g_I \mu_N M_I H \quad ; \quad M_I = \pm 3/2, \pm 1/2$$

$$E_{-3/2} = -\frac{3}{2} g_I \mu_N H - \frac{e^2 q Q}{8}\left(3\cos^2\theta - 1\right)$$

$$E_{-1/2} = -\frac{1}{2} g_I \mu_N H + \frac{e^2 q Q}{8}\left(3\cos^2\theta - 1\right)$$

$$E_{1/2} = \frac{1}{2} g_I \mu_N H + \frac{e^2 q Q}{8}\left(3\cos^2\theta - 1\right)$$

$$E_{3/2} = \frac{3}{2} g_I \mu_N H - \frac{e^2 q Q}{8}\left(3\cos^2\theta - 1\right)$$

Because we will need them later, we now compute to first order the eigenfunctions of our energy levels using: We will compute transitions to the second order:

$$|\psi_{M_I}\rangle = |\psi^{(0)}_{M_I}\rangle + \sum_{M_I' \neq M_I} \frac{|\psi^{(0)}_{M_I'}\rangle\langle\psi^{(0)}_{M_I'}|\mathcal{H}_Q|\psi^{(0)}_{M_I}\rangle}{E^{(0)}_{M_I} - E^{(0)}_{M_I'}}$$

Since we will be concerned only with allowed transitions or selection rules, we need only consider if $\langle \psi^{(1)}_{M_I'} | \mathcal{H}_Q | \psi^{(0)}_{M_I} \rangle$ vanishes or not and not be concerned with its actual value which will be some constant.

Now, the transition operator will be of the form $\vec{I} \cdot \vec{h}$ in the field system. Since we need only $\vec{h} \perp \vec{H}$, we can choose $\vec{h}$ to be in the x or X direction without loss of generality. Hence the interaction is of the form $I_x \rightarrow I_+ + I_-$ in the field system. Then to discover the selection rules, we must discuss matrix elements of the form:

$$\langle \psi_{M_I'} | I_\pm | \psi_{M_I} \rangle$$

We now return to the problem of finding $|\psi_{M_I}\rangle$. We will now use $|\psi^{(0)}_{M_I}\rangle = |M_I\rangle$. From the form of $\mathcal{H}_Q$, we now see that the following values of $\langle M_I' | \mathcal{H}_Q | M_I \rangle$ are non-vanishing:

$\langle M_I' | \mathcal{H}_Q | M_I \rangle$

M_I / M_I'	$-3/2$	$-1/2$	$1/2$	$3/2$
$-3/2$	×	×	×	
$-1/2$	×	×	×	×
$1/2$	×	×	×	×
$3/2$		×	×	×

Hence:

$$|\psi_{-3/2}\rangle = |-3/2\rangle + C^{-3/2}_{-1/2}|-1/2\rangle + C^{-3/2}_{1/2}|1/2\rangle$$

$$|\psi_{-1/2}\rangle = |-1/2\rangle + C^{-1/2}_{-3/2}|-3/2\rangle + C^{-1/2}_{1/2}|1/2\rangle + C^{-1/2}_{3/2}|3/2\rangle$$

$$|\psi_{1/2}\rangle = |1/2\rangle + C^{1/2}_{-3/2}|-3/2\rangle + C^{1/2}_{-1/2}|-1/2\rangle + C^{1/2}_{3/2}|3/2\rangle$$

$$|\psi_{3/2}\rangle = |3/2\rangle + C^{3/2}_{-1/2}|-1/2\rangle + C^{3/2}_{1/2}|1/2\rangle$$

Since the interaction is of the form $I_\pm$, we will only have transitions among those states $|\psi_{M_I}\rangle$ which have components differing by ± 1. The following table of allowed transitions is then obvious:

$\psi_{3/2} \leftrightarrow \psi_{-3/2}$	$\psi_{1/2} \leftrightarrow \psi_{-3/2}$
$\psi_{3/2} \leftrightarrow \psi_{-1/2}$	$\psi_{1/2} \leftrightarrow \psi_{-1/2}$
$\psi_{3/2} \leftrightarrow \psi_{1/2}$	$\psi_{-1/2} \leftrightarrow \psi_{-3/2}$

We see that all possible transitions can occur for some general θ. Of course, the $C^{M_I}_{M_I'}$ above depend on θ and some of them will vanish for judiciously chosen values of θ.

To accurately sketch the resonance absorption peaks, one needs to know the values of the $C^{M_I}_{M_I'}$. From the Hermitean character of $\mathcal{H}$ and from the first order form of the wave function, we know $C^{M_I}_{M_I'} = -C^{*M_I'}_{M_I}$.

In the calculations to follow, the following table will be convenient:

$\langle M_I' | I_\pm^2 | M_I \rangle$; $\langle M_I' | I_\pm | M_I \rangle$

M_I' \ M_I	$-3/2$	$-1/2$	$1/2$	$3/2$
$-3/2$		I_+ $\sqrt{3}$	I_-^2 $2\sqrt{3}$	
$-1/2$	I_+ $\sqrt{3}$		I_- 2	I_-^2 $2\sqrt{3}$
$1/2$	I_+^2 $2\sqrt{3}$	I_+ 2		I_- $\sqrt{3}$
$3/2$		I_+^2 $2\sqrt{3}$	I_+ $\sqrt{3}$	

With this we can now form the table of $\langle M_I' | \mathcal{H}_Q | M_I \rangle$ disregarding the diagonal. Define $A = \frac{+e^2qQ}{12}\frac{3}{2} = \frac{e^2qQ}{8}$ so that:

$$\langle M_I' | \mathcal{H}_Q | M_I \rangle_{M_I' \neq M_I} = A \langle M_I' | \frac{\sin\theta\cos\theta}{2}\left[I_z(I_+ - I_-) + (I_+ - I_-)I_z\right] + \frac{\sin^2\theta}{2}(I_+^2 + I_-^2) | M_I \rangle$$

$$= \frac{A\sin\theta\cos\theta}{2} 2 M_I' M_I \langle M_I' | I_+ - I_- | M_I \rangle + \frac{A\sin^2\theta}{2}\langle M_I' | (I_+^2 + I_-^2) | M_I \rangle$$

$$\langle -3/2 | \mathcal{H}_Q | -1/2 \rangle = \frac{A\sin\theta\cos\theta}{2} 2\left(-\tfrac{3}{2}\right)\left(-\tfrac{1}{2}\right)\left(-\sqrt{3}\right) = -\frac{3\sqrt{3}}{4} A\sin\theta\cos\theta$$

$$\langle -1/2 | \mathcal{H}_Q | 1/2 \rangle = \frac{A\sin\theta\cos\theta}{2} 2\left(-\tfrac{1}{2}\right)\left(\tfrac{1}{2}\right)(-2) = \frac{1}{2} A\sin\theta\cos\theta$$

$$\langle 1/2 | \mathcal{H}_Q | 3/2 \rangle = \frac{A\sin\theta\cos\theta}{2} 2\left(\tfrac{1}{2}\right)\left(\tfrac{3}{2}\right)\left(-\sqrt{3}\right) = -\frac{3\sqrt{3}}{4} A\sin\theta\cos\theta$$

$$\langle -3/2 | \mathcal{H}_Q | 1/2 \rangle = \frac{A\sin^2\theta}{2} \cdot 2\sqrt{3} = \sqrt{3}\, A\sin^2\theta$$

$$\langle -1/2 | \mathcal{H}_Q | 3/2 \rangle = \sqrt{3}\, A\sin^2\theta$$

Now define: $B = \frac{A}{\text{Since Now } H = \gamma}$, thus:

