GROUP THEORY
- WHITE -

PHYSICS 264

GROUP THEORY AND QUANTUM MECHANICS

INSTRUCTOR: WHITE J256: TTS 10

LECTURE 1: 2-6-62

Texts:

Wigner: GT and Atomic Spectra
Hiene: GT and QM
Hammermesh: GT
Lyubarskii: Applications of GT in Physics
Bauer: Ann. de l'Institute H. Poincaré (1933)
Weyl: GT and QM
A. Speiser: Die Theorie der Gruppen von Endlicher Ordnung, 4 Auflagl
Van der Waerden: Die Gruppen Theoretisch methode in der Quantenmechanik
Echart: RMP 2
Dirac: Quantum Theory of Many Election Systems PRS 123
Koster: Class Notes

Applications of Group Theory:

Normal modes of vibration
Spectra: Angular Momentum
Selection Rules
Degeneracy Splitting
Dirac Election
Solids: Band Theory
Symmetric Top Model
Continuous Groups: Invariance of Hamiltonian

The primary emphasis here will be on finite groups and matrix representation.

Reference: Chapters 7 and 8 in Wigner

Formation of a Group:

We need the operations a and b which can be algebraic or operations of any type. We first need the unit element:

1) $e_\ell a = a = a e_r$
(e_ℓ: left; e_r: right)

$e_\ell = e_\ell e_r = e_r$, hence $e_\ell = e_r$ and we need denote the unit operation only by e. e cannot be the numbers $2, 3, 4, \cdots$.

2) Associative law:

Given the operations a b c:

$$a(bc) = (ab)c$$

This does not hold for complex conjugation because:

$$b^* c^* = K(bc) \neq (Kb)c = b^* c$$

3) The operation must have an inverse:

Left inverse: $a\bar{e}^1 a = e$. Note $\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$ is not valid

The left inverse is the same as the right inverse:

$$\underbrace{(a\bar{e}^1)_\ell^{-1} a\bar{e}^1 a}_{e} \underbrace{a\bar{e}^1}_{e} = e \quad , \text{ or: } a a\bar{e}^1 = e$$

hence we can write $aa^{-1} = e$

If abc means $a+b+c$, and the elements are: $\cdots -2, -1, 0, 1, 2, \cdots$ then we see that $e = 0$ and the inverses are negative numbers.

4) Closure: each "product" must give another element of the group.

The above four conditions must be satisfied if the operations are to form a group.

As an example, consider the 2 element group E, A:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad ; \quad A = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These two satisfy all the requirements for a group. The multiplication table:

	E	A
E	E	A
A	A	E

Now consider adding the new element: $B = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}$

Multiply together and form new elements:

$$AB = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix} = D$$

$$DA = \frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix} = C$$

$$AC = \frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix} = F$$

Now E, A, B, C, D, F satisfy all the requirements for a group. Form the multiplication table:

$BC = BAF = D$
$BD = BBC = C$
$BF = BBA = A$
$CB = CAD = DD = F$
$CD = CBC = DC$

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

LECTURE 2 : 2-8-62

All we really need to know about a group in abstract is its multiplication table. Use the previous table:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

The "order" of the group is $h = 6$

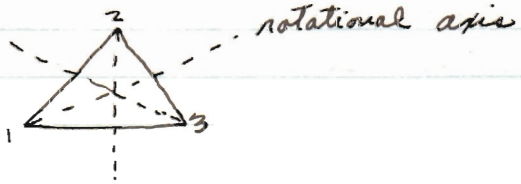
This is also the multiplication table for the group of all the permutations of three objects:

123	123	123	123	123	123
123	213	132	321	312	231
E	A	B	C	D	F

$AB = 312 = D$

$DAB = 231 = DD = F$, etc

The three object permutation group is another "realization" of the above multiplication table. Another realization is the symmetry operations on an equilateral triangle:



The rotation about the symmetry axis can also be interpreted as permutations of the triangle points.

Abstract Group Theory

We forget about "realizations" and become concerned with just the multiplication table. With our MT, no element appears more than once in any column or row. This is called the Rearrangement Theorem. Call the whole group H:

$$H = \{E, A, B, C, D, F\}$$

Multiply H by any element X: $XH = H$ for any X in H (Rearrangement Theorem). We get the same elements back but in different order, providing the group has closure. $AB = C$ is unique because there is only one intersection in the MT.