$$C_{-1/2}^{-3/2} = \frac{\langle -1/2 | \mathcal{H}_Q | -3/2 \rangle}{\gamma(-\frac{3}{2}+\frac{1}{2})} = C_{-3/2}^{-1/2} = \frac{3\sqrt{3}}{2} B \sin\theta\cos\theta$$

$$C_{1/2}^{-3/2} = \frac{\langle 1/2 | \mathcal{H}_Q | -3/2 \rangle}{\gamma(-\frac{3}{2}-\frac{1}{2})} = C_{-3/2}^{1/2} = -\frac{\sqrt{3}}{2} B \sin^2\theta$$

$$C_{1/2}^{-1/2} = \frac{\langle 1/2 | \mathcal{H}_Q | -1/2 \rangle}{\gamma(-\frac{1}{2}-\frac{1}{2})} = C_{-1/2}^{1/2} = -\frac{1}{2} B \sin\theta\cos\theta$$

$$C_{3/2}^{-1/2} = \frac{\langle 3/2 | \mathcal{H}_Q | -1/2 \rangle}{\gamma(-\frac{1}{2}-\frac{3}{2})} = C_{-1/2}^{3/2} = -\frac{\sqrt{3}}{2} B \sin^2\theta$$

$$C_{3/2}^{1/2} = \frac{\langle 3/2 | \mathcal{H}_Q | 1/2 \rangle}{\gamma(\frac{1}{2}-\frac{3}{2})} = C_{1/2}^{3/2} = \frac{3\sqrt{3}}{2} B \sin\theta\cos\theta$$

Transitions:

$\psi_{3/2} \leftrightarrow \psi_{-3/2}$:

$$\langle \psi_{3/2} | I_\pm | \psi_{-3/2} \rangle = C_{1/2}^{-3/2} \langle 3/2 | I_+ | 1/2 \rangle + C_{-1/2}^{3/2} \langle -1/2 | I_+ | -3/2 \rangle + C_{-1/2}^{3/2} C_{1/2}^{-3/2} \langle -1/2 | I_- | 1/2 \rangle + C_{1/2}^{3/2} \langle 1/2 | I_+ | -1/2 \rangle C_{-1/2}^{-3/2}$$

$$= \sqrt{3} \cdot -\frac{\sqrt{3}}{2} B \sin^2\theta + \sqrt{3} \cdot -\frac{\sqrt{3}}{2} B \sin^2\theta + 2 \cdot -\frac{\sqrt{3}}{2} B \sin^2\theta \cdot -\frac{\sqrt{3}}{2} B \sin^2\theta + 2 \cdot \frac{3\sqrt{3}}{2} B \sin\theta\cos\theta \cdot \frac{3\sqrt{3}}{2} B \sin\theta\cos\theta$$

$$= -3B\sin^2\theta + \frac{3}{2} B^2 \sin^4\theta - \frac{27}{2} B^2 \sin^2\theta\cos^2\theta$$

It appears as if the transition amplitudes admit of no simple form, thus we just plot a rough sketch of the resonance absorption peaks in order to save time; that is, we assume all peaks are δ functions.

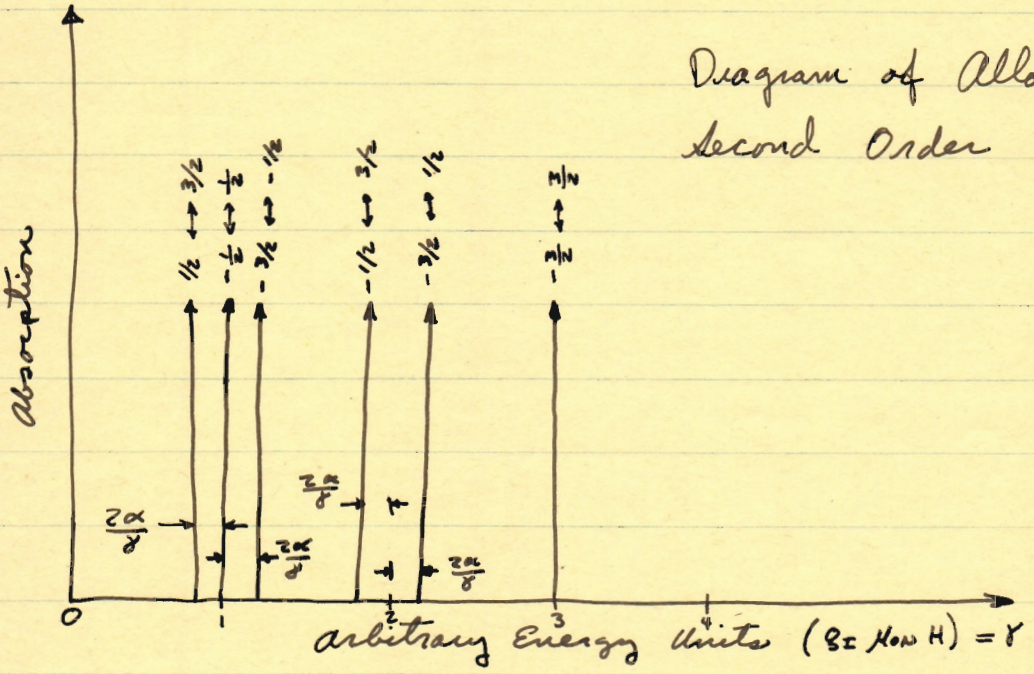
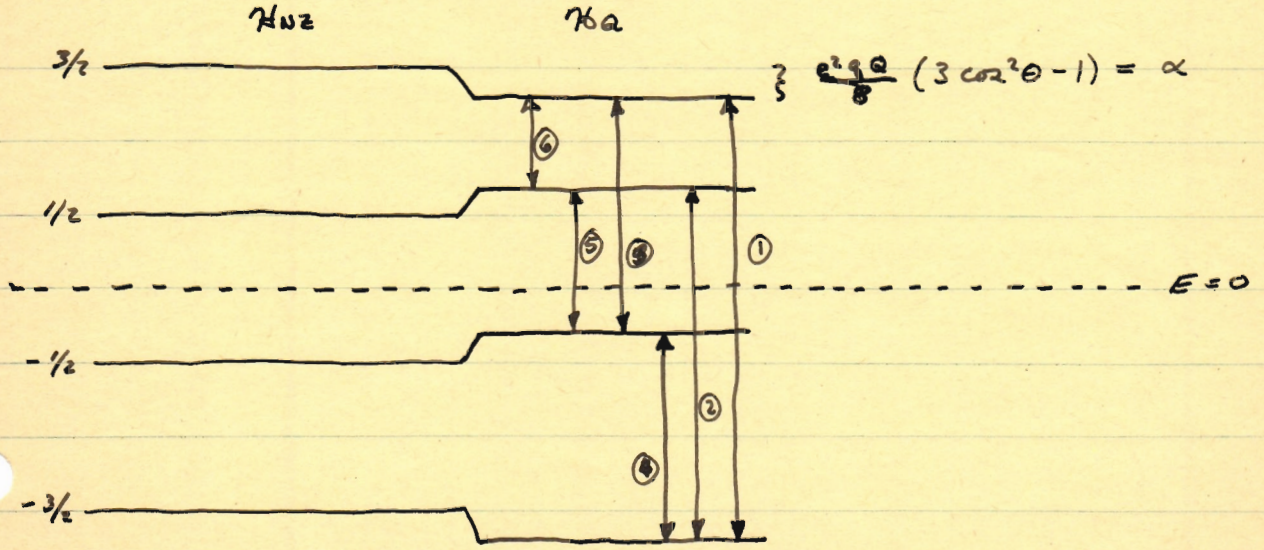


Diagram of Allowed Second Order Transitions

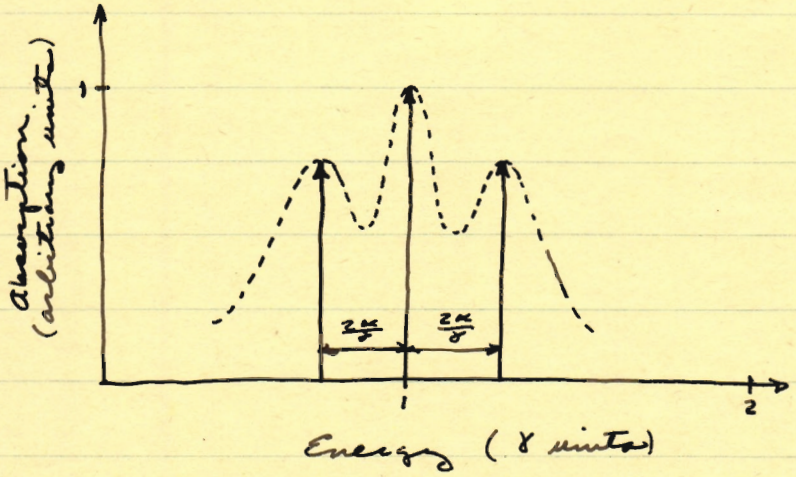
Energy Diagram



To calculate the allowed first order transitions, we can refer directly to the table for $\langle M\pm | I_\pm | M_z \rangle$. We find:

First Order Allowed Transitions	Relative Intensity ($\lvert\langle M\pm \lvert I_\pm \rvert M_z\rangle\rvert^2$)
$\psi_{-3/2} \leftrightarrow \psi_{-1/2}$	3
$\psi_{-1/2} \leftrightarrow \psi_{1/2}$	4
$\psi_{1/2} \leftrightarrow \psi_{3/2}$	3

Thus we see the transitions ④, ⑤ and ⑥ are allowed. If we include a little damping, a sketch of the resonance spectrum will be as follows:



Applied Physics 296

Due: May 21, 1962

1. Start with the effective mass Hamiltonian for the four-fold degenerate valence bands of Ge or Si, in the presence of a magnetic field $\vec{H}$,

$$\mathcal{H} = -\frac{1}{m}\left[\left(\gamma_1 + \frac{5}{2}\gamma_2\right)\frac{\vec{P}^2}{2} - \gamma_2\left(J_x^2 P_x^2 + J_y^2 P_y^2 + J_z^2 P_z^2\right)\right.$$

$$-2\gamma_3\left(\{J_x J_y\}\{P_x P_y\} + \{J_y J_z\}\{P_y P_z\} + \{J_z J_x\}\{P_z P_x\}\right)$$

$$\left. + \frac{e\hbar}{c}\,K\vec{J}\cdot\vec{H} + \frac{e\hbar}{c}\,q\left(J_x^3 H_x + J_y^3 H_y + J_z^3 H_z\right)\right].$$

The symbol $\{P_x P_y\}$, etc. means $\frac{1}{2}\left(P_x P_y + P_y P_x\right)$.

The angular momentum 3/2 matrices J_x, J_y, J_z are,

$$J_z = \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}$$

$$J_x = 1/2 \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$J_y = \frac{1}{2i} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

Show that in the limit of $\vec{H} \to 0$, the solution of the eigenvalue problem,

$\mathcal{H}_{\downarrow} = E_{\downarrow}$ has the four roots,

$$E = \frac{-\hbar^2}{2m}\left[Ak^2 + \sqrt{B^2k^4 + c^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)}\ \right] - \text{twice}$$

$$E = \frac{\hbar^2}{2m}\left[\ Ak^2 - \sqrt{B^2k^4 + c^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)}\ \right] - \text{twice},$$

where

$$\begin{cases} A = \gamma_1 \\ B^2 = (2\gamma_2)^2 \\ C^2 = 12(\gamma_3^2 - \gamma_2^2). \end{cases}$$

2. Suppose an electron moves in a magnetic field H in kinetic momentum space, on a constant energy surface,

$$E = \frac{1}{2m}\left(P_x^2\alpha_{11} + P_y^2\alpha_{22} + P_z^2\alpha_{33}\right).$$

The magnetic field is,

$$H = H[\alpha\hat{x} + \beta\hat{y} + \alpha\hat{z}].$$

Write out the classical equation of motion of an electron,

$$\frac{d\vec{P}}{dT} = \frac{e}{c}\,\nabla_p E \times \vec{H}\ .$$

Assume that the motion of the electron in P space is periodic and goes as $e^{i\,\omega_c t}$.

From the consistency condition for the motion, show that

$\omega_c = \dfrac{eH}{m^*_c C}$, where

$$\frac{m}{m^*_c} = \left(\hat{H}\ .\ \overleftrightarrow{\alpha}^{-1}\ .\ \hat{H}\ |\alpha|\right)^{1/2}$$

3. For the case of a two-fold degenerate band j coupled to one other two-fold degenerate band u, and neglecting the free electron contributions, we

have the effective mass equation,

$$\left[\frac{1}{2m} \vec{P} \cdot \overleftrightarrow{\alpha} \cdot \vec{P} + \mu_o \vec{S} \cdot \overleftrightarrow{g} \cdot H - E \right] f_j(\vec{r}) = 0,$$

where

$$\overleftrightarrow{\alpha} = 2m \frac{(\vec{t}_{j\mu}\vec{t}_{j\mu} + \vec{u}_{j\mu}\vec{u}_{j\mu} + \vec{v}_{j\mu}\vec{v}_{j\mu} + w_{j\mu}w_{j\mu})}{E_j^o - E_\mu^o}$$

$$\overleftrightarrow{g} = \frac{2m}{(E_j^o - E_\mu^o)} \left[\hat{x} (\vec{v}_{j\mu} x \vec{w}_{j\mu} + \vec{u}_{j\mu} x \vec{t}_{j\mu}) \right.$$

$$\left. + \hat{y}(\vec{w}_{j\mu} x \vec{u}_{j\mu} + \vec{v}_{j\mu} x \vec{t}_{j\mu}) + \hat{z}(\vec{u}_{j\mu} x \vec{v}_{j\mu} + \vec{w}_{j\mu} x \vec{t}_{j\mu}) \right] .$$

The expressions for the effective cyclotron resonance mass and the effective spin resonance mass are,

$$\left(\frac{m}{m_c^*}\right) = (\hat{H} \cdot \vec{\alpha}^{-1} \cdot \hat{H} \, |a|)^{1/2}$$

$$\left(\frac{m}{m_s^*}\right) = 1/2(\hat{H} \cdot \tilde{\overleftrightarrow{g}} \cdot \overleftrightarrow{g} \cdot \hat{H})^{1/2}$$

Show that for this simple case, $m_c^* = m_s^*$ for any direction of applied field.