Proof:

Assume $XA = XB$ and use the fact that X^{-1} is in the group. This demands:

$$X^{-1}XA = X^{-1}XB \quad \text{or} \quad EA = EB \quad \text{or} \quad A = B$$

which demonstrates the uniqueness. Note that the elements do not commute. The group is called Abelian if all $AB = BA$ for A, B in the group.

The powers of an element will eventually yield E. That is, if:

$$D^n = E \; ; \; D^{n+1} = D$$

What is n? From the MT: $D^2 = F$; $D^3 = DF = E$; $n = 3$. Note that for A, $n = 2$ and for E, $n = 1$. The rest follow directly. For the inverse, $DD^{n-1} = D^n = E$.

The products of D form an Abelian sub-group:

D, D^2, D^3
$\downarrow \quad \downarrow$
$F \quad E$

That this is true can be seen from: $D^nD^m = D^{n+m} = D^{m+n} = D^mD^n$. Call the subgroup B.

Cosets: Right coset: BX for X in H

If X is in B, $BX = B$. Suppose now some element not in B gives an element in B:

$B_i X = B_j$; but $X = B_i^{-1} B_j$, so that X has to be in B (since B_i^{-1} is in B and B_j is in B).

Can $B_i X = B_j X$?; $B_i = B_j$ hence the elements in the coset are distinct if the elements in H are.

What about other cosets? We have BX, X in B. BY is another coset (Y not in B).

What about elements in common?

Suppose: $B_i X = B_j Y$; $XY^{-1} = B_i^{-1} B_j$ in B.

Also: $B_i = B_j YX^{-1}$. Multiply this by all other elements in B:

$$B B_i = B B_j YX^{-1}$$

$$B = BYX^{-1}; \quad BX = BY$$

hence the cosets are the same and the cosets of the group are distinct with no common element. So the group can be subdivided into distinct subgroups.

Suppose g is the order of B, then $\frac{h}{g} = l$, an integer. If h is a prime number, we can only have E and itself for a subgroup. Also, if h is prime, it must be Abelian and cyclic.

Now consider $X^{-1}AX = B$ or $AX = XB$. A and B are said to be conjugately related.

Class: $X^{-1}AX = B$

If we consider all the elements generated from A by letting X run thru the group H we have what is called a class.

What is the class of A? Use the MT:

(AAA) $EA = A$

(EAE) $AE = A$

(DAD) $BD = C$

(FAF) $CF = B$

(BAB) $FB = C$

(CAC) $DC = B$

The class of A is A, B, C but no identity.

For an Abelian group:

$$X^{-1}AX = X^{-1}XA = A$$

LECTURE 3 : 2-10-62

Classes :

The classes of our example group are : E

D, F

A, B, C

What about the combination of classes? E, D, F forms a group. This is called a self-conjugate subgroup. All subgroups of an Abelian group are self-conjugate. Call the self-conjugate sub-group R, then :

$$RA = AA^{-1}RA = AR$$

so the right and left cosets are identical. So far we have only used the "multiplicative" form for element combination. We now introduce "addition", so that we can write a set of elements as a sum of the elements :

$$R = R_1 + R_2 + \cdots + R_n$$

$$R = RR = (R_1 + R_2 + \cdots + R_n)(R_1 + R_2 + \cdots + R_n) = R_1^2 + R_1R_2 + R_2R_1 + \cdots + R_n^2$$

Continuing :

$$RR = R$$

$$RARA^{-1} = RR = R$$

$$\underbrace{RA}_{\text{two different cosets}}\underbrace{RB} = RARA^{-1}AB = RRAB = \underbrace{RAB}_{\text{another coset}}$$

Hence the cosets form a group, only if we have a self-conjugate subgroup. This group of cosets of self-conjugate sub-groups is called a factor group. Correspondences between cosets and factor groups :

Cosets		Factor Group
R	$\rightarrow$	$\bar{E}$
$AR = RA$	$\rightarrow$	$\bar{A}$
$RARB$	$\rightarrow$	$\bar{A}\bar{B} = \overline{AB}$

We will need these later.