AP 296

Assignment Number 4

Paul M. Grant

Problem 1

The effective mass Hamiltonian for the 4-fold degenerate valence bands of Si and Ge, in the presence of a magnetic field is:

$$\mathcal{H} = -\frac{1}{m}\left[\left(\gamma_1 + \frac{5}{2}\gamma_2\right)\frac{\vec{P}^2}{2} - \gamma_2\left(J_x^2 P_x^2 + J_y^2 P_y^2 + J_z^2 P_z^2\right)\right.$$

$$-2\gamma_3\left(\{J_x, J_y\}\{P_x, P_y\} + \{J_y, J_z\}\{P_y, P_z\} + \{J_z, J_x\}\{P_z, P_x\}\right)$$

$$\left. + \frac{e\hbar}{c}\kappa\,\vec{J}\cdot\vec{H} + \frac{e\hbar}{c}q\left(J_x^3 H_x + J_y^3 H_y + J_z^3 H_z\right)\right]$$

Now, in the limit of $\vec{H} \to 0$, we have $P_x \to \hbar k_x$, etc, and the Hamiltonian becomes:

$$\mathcal{H} = -\frac{\hbar^2}{m}\left[\left(\gamma_1 + \frac{5}{2}\gamma_2\right)\frac{\hbar^2 k^2}{2} - \gamma_2\hbar^2\left(J_x^2 k_x^2 + J_y^2 k_y^2 + J_z^2 k_z^2\right)\right.$$

$$\left. -2\gamma_3\hbar^2\left(\{J_x, J_y\}k_x k_y + \{J_y, J_z\}k_y k_z + \{J_z, J_x\}k_z k_x\right)\right]$$

and the appropriate $J = 3/2$ matrices are:

$$J_z = \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}; \quad J_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}; \quad J_y = \frac{1}{2i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

now:

$$J_x^2 = \frac{1}{4}\begin{pmatrix} 3 & 0 & 2\sqrt{3} & 0 \\ 0 & 7 & 0 & 2\sqrt{3} \\ 2\sqrt{3} & 0 & 7 & 0 \\ 0 & 2\sqrt{3} & 0 & 3 \end{pmatrix}; \quad J_y^2 = -\frac{1}{4}\begin{pmatrix} -3 & 0 & 2\sqrt{3} & 0 \\ 0 & -7 & 0 & 2\sqrt{3} \\ 2\sqrt{3} & 0 & -7 & 0 \\ 0 & 2\sqrt{3} & 0 & -3 \end{pmatrix}$$

$$J_z^2 = \frac{1}{4}\begin{pmatrix} +9 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +9 \end{pmatrix}$$

$$J_x J_y = \frac{1}{4i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix} = \frac{1}{4i}\begin{pmatrix} -3 & 0 & 2\sqrt{3} & 0 \\ 0 & -1 & 0 & 2\sqrt{3} \\ -2\sqrt{3} & 0 & 1 & 0 \\ 0 & -2\sqrt{3} & 0 & 3 \end{pmatrix}$$

$$J_y J_x = \frac{1}{4i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} = \frac{1}{4i}\begin{pmatrix} 3 & 0 & 2\sqrt{3} & 0 \\ 0 & 1 & 0 & 2\sqrt{3} \\ -2\sqrt{3} & 0 & -1 & 0 \\ 0 & -2\sqrt{3} & 0 & -3 \end{pmatrix}$$

$$\{J_x, J_y\} = \frac{1}{8i}\cdot 4\begin{pmatrix} 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & -\sqrt{3} & 0 & 0 \end{pmatrix} = \frac{1}{2i}\begin{pmatrix} 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & -\sqrt{3} & 0 & 0 \end{pmatrix} = \frac{\sqrt{3}}{2i}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

$$J_y J_z = \frac{1}{4i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} = \frac{1}{4i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -3\sqrt{3} & 0 & -2 & 0 \\ 0 & -2 & 0 & -3\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$J_z J_y = \frac{1}{4i}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix} = \frac{1}{4i}\begin{pmatrix} 0 & 3\sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & -\sqrt{3} \\ 0 & 0 & 3\sqrt{3} & 0 \end{pmatrix}$$

$$\{J_y, J_z\} = \frac{\sqrt{3}}{2i}\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$J_z J_x = \frac{1}{4}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix} = \frac{1}{4}\begin{pmatrix} 0 & 3\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & -\sqrt{3} \\ 0 & 0 & -3\sqrt{3} & 0 \end{pmatrix}$$

$$J_x J_z = \frac{1}{4}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} = \frac{1}{4}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 3\sqrt{3} & 0 & -2 & 0 \\ 0 & 2 & 0 & -3\sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

$$\{J_z, J_x\} = \frac{\sqrt{3}}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

The secular equation is then:

	3/2	1/2	−1/2	−3/2
3/2	$\frac{-\hbar^2 k^2}{2m}(\gamma_1 + \frac{5}{2}\gamma_2)$ $+ \frac{\hbar^2 \gamma_2}{4m}(3k_x^2 + 3k_y^2 + 9k_z^2)$ $-\varepsilon$	$\frac{\sqrt{3}\gamma_3 \hbar^2}{m} k_z (k_x - \iota k_y)$	$\frac{\sqrt{3}\gamma_3 \hbar^2}{m} \frac{k_x k_y}{\iota}$ $+ \frac{\sqrt{3}\gamma_2 \hbar^2}{2m}(k_x^2 + k_y^2)$	0
1/2	$\frac{\sqrt{3}\gamma_3 \hbar^2}{m} k_z (k_x + \iota k_y)$	$\frac{-\hbar^2 k^2}{2m}(\gamma_1 + \frac{5}{2}\gamma_2)$ $+ \frac{\hbar^2 \gamma_2}{4m}(7k_x^2 + 7k_y^2 + k_z^2)$ $-\varepsilon$	0	$\frac{\sqrt{3}\gamma_3 \hbar^2}{m} \frac{k_x k_y}{\iota}$ $+ \frac{\sqrt{3}\gamma_2 \hbar^2}{2m}(k_x^2 + k_y^2)$
−1/2	$-\frac{\sqrt{3}\gamma_3 \hbar^2}{m} \frac{k_x k_y}{\iota}$ $+ \frac{\sqrt{3}\gamma_2 \hbar^2}{2m}(k_x^2 + k_y^2)$	0	$\frac{\hbar^2 k^2}{2m}(\gamma_1 + \frac{5}{2}\gamma_2)$ $+ \frac{\hbar^2 \gamma_2}{4m}(7k_x^2 + 7k_y^2 + k_z^2)$ $-\varepsilon$	$-\frac{\sqrt{3}\gamma_3 \hbar^2}{m} k_z (k_x - \iota k_y)$
−3/2	0	$-\frac{\sqrt{3}\gamma_3 \hbar^2}{m} \frac{k_x k_y}{\iota}$ $+ \frac{\sqrt{3}\gamma_2 \hbar^2}{2m}(k_x^2 + k_y^2)$	$-\frac{\sqrt{3}\gamma_3 \hbar^2}{m} k_z (k_x + \iota k_y)$	$\frac{-\hbar^2 k^2}{2m}(\gamma_1 + \frac{5}{2}\gamma_2)$ $+ \frac{\hbar^2 \gamma_2}{4m}(3k_x^2 + 3k_y^2 + 9k_z^2)$ $-\varepsilon$

Define the following quantities:

$$A = -\frac{\hbar^2 k^2}{2m}\left(\gamma_1 + \frac{5}{2}\gamma_2\right)$$

$$B = \frac{\hbar^2 \gamma_2}{4m}\left(3k_x^2 + 3k_y^2 + 9k_z^2\right)$$

$$C = \frac{\hbar^2 \gamma_2}{4m}\left(7k_x^2 + 7k_y^2 + k_z^2\right)$$

$$E = \frac{\sqrt{3}\,\gamma_3 \hbar^2}{m} k_z \left(k_x - i k_y\right)$$

$$F = \frac{\sqrt{3}\,\gamma_3 \hbar^2}{m} \frac{k_x k_y}{i} + \frac{\sqrt{3}\,\gamma_2 \hbar^2}{2m}\left(k_x^2 - k_y^2\right)$$

Then the secular equation becomes:

$$\begin{vmatrix} A+B-\varepsilon & E & F & 0 \\ E^* & A+C-\varepsilon & 0 & F \\ F^* & 0 & A+C-\varepsilon & -E \\ 0 & F^* & -E^* & A+B-\varepsilon \end{vmatrix} = 0$$

$$(A+B-\varepsilon)\underbrace{\begin{vmatrix} A+C-\varepsilon & 0 & F \\ 0 & A+C-\varepsilon & -E \\ F^* & -E^* & A+B-\varepsilon \end{vmatrix}}_{\text{I}} - E^*\underbrace{\begin{vmatrix} E & F & 0 \\ 0 & A+C-\varepsilon & -E \\ F^* & -E^* & A+B-\varepsilon \end{vmatrix}}_{\text{II}}$$

$$+ F^* \begin{vmatrix} E & F & 0 \\ A+C-\varepsilon & 0 & F \\ F^* & -E^* & A+B-\varepsilon \end{vmatrix} = 0$$

III

$$I = (A+C-\varepsilon)\begin{vmatrix} A+C-\varepsilon & -E \\ -E^* & A+B-\varepsilon \end{vmatrix} + F^* \begin{vmatrix} 0 & F \\ A+C-\varepsilon & A+B-\varepsilon \end{vmatrix}$$

$$= (A+C-\varepsilon)\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2\right\} - (A+C-\varepsilon)F^2$$

$$= (A+C-\varepsilon)\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2 - F^2\right\}$$

$$II = E\begin{vmatrix} A+C-\varepsilon & -E \\ -E^* & A+B-\varepsilon \end{vmatrix} + F^* \begin{vmatrix} F & 0 \\ A+C-\varepsilon & -E \end{vmatrix}$$

$$= E\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2\right\} - EF^2$$

$$= E\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2 - F^2\right\}$$

$$III = E^*\left\{FE^*\right\} - F\left\{(A+C-\varepsilon)(A+B-\varepsilon) - F^2\right\}$$

$$= -F\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2 - F^2\right\}$$

The secular equations resolves beautifully to:

$$\left\{(A+C-\varepsilon)(A+B-\varepsilon) - E^2 - F^2\right\}^2 = 0$$

Hence there are two double roots.

Now, we have the quadratic:

$$\mathcal{E}^2 - (2A+B+C)\mathcal{E} + A^2 + AC + AB + BC - E^2 - F^2 = 0$$

$$2A + B + C = -\frac{\hbar^2 k^2}{2m}(2\gamma_1 + 5\gamma_2) + 5\gamma_2 \frac{\hbar^2 k^2}{2m}$$

$$= -2A \frac{\hbar^2 k^2}{2m} \quad \text{where now } A = \gamma_1$$

$$A^2 + A(B+C) + BC - E^2 - F^2$$

$$= \left(\frac{\hbar^2 k^2}{2m}\right)^2 \left(\gamma_1 + \frac{5}{2}\gamma_2\right)^2 - \frac{\hbar^2 k^2}{2m}\left(\gamma_1 + \frac{5}{2}\gamma_2\right)\left(5\gamma_2 \frac{\hbar^2 k^2}{2m}\right)$$

$$+ \left(\frac{\hbar^2 \gamma_2}{4m}\right)^2 (3k_x^2 + 3k_y^2 + 9k_z^2)(7k_x^2 + 7k_y^2 + k_z^2)$$

$$- 3\left(\frac{\gamma_3 \hbar^2}{m}\right)^2 (k_z^2 k_x^2 + k_z^2 k_y^2) - 3\left(\frac{\hbar^2}{2m}\right)^2 \left(\gamma_3^2 4 k_x^2 k_y^2 + \gamma_2^2 [k_x^4 + k_y^4 - 2k_x^2 k_y^2]\right)$$

$$= \left(\frac{\hbar^2 k^2}{2m}\right)^2 \left(\gamma_1^2 + 5\gamma_1\gamma_2 + \frac{25}{4}\gamma_2^2 - 5\gamma_1\gamma_2 - \frac{25}{2}\gamma_2^2\right)$$

$$+ \left(\frac{\hbar^2}{2m}\right)^2 \frac{\gamma_2^2}{4} (21k_x^4 + 21k_y^4 + 9k_z^4 + 42k_x^2 k_y^2 + 66k_x^2 k_z^2 + 66k_y^2 k_z^2)$$

$$- 3\left(\frac{\hbar^2}{2m}\right)^2 \left[4\gamma_3^2 (k_z^2 k_x^2 + k_z^2 k_y^2 + k_x^2 k_y^2) + \gamma_2^2 (k_x^4 + k_y^4 - 2k_x^2 k_y^2)\right]$$

$$A^2 + A(B+C) + BC - E^2 - F^2$$

$$= \left(\frac{\hbar^2 k^2}{2m}\right)^2 \left(\gamma_1^2 - \frac{25}{4}\gamma_2^2\right) + \frac{1}{4}\left(\frac{\hbar^2}{2m}\right)^2 \Big[\gamma_2^2 \left(21 k_x^4 + 21 k_y^4 + 9 k_z^4 \right.$$

$$\left. + 42 k_x^2 k_y^2 + 66 k_x^2 k_z^2 + 66 k_y^2 k_z^2 - 12 k_x^4 - 12 k_y^4 + 24 k_x^2 k_y^2 \right)$$

$$- 48 \gamma_3^2 \left(k_z^2 k_x^2 + k_z^2 k_y^2 + k_x^2 k_y^2\right) \Big]$$

$$= \frac{1}{4}\left(\frac{\hbar^2 k^2}{2m}\right)^2 (4\gamma_1^2 - 25\gamma_2^2) + \frac{1}{4}\left(\frac{\hbar^2}{2m}\right)^2 \Big[\gamma_2^2 \left(9k^4 + 48\{k_x^2 k_z^2 + k_x^2 k_y^2 + k_y^2 k_z^2\}\right)$$

$$- 48 \gamma_3^2 \left(k_x^2 k_z^2 + k_z^2 k_y^2 + k_x^2 k_y^2\right) \Big]$$

$$= \gamma_1^2 \left(\frac{\hbar^2 k^2}{2m}\right)^2 - \left(\frac{\hbar^2}{2m}\right)^2 \left[4\gamma_2^2 k^4 + 12(\gamma_3^2 - \gamma_2^2)(k_x^2 k_z^2 + k_x^2 k_y^2 + k_y^2 k_z^2) \right]$$

Define: $B = 2\gamma_2$; $C^2 = 12(\gamma_3^2 - \gamma_2^2)$

Then the quadratic becomes:

$$\varepsilon^2 + 2A\frac{\hbar^2 k^2}{2m}\varepsilon + \left\{ A^2\left(\frac{\hbar^2 k^2}{2m}\right)^2 - \left(\frac{\hbar^2}{2m}\right)^2 \left[B^2 k^4 + C^2(k_x^2 k_z^2 + k_x^2 k_y^2 + k_y^2 k_z^2) \right] \right\} = 0$$

The solution is obviously:

$$\varepsilon = -\frac{\hbar^2}{2m}\left[Ak^2 \pm \left\{ B^2 k^4 + C^2(k_x^2 k_z^2 + k_x^2 k_y^2 + k_y^2 k_z^2) \right\}^{1/2} \right]$$

where there are also two identical roots for the $\pm$ sign each.