Commutative Groups : (not in Wigner) :

Look at :

$$AB\ "C" = BA$$

We ask what "C" is needed and we see it is D.

Furthermore :

$$\underbrace{AC}_{F}\ \underset{F}{"C"} = \underbrace{CA}_{D}$$

$$DF\ \underset{E}{"C"} = FD$$

$$\underbrace{AD}_{B}\ \underset{D}{"C"} = \underbrace{DA}_{C}$$

Exercise (1) : Prove that the factor group of the commutator group is Abelian. To form the commutator group, form all products of commutators and force closure. The commutator is certainly an element of the group since $"C" = D^{-1}A^{-1}DA$. To do the problem, we must also prove that the commutator is self-conjugate.

What is the order of the factor group? $l = \frac{h}{r}$, where r is the order of R.

Homomorphism :

We have example above. The elements of one large group map into one element of a small group as above. The relations among the sets of elements in each group must be identical. These two conditions suffice to define homomorphism. Look at correspondences involved in homomorphism:

$E \to \bar{E}$ because $EE = E \to \bar{E} = \bar{E}\bar{E}$

$A^{-1} \to \bar{A}^{-1}$

$$\left.\begin{array}{l} A^{-1}A \to "\bar{A}^{-1}"\,\bar{A} \\ \downarrow \quad\quad \downarrow \\ E \to \bar{E} \end{array}\right\} "\bar{A}^{-1}" = \bar{A}^{-1}$$

Totality : $E_1 E_2 = E \to \bar{E}$; $E_1 \to \bar{E}$; $E_2 \to \bar{E}$

$E_1 = E_2 E_2 \to \bar{E}\bar{E} = \bar{E}$

$$\underbrace{X^{-1} E_2 X}_{E_2} \to \bar{X}^{-1}\bar{E}\bar{X} = \bar{E}$$

LECTURE 4 : 2-13-62

Homomorphisms: $\{E_\alpha\} \to \bar{E}$; $\{\ \}$ are invariant subgroups

$\{A_\alpha\} \to \bar{A}$

$A_\alpha B_\beta \to \bar{A}\bar{B} = \overline{AB}$

$\{A_\alpha^{-1}\} \to \bar{A}^{-1}$

Now: $E_\alpha = A_\alpha A_\beta^{-1} \to \bar{E}$

Then: $E_\alpha A_\beta = A_\alpha$

$E_\alpha A_\beta = X$; $E_\alpha = X A_\beta^{-1}$; X must be in $\{A_\alpha\}$

The set $\{A_\alpha\}$ is just a left coset of the invariant subgroup $\{E_\alpha\}$ as shown above.

Representation Theory

We will be concerned with matrix representations. Two kinds of representations; faithful and unfaithful. (1) is unfaithful because it is same for all elements. A faithful representation has distinct matrices for each element.

Our previous 2×2 matrix representation is a faithful representation.

The determinants of E, A, B, C, D, F also give a representation: det A det B = det(AB) = det D, that is, it obeys the MT.

Consider the 3×3 representation:

$E = \begin{pmatrix} 1&0&0\\ 0&1&0\\ 0&0&1 \end{pmatrix}$; $A = \begin{pmatrix} 1&0&0\\ 0&-1&0\\ 0&0&-1 \end{pmatrix}$; etc, where $\begin{pmatrix} \times&\times&\times\\ \times&\times&\times\\ \times&\times&\times \end{pmatrix}$ is the determinant of the previous 2×2 matrices. See if they give a representation:

$B = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0\\ \frac{1}{2}\sqrt{3} & \frac{1}{2} & 0\\ 0 & 0 & -1 \end{pmatrix}$; $AB = \begin{pmatrix} \begin{pmatrix} 1&0\\ 0&-1 \end{pmatrix} & 0\\ 0\ 0 & -1 \end{pmatrix} \begin{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & 1/2 \end{pmatrix} & 0\\ 0\ 0 & -1 \end{pmatrix} = \begin{pmatrix} (\ ) & \\ & (\ ) \end{pmatrix}$

so we do have a representation that obeys the MT.