Problem 2

Consider the ellipsoidal energy surface:

$$E = \frac{1}{2m}\left(P_x^2 \alpha_{11} + P_y^2 \alpha_{22} + P_z^2 \alpha_{33}\right)$$

and the magnetic field:

$$\vec{H} = H\left(\alpha \hat{x} + \beta \hat{y} + \gamma \hat{z}\right)$$

α, β, γ being direction cosines. The classical equation of motion is:

$$\frac{d\vec{P}}{dt} = \frac{e}{c} \nabla_p E \times \vec{H}$$

Now:

$$\nabla_p E = \frac{1}{m}\left(P_x \alpha_{11} \hat{x} + P_y \alpha_{22} \hat{y} + P_z \alpha_{33} \hat{z}\right)$$

and:

$$\nabla_p E \times \vec{H} = \frac{H}{m}\begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ P_x\alpha_{11} & P_y\alpha_{22} & P_z\alpha_{33} \\ \alpha & \beta & \gamma \end{vmatrix}$$

$$= \frac{H}{m}\left\{\left(\gamma P_y \alpha_{22} - \beta P_z \alpha_{33}\right)\hat{x} + \left(\alpha P_z \alpha_{33} - \gamma P_x \alpha_{11}\right)\hat{y} + \left(\beta P_x \alpha_{11} - \alpha P_y \alpha_{22}\right)\hat{z}\right\}$$

This gives rise to the following three equations:

$$\frac{dP_x}{dt} = \frac{eH}{mc}\left(\gamma P_y \alpha_{22} - \beta P_z \alpha_{33}\right)$$

$$\frac{dP_y}{dt} = \frac{eH}{mc}\left(\alpha P_z \alpha_{33} - \gamma P_x \alpha_{11}\right)$$

$$\frac{dP_z}{dt} = \frac{eH}{mc}\left(\beta P_x \alpha_{11} - \alpha P_y \alpha_{22}\right)$$

Assuming that the motion is periodic so that $\vec{P} \sim e^{i\omega_c t}$ we have, defining $\omega_0 = \frac{eH}{mc}$

$$i\omega_c P_x = \omega_0 (\gamma P_y \alpha_{22} - \beta P_z \alpha_{33})$$

$$i\omega_c P_y = \omega_0 (\alpha P_z \alpha_{33} - \gamma P_x \alpha_{11})$$

$$i\omega_c P_z = \omega_0 (\beta P_x \alpha_{11} - \alpha P_y \alpha_{22})$$

Now the determinant of the coefficients of the P's must vanish:

$$\begin{vmatrix} i\omega_c & -\omega_0 \gamma \alpha_{22} & \omega_0 \beta \alpha_{33} \\ \omega_0 \gamma \alpha_{11} & i\omega_c & -\omega_0 \alpha \alpha_{33} \\ -\omega_0 \beta \alpha_{11} & \omega_0 \alpha \alpha_{22} & i\omega_c \end{vmatrix} = 0$$

$$i\omega_c \left(-\omega_c^2 + \omega_0^2 \alpha^2 \alpha_{22} \alpha_{33}\right) - \omega_0 \gamma \alpha_{11} \left(-i\omega_c \omega_0 \gamma \alpha_{22} - \omega_0^2 \alpha \beta \alpha_{22} \alpha_{33}\right)$$

$$- \omega_0 \beta \alpha_{11} \left(+\omega_0^2 \gamma \alpha \alpha_{22} \alpha_{33} - i\omega_c \omega_0 \beta \alpha_{33}\right) = 0$$

Or: $$-\omega_c^2 + \omega_0^2 \alpha^2 \alpha_{22} \alpha_{33} + \omega_0^2 \gamma^2 \alpha_{11} \alpha_{22} + \omega_0^2 \beta^2 \alpha_{11} \alpha_{33} = 0$$

or: $$\omega_c = \omega_0 \left[\alpha^2 \alpha_{22} \alpha_{33} + \beta^2 \alpha_{11} \alpha_{33} + \gamma^2 \alpha_{11} \alpha_{22} \right]^{1/2}$$

Suppose we write ω_c in the form: $\omega_c = \frac{eH}{m_c^* c}$, then we readily see that:

$$\frac{m}{m_c^*} = \left[\alpha^2 \alpha_{22} \alpha_{33} + \beta^2 \alpha_{11} \alpha_{33} + \gamma^2 \alpha_{11} \alpha_{22} \right]^{1/2}$$

To put this in another way, note that:

$$\overleftrightarrow{\alpha} = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \quad ; \quad \overleftrightarrow{\alpha}^{-1} = \begin{pmatrix} \frac{1}{\alpha_{11}} & 0 & 0 \\ 0 & \frac{1}{\alpha_{22}} & 0 \\ 0 & 0 & \frac{1}{\alpha_{33}} \end{pmatrix}$$

$$\hat{H} = \alpha \hat{x} + \beta \hat{y} + \gamma \hat{z}$$

$$|\overleftrightarrow{\alpha}| = \alpha_{11}\ \alpha_{22}\ \alpha_{33}$$

Now form:

$$\hat{H} \cdot \overleftrightarrow{\alpha}^{-1} \cdot \hat{H}\ |\overleftrightarrow{\alpha}|$$

$$= \left(\frac{\alpha^2}{\alpha_{11}} + \frac{\beta^2}{\alpha_{22}} + \frac{\gamma^2}{\alpha_{33}} \right) \alpha_{11}\ \alpha_{22}\ \alpha_{33}$$

$$= \alpha^2 \alpha_{22} \alpha_{33} + \beta^2 \alpha_{11} \alpha_{33} + \gamma^2 \alpha_{11} \alpha_{22}$$

Hence, we can write finally:

$$\boxed{\frac{m}{m_c} = \left[\hat{H} \cdot \overleftrightarrow{\alpha}^{-1} \cdot \hat{H}\ |\overleftrightarrow{\alpha}| \right]^{1/2}}$$

Problem 3

We are considering two 2-fold degenerate bands coupled to each other, giving the effective mass equation:

$$\left[\frac{1}{2m}\,\vec{P}\cdot\overleftrightarrow{\alpha}\cdot\vec{P} + \mu_0\,\vec{S}\cdot\overleftrightarrow{\beta}\cdot\vec{H} - E\right] f_j(\vec{r}) = 0$$

where:

$$\overleftrightarrow{\alpha} = 2m\,\frac{(\vec{t}_{j\mu}\vec{t}_{j\mu} + \vec{u}_{j\mu}\vec{u}_{j\mu} + \vec{v}_{j\mu}\vec{v}_{j\mu} + \vec{w}_{j\mu}\vec{w}_{j\mu})}{E_j^\circ - E_\mu^\circ}$$

and:

$$\overleftrightarrow{\beta} = \frac{2m}{E_j^\circ - E_\mu^\circ}\Big[\hat{x}\,(\vec{v}_{j\mu}\times\vec{w}_{j\mu} + \vec{u}_{j\mu}\times\vec{t}_{j\mu}) + \hat{y}\,(\vec{w}_{j\mu}\times\vec{u}_{j\mu} + \vec{v}_{j\mu}\times\vec{t}_{j\mu}) + \hat{z}\,(\vec{u}_{j\mu}\times\vec{v}_{j\mu} + \vec{w}_{j\mu}\times\vec{t}_{j\mu})\Big] \times 2$$

my mistake by factor of 2.

Furthermore: $\left(\frac{m}{m_c^*}\right) = (\hat{H}\cdot\overleftrightarrow{\alpha}^{-1}\cdot\hat{H}\,|\overleftrightarrow{\alpha}|)^{1/2}$

$$\left(\frac{m}{m_s^*}\right) = \frac{1}{2}(\hat{H}\cdot\tilde{\overleftrightarrow{\beta}}\,\overleftrightarrow{\beta}\cdot\hat{H})^{1/2}$$

Now, to show that $m_s^* = m_c^*$ for this simple case, we need to show:

$$|\overleftrightarrow{\alpha}|\,\overleftrightarrow{\alpha}^{-1} = \frac{1}{4}\,\tilde{\overleftrightarrow{\beta}}\,\overleftrightarrow{\beta}$$

It will probably be best to use matrix notation for the dyads involved.

Define: $A = \dfrac{2m}{E_j^\circ - E_i^\circ}$

Now: $(\vec{\vec{\alpha}}^{-1})_{ij} = \dfrac{M_{ji}(\vec{\vec{\alpha}})}{|\vec{\vec{\alpha}}|}$; $M_{ji}(\vec{\vec{\alpha}}) = \begin{cases} \epsilon_{imn}\alpha_{2m}\alpha_{3n} ; & j=1 \\ \epsilon_{imn}\alpha_{1m}\alpha_{3n} ; & j=2 \\ \epsilon_{imn}\alpha_{1m}\alpha_{2m} ; & j=3 \end{cases}$

where $M_{ji}(\vec{\vec{\alpha}})$ is the signed minor of ji in the matrix for $\vec{\vec{\alpha}}$.

$$(\tilde{\vec{\vec{\varsigma}}}\,\vec{\vec{\varsigma}})_{ij} = \tilde{\varsigma}_{ik}\varsigma_{kj} = \varsigma_{ki}\varsigma_{kj}$$

In what follows, we suppress the indices j, n as they do not concern the problem at hand.

We then write:

$$(\vec{\vec{\alpha}})_{ij} = A\left[t_i t_j + u_i u_j + v_i v_j + w_i w_j\right]$$

$$(\vec{\vec{\varsigma}})_{ij} = A\left\{\delta_{i1}e_i\left(v_k w_\ell + u_k t_\ell\right) + \delta_{i2}e_i\left(w_k u_\ell + v_k t_\ell\right) + \delta_{i3}e_i\left(u_k v_\ell + w_k t_\ell\right)\right\}\epsilon_{jk\ell}$$

or: $(\vec{\vec{\varsigma}})_{ij} = A\,\epsilon_{jk\ell}\,e_i\left\{\delta_{i1}\left(v_k w_\ell + u_k t_\ell\right) + \delta_{i2}\left(w_k u_\ell + v_k t_\ell\right) + \delta_{i3}\left(u_k v_\ell + w_k t_\ell\right)\right\}$

$$(\tilde{\vec{\vec{\varsigma}}}\,\vec{\vec{\varsigma}})_{ij} = \varsigma_{ki}\varsigma_{kj} = \left[A\,\epsilon_{ik\ell}\,e_k\left\{\delta_{n1}\left(v_k w_\ell + u_k t_\ell\right) + \delta_{n2}\left(w_k u_\ell + v_k t_\ell\right)\right.\right.$$

$$\left.\left. + \delta_{n3}\left(u_k v_\ell + w_k t_\ell\right)\right\}\right]\left[A\,\epsilon_{jmn}\,e_n\left\{\delta_{n1}\left(v_m w_n + u_m t_n\right) + \delta_{n2}\left(w_m u_n + v_m t_n\right)\right.\right.$$

$$\left.\left. + \delta_{n3}\left(u_m v_n + w_m t_n\right)\right\}\right]$$

Then:

$$(\vec{\vec{S}}\,\vec{\vec{S}})_{ij} = A^2 \epsilon_{ikl}\epsilon_{jmn}\{(V_k W_l + U_k t_l)(V_m W_n + U_m t_n)$$

$$+ (W_k U_l + V_k t_l)(W_m U_n + V_m t_n) + (U_k V_l + W_k t_l)(U_m V_n + W_m t_n)\}$$

Now:

$$|\vec{\vec{\alpha}}|(\vec{\vec{\alpha}}^{-1})_{ij} = M_{ji}(\vec{\vec{\alpha}}) = \frac{1}{2}\epsilon_{ikl}\epsilon_{jmn}\alpha_{mk}\alpha_{nl}$$

$$= \frac{A^2}{2}\epsilon_{ikl}\epsilon_{jmn}[t_m t_k + U_m U_k + V_m V_k + W_m W_k][t_n t_l + U_n U_l$$

$$+ V_n V_l + W_n W_l]$$

It is easily seen that products like $\epsilon_{ikl}\epsilon_{jmn} t_m t_k t_n t_l$ vanish.

Now $|\vec{\vec{\alpha}}|(\vec{\vec{\alpha}}^{-1})_{ij}$ contains products of the type:

$$U_m U_k t_n t_l + V_m V_k t_n t_l + W_m W_k t_n t_l$$
$$+ U_n U_l t_m t_k + U_n U_l V_m V_k + U_n U_l W_m W_k$$
$$+ t_m t_k V_n V_l + U_m U_k V_n V_l + W_m W_k V_n V_l$$
$$+ W_n W_l t_m t_k + W_n W_l U_m U_k + W_n W_l V_m V_k$$

$$= 2[U_m U_k t_n t_l + V_m V_k t_n t_l + W_m W_k t_n t_l$$
$$+ U_n U_l V_m V_k + U_n U_l W_m W_k + W_m W_k V_n V_l]$$

whereas $(\overleftrightarrow{\beta}\vec{\beta})_{ij}$ contains the products:

$$V_\alpha V_m W_\epsilon W_n + V_\alpha W_\epsilon U_m t_n + V_m W_n U_\alpha t_\epsilon + U_\alpha U_m t_\epsilon t_n$$
$$+ W_\alpha W_m U_\epsilon U_n + V_m W_\alpha U_\epsilon t_n + V_\alpha W_m U_n t_\epsilon + V_\alpha V_m t_\epsilon t_n$$
$$+ U_\alpha U_m V_\epsilon V_n + V_\epsilon W_m U_\alpha t_n + V_n W_\alpha U_m t_\epsilon + W_\alpha W_m t_\epsilon t_n$$

It is again easily seen that the cross-terms will drop out under complete permutation of the indices. Hence we immediately see:

$$|\overleftrightarrow{\alpha}| \overleftrightarrow{\alpha}^{-1} = \overleftrightarrow{\beta}\vec{\beta}$$

It appears that there is a misprint on the homework sheet, especially since the expression for $\frac{m}{m_s^*}$ does not check against the lecture notes or this result. From lecture:

$$\frac{m}{m_s^*} = (\hat{H}\cdot\overleftrightarrow{\alpha}^{-1}\cdot\hat{H}\,|\overleftrightarrow{\alpha}|)^{1/2}$$

$$\frac{m}{m_s^*} = (\hat{H}\cdot\overleftrightarrow{\beta}\vec{\beta}\cdot\hat{H})^{1/2} \quad \text{(no factor of } \tfrac{1}{2} \text{ as indicated on sheet)}$$

The results then show that $m_s^* = m_c^*$.

There is factor $\frac{1}{2}$ here. But there is factor of 2 in expression for $\vec{q}$. ✓

Applied Physics 296

Final Examination

Tuesday, June 5, 1962

1. Define and Discuss briefly the following physical concepts:
   a. De-Haas Van-Alphen effect
   b. Spatial acoustic resonance
   c. Open orbits
   d. Knight Shift
   e. Dressed interaction

2. Discuss the content of the following theorems:
   a. Kramers' theorem
   b. Generalization of Kramers' theorem for band states in a crystal with inversion symmetry
   c. Jahn-Teller theorem
   d. Van Leeuwen's theoren

Do <u>three</u> of the following <u>four</u> problems.

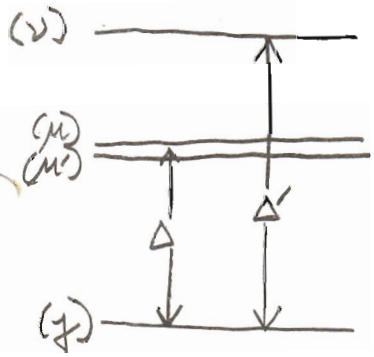
3. Starting with the interaction Hamiltonian,

$$\mathcal{H} = \frac{1}{2m}\left(\vec{P} + \frac{e}{c}\vec{A}_n\right)^2 - \vec{\mu}_S \cdot \nabla \times \vec{A}_n \quad ,$$

for an electron interacting with a nuclear vector potential $\vec{A}_n$, derive the magnetic hyperfine interaction, including the contact term. Make use of the expression,

$\vec{A}_n = \vec{\mu}_n \times \frac{\vec{r}}{r^3}$, far from the nucleus; and ignore any nuclear structure effects.