Consider a Unitary Transformation on the elements of the group:

$$U^{\dagger} A U$$

gives also a representation. More generally; take similitude transformation:

$$S^{-1}AS: \quad S^{-1}ASS^{-1}BS = S^{-1}ABS = S^{-1}DS$$

so this obeys the MT. The unitary transformation is a special group.

In the matrix representation of a group element, we can think of the matrix as representing a transformation on some set of basis vectors. Consider the transformation from one basis system to another:

$$F = \sum_i a_i \hat{u}_i = \sum_{ijk} \underbrace{a_i A_{ij}}\ \underbrace{(A^{-1})_{jk}\ \hat{u}_k}$$

$$\bar{a}_k = \sum_j a_j A_{jk} \quad \text{(new components)} \qquad \hat{\bar{u}}_j = \sum_k (A^{-1})_{jk}\,\hat{u}_k \quad \text{(new basis)}$$

If we think of our 3×3 representation, we see that the z axis is not mixed in with x and y. This is known as the reduced form: All elements are of form:

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

so we see no mixing of z with x, y.

However, suppose we have to perform a similitude Transformation:

$$x' = Ax \ ; \quad \underbrace{S^{-1}x'}_{\bar{x}'} = \underbrace{S^{-1}AS}_{\bar{A}}\ \underbrace{S^{-1}x}_{\bar{x}}$$

However, now we do not any longer have a reduced form in $\bar{A}$ as the similitude transformation destroys.

The essential problem in finite groups is to find the reduced forms for the elements of the group.

LECTURE 5 : 2-15-62

Representation Theory:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

or:
$$x' = x\cos\theta + y\sin\theta$$
$$y' = -x\sin\theta + y\cos\theta$$

We can write this as:

$$x' \pm iy' = x(\cos\theta \mp i\sin\theta) + y(\sin\theta \pm i\cos\theta)$$

$$= x(\cos\theta \mp i\sin\theta) \pm iy(\mp i\sin\theta + \cos\theta)$$

$$= (x \pm iy)(\cos\theta \mp i\sin\theta) = (x \pm iy)e^{\mp i\theta}$$

Thus we have found an invariant subgroup:

$$\left.\begin{aligned} (x'+iy') &= (x+iy)e^{-i\theta} \\ (x'-iy') &= (x-iy)e^{i\theta} \end{aligned}\right\} \quad \begin{pmatrix} x'+iy' \\ x'-iy' \end{pmatrix} = \begin{pmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{pmatrix} \begin{pmatrix} x+iy \\ x-iy \end{pmatrix}$$

or:
$$\begin{pmatrix} x'+iy' \\ ix'+y' \end{pmatrix} = \begin{pmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{pmatrix} \begin{pmatrix} x+iy \\ ix+y \end{pmatrix}$$

Now write: $(x') = R(x)$

$$S(x') = \underbrace{S R S^{-1}}_{\begin{pmatrix} e^{-i\theta} & 0 \\ 0 & e^{i\theta} \end{pmatrix}} S(x) \quad ; \quad S(x) = \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x+iy \\ ix+y \end{pmatrix}$$

We have reduced the representation.

For the 3-D rotation of $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ there is now further reducible representation than the original rotation representation.

What about the relations of the second order combinations of x, y, z: $x^2, y^2, z^2, xy, yz, zx$.

Note that the quantity $x^2+y^2+z^2 = r^2 = \sum_i x_i x_i$

$= x^T x = \overline{x}(x)$ is invariant under all rotations.

$\underbrace{x^T R^T}_{x'^T} \underbrace{R x}_{x'}$

But R is orthogonal: Then: $x'^T x' = x^T x$

We can reduce, because of invariance of $x^2+y^2+z^2$, into 5 elements:

$x^2 - y^2$
$x^2 + y^2 - 2z^2$
xy
yz
zx

} As long as $x^2+y^2+z^2$ is linearly independent of these. $x^2+y^2+z^2$ then provides the 6th quantity.

Call these 6 quantities the vector v: We can write the rotation:

$$v' = D(R)\, v$$
$$S v' = S D S^{-1} S v$$
$$\bar{v}' = S D S^{-1} \bar{v}$$

Original basis:

$D \sim \begin{pmatrix} 1 & 1 & 1 & 0 & 0 & 0 \\ & & & & & \\ & & & & & \end{pmatrix}$ combines x^2, y^2, z^2

$$SDS^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

This will true for every representation in that it can be reduced into at least this form.

We could also have as a basis:

$$\begin{pmatrix} x_1 x_2 \\ y_1 y_2 \\ z_1 z_2 \\ x_1 y_2 \\ y_1 x_2 \\ y_1 z_2 \\ z_1 y_2 \\ z_1 x_2 \\ z_2 x_1 \end{pmatrix} = M$$

We will see $X_1^T X_2$ is invariant under all rotations:

$$X_1^T X_2 : \quad \underbrace{X_1^T R^T}_{\bar{X}_1^T} \underbrace{R X_2}_{\bar{X}_2} = X_1^T X_2$$

Original basis: $D = \begin{pmatrix} 111 & 000 & 000 \end{pmatrix}$

Now look at: $\vec{r}_1 \times \vec{r}_2 = \begin{cases} x_1 y_2 - y_1 x_2 \\ y_1 z_2 - z_1 y_2 \\ z_1 x_2 - z_2 x_1 \end{cases}$

Note that this is an invariant space because antisymmetric functions rotate into antisymmetric functions:
The other subspace is:

$x_1 y_2 + y_1 x_2$

$y_1 z_2 + z_1 y_2$

$z_1 x_2 + z_2 x_1$

$x_1 x_2 - y_1 y_2$

$x_1 x_2 + y_1 y_2 - 2 z_1 z_2$

Hence, the representation reduces to:

$$SDS^{-1} = \begin{pmatrix} 1 & 0 & \\ 0 & 3 & 0 \\ & 0 & 5 \end{pmatrix}$$

Exercise (2): Find explicit irreducible representations for the direct product representation $t \otimes t$ of the t group, where the t group is the one we have been working with in two dimensions of x_1, x_2; y_1, y_2

LECTURE 6: 2-17-62

Methods of Finding Irreducible Representations

We work with unitary representations only. That is, we stipulate that any nonsingular representation is equivalent to a unitary representation.

Proof:

$A_R A_R^+$ (product of group element)

$(A_R A_R^+)^+ = A_R A_R$ = hermitean.

The same is true for: $H = \sum_R A_R A_R^+$

Any hermitean matrix can be diagonalized by a unitary transformation:

$$d = U^+ H U = \sum_R \underbrace{U^+ A_R U}_{\bar{A}_R} \underbrace{U^+ A_R^+ U}_{\bar{A}_R^+}$$

$$\bar{A}_R^+ = (U^+ A_R U)^+ = U^+ A_R^+ U$$

Now: $d^+ = d$

The diagonal elements of d are real and given by:

$$d_{ii} = \sum_R \sum_j (\bar{A}_R)_{ij} (\bar{A}_R^+)_{ji} = \sum_R \sum_j (\bar{A}_R)_{ij} (\bar{A}_R^+)_{ij}$$

We cannot have any $d_{ii} = 0$ as this would mean some A_R is singular which we disallow. Thus we can form d^{-1} and in fact $d^{-1/2}$:

$$d^{-1/2} = \begin{pmatrix} \frac{1}{\sqrt{d_1}} & & 0 \\ & \frac{1}{\sqrt{d_2}} & \\ 0 & & \ddots \end{pmatrix}$$

Form: $\tilde{\bar{A}}_R = d^{-1/2} \bar{A}_R d^{1/2}$

Does $\tilde{\bar{A}}_R \tilde{\bar{A}}_R^+ = 1$?

Use $(d^{1/2})^+ = (d^{1/2})^T = d^{1/2}$:

Then: $\bar{\bar{A}}_x \bar{\bar{A}}_x^+ = d^{-1/2} \bar{A}_x d^{1/2} d^{1/2} \bar{A}_x^+ d^{-1/2}$

$= d^{-1/2} \bar{A}_x \left(\sum_\ell \bar{A}_\ell \bar{A}_\ell^+ \right) \bar{A}_x^+ d^{-1/2}$

$= d^{-1/2} \sum_\ell (\bar{A}_x \bar{A}_\ell)(\bar{A}_\ell^+ \bar{A}_x^+) d^{-1/2}$

These products merely generate other members of the group uniquely by the rearrangement theorem.