4. An ion with L = 3, S = 1, is in a crystal field of tetragonal symmetry. The spectrum of crystal field states of importance is:



(j) is orbitally non-degenerate, (μ) is 2-fold orbitally degenerate, and (ν) is orbitally non-degenerate. The wave functions for these states are,

$$\psi_{(j)} = \frac{\psi_{+2} - \psi_{-2}}{\sqrt{2}}$$

$$\begin{cases} \psi_{(\mu)} = \sqrt{\frac{3}{8}}\psi_{+3} - \sqrt{\frac{5}{8}}\psi_{-1} \\ \psi_{(\mu')} = \sqrt{\frac{3}{8}}\psi_{-3} - \sqrt{\frac{5}{8}}\psi_{+1} \end{cases}$$

$$\psi_{(\nu)} = \frac{\psi_{+2} + \psi_{-2}}{\sqrt{2}} .$$

Treat the effect of the perturbation terms,

$$\mathcal{H} = \lambda \vec{L}\cdot\vec{S} + \mu_0(\vec{L}+2\vec{S})\cdot\vec{H} ,$$

to derive a spin Hamiltonian of the form,

$$\mathcal{H} = D S_z^2 + g_{11}\mu_0 H_z S_z + g_\perp \mu_0 (H_x S_x + H_y S_y) .$$

Evaluate the coefficients D, g_{11}, $g_\perp$ in terms of λ, Δ, Δ'. Make use of the raising and lowering operator relations for L = 3,

$$L^+ \psi_M = \sqrt{(3-M)(3+M+1)}\ \psi_{M+1}$$

$$L^- \psi_M = \sqrt{(3+M)(3-M+1)}\ \psi_{M-1} .$$

5. a. Consider an ellipsoidal energy-momentum relation,

$$\mathcal{E} = \frac{1}{2m_{11}}(p_x^2 + p_y^2) + \frac{1}{2m_\perp} p_z^2 .$$

Using the result,

$$m_c^* = \frac{1}{2\pi}\left(\frac{\partial A}{\partial \mathcal{E}}\right) ,$$

find the effective mass for an orbit about the middle of the ellipsoid, for H along the principal axis of the ellipsoid; and for H at right angles to the principle axis of the ellipsoid.

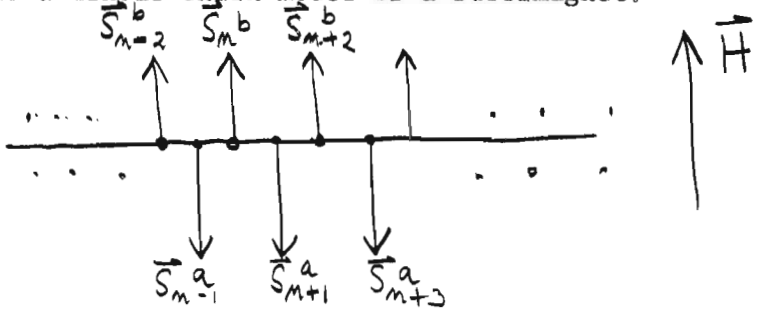
b. Consider an energy-momentum relation,

$$\mathcal{E} = \frac{1}{2m}\left[\vec{p}^2 + B\vec{p}^4\right] ,$$

with B a small constant.

Find the effective mass for an orbit around the middle of a constant energy surface, to first order in B. What is the cyclotron resonance frequency for a Fermi surface of energy E_F? Would you expect to see a sharp resonance for a Boltzmann distribution of carriers?

6. Take a linear chain model of a ferrimagnet:



The Hamiltonian for the problem is,

$$\mathcal{H} = \sum_n 2\mu_0 \vec{S}^a_n \cdot \vec{H} + \sum_{n'} 2\mu_0 \vec{S}^b_{n'} \cdot \vec{H} + \sum_{n,n'} 2 J_{nn'} \vec{S}^a_n \cdot \vec{S}^b_{n'} \; .$$

Assume nearest neighbor antiferromagnetic exchange coupling. The magnitudes of spins on the sublattices are S^a, S^b. From the operator relations,

$$\frac{d\vec{S}^a_n}{dt} = \frac{1}{i\hbar}\left[\mathcal{H}, \vec{S}^a_n\right]$$

$$\frac{d\vec{S}^b_n}{dt} = \frac{1}{i\hbar}\left[\mathcal{H}, \vec{S}^b_n\right] \; ,$$

obtain equations of motion. Interpret these classically, and find the small amplitude spin wave dispersion relations of the system. What are the uniform mode (k = 0) resonant frequencies of the system?

APPLIED PHYSICS 243b

SOLID STATE ELECTRONICS

OUTLINE OF LECTURES

SPRING 1962

I. PHYSICAL BASIS OF MAGNETIC PROPERTIES

A. Atomic Sources of Magnetism (3)*

1. Introduction and classification of magnetic materials

2. Diamagnetism and the Larmor Theorem

3. Permanent moments of ions, atoms and molecules; exclusion principle and Hund's Rule, g-factor

B. Paramagnetic Behavior (3)

1. Statistical theory of magnetism; Langevin and Brillouin functions

2. Quantum theory of paramagnetism

3. Crystalline electric field effects

C. Ferromagnetic Behavior (6)

1. Internal magnetic fields; Weiss molecular field and its consequences

2. Exchange energy and its role in magnetism; superexchange

3. Spin arrangements in solids; ferro, ferri-, and antiferromagnetism

4. Spin wave description of ferromagnetism

5. Other contributions to magnetic energy; demagnetizing fields, magnetocrystalline anisotropy and magnetostriction

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* Numbers in parantheses ( ) indicate approximate number of lectures on a topic.

D. Magnetic Domain Theory (3)

1. Domain walls and domain configurations

2. Domain dynamics; rotation and wall motion

3. Application to the magnetization process; hysteresis, initial permeability, coercive field, remanent flux, etc.

E. Magnetic Resonance and Gyromagnetic Properties (6)

1. Paramagnetic resonance; macroscopic and microscopic approach

2. Ferromagnetic resonance; uniform mode resonance conditions and permeability tensor

3. Other resonance phenomena; sublattice effects and magnetostatic modes

4. Loss mechanisms; resonance linewidth and rf initial permeability

5. High power effects; stable and unstable behavior

F. Important Magnetic Materials (2)

1. Paramagnetic salts

2. Ferromagnetic metals and thin films

3. Magnetic oxides

II. PHYSICAL BASIS OF DIELECTRIC PROPERTIES (2)

A. Elementary Atomic Theory of Dielectric Properties

1. Classification of dielectric materials

2. Local electric fields; Clausius-Mosotti and Langevin formula

3. Polarization mechanisms and the susceptibility dispersion spectrum

B. Ferroelectricity and Piezoelectricity (4)

1. Sources of spontaneous polarization; $\frac{4}{3}\pi$ catastrophe
2. Ferroelectric domain structure and domain dynamics
3. Crystal structure and tensor relationships in piezoelectrics

III. SOME APPLICATIONS OF MAGNETIC AND DIELECTRIC PHENOMENA

A. Passive Microwave Ferrite Devices (5)

1. Solutions of Maxwell's equations in gyromagnetic media
2. Faraday rotation devices; isolator, circulator, switch
3. Birefringence and anisotropic scattering; resonance isolator, field displacement, differential phase shift circulator, Y-type circulator
4. Non-linear devices; frequency multiplier, limiter

B. Microwave Amplifiers (2)

1. Masers; discussion of noise figure
2. Parametric amplifier and converter

C. Low Frequency Magnetic and Dielectric Devices (3)

1. Switching applications in computers
2. Computer memory devices
3. Saturable reactors, magnetic and dielectric amplifiers

D. Electromechanical Devices (1)

1. Transducers
2. Resonators