$= d^{-1/2} \left(\sum_m \bar{A}_m \bar{A}_m^+ \right) d^{-1/2} = I$

Thus we have found another unitary representation given by:

$$\bar{\bar{A}}_x = d^{-1/2} U^+ A_x U d^{-1/2}$$

This completes the proof.

Schur's Fundamental Lemma:

Begin with a unitary representation. Suppose we have found a matrix M such that:

$$M D^{(1)}(R) = D^{(2)}(R) M$$

(Reminescent of quantum commutators)

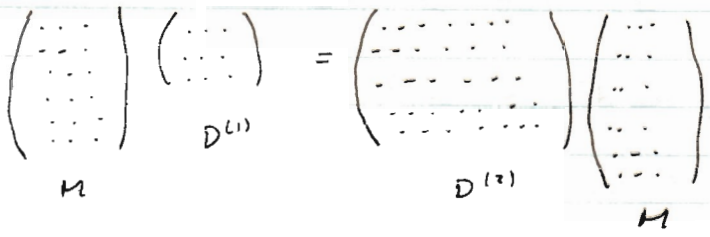
If $D(R)$ is irreducible, then Schur's Lemma says that either $M=0$ or $D^{(1)}(R) = D^{(2)}(R)$ are equivalent for all R in which case $M = cI$:

$$I = \begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & \ddots \end{pmatrix}$$

Proof:

It is possible that $D^{(1)}$, $D^{(2)}$ have different dimensions.

By the rules of matrix products, we must have the form:



Form: $M\, D^{(1)}(R)^{+} M^{+} = M M^{+} D^{(2)}(R)^{+}$

$$M D^{(1)}(R)^{+} = D^{(2)}(R)^{+} M$$
$$D^{(1)}(R^{-1}) = D^{(1)}(R)^{+}$$

Then: $D^{(2)}(R)^{+} M M^{+} = M M^{+} D^{(2)}(R)^{+}$ for all R

M is hermitean. Bring the above M into diagonal form; (MM^{+} is hermitean):

$$V^{+} D^{(2)}(R)^{+} V V^{+} M' V = V^{+} M' V V^{+} D^{(2)}(R)^{+} V$$

$$\begin{pmatrix} m_1 & & \\ & m_2 & 0 \\ & 0 & \ddots \end{pmatrix}$$

Then we have the form: $\bar{D}\, m = m\, \bar{D}$

$$\begin{pmatrix} d_{11} & d_{12} & \cdots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} m_1 & & \\ & m_2 & 0 \\ & 0 & \ddots \end{pmatrix} = \begin{pmatrix} m_1 & & \\ & m_2 & 0 \\ & 0 & \ddots \end{pmatrix} \begin{pmatrix} d_{11} & d_{12} & \cdots \\ \vdots & \vdots & \end{pmatrix}$$

Suppose $m_1 = m_2$, Then d_{12} must $= 0$, in fact $d_{1n} = 0$ and $d_{n1} = 0$

so we have reduced $D(R)$ somewhat. For completely irreducible $D(R)$ all elements of m are equal and we have shown the proof.

Call the dimension of $D^{(l)}(R)$, l.

1) $l_1 = l_2$; $m' \neq 0$; where $m = m'\, I$, then M is nonsing. because $\det M \neq 0$ and then $D^{(1)}(R) = M^{-1} D^{(2)}(R) M$
2) $l_1 = l_2$; $m' = 0$, then $M' = 0$, $\therefore M = 0$
3) $l_1 \neq l_2$; M not square, make square into N. Show: $0 = \det(MM^{+}) = \det(NN^{+}) = \det N \det N^{+} = 0$; $M = 0$ due to same as (2).

LECTURE 7: 2-19-62

Absent

LECTURE 8 : 12-24-62

$$\sum_R D^{(\lambda)}_{\alpha\beta}(R)\, D^{(\lambda)}_{\gamma\delta}(R)^* = \frac{h}{l_\lambda}\,\delta_{\alpha\gamma}\,\delta_{\beta\delta}$$

Orthogonality Relation

$$M = \sum_R D^{(\lambda)}(R) \times D^{(\lambda)}(R^{-1})$$

$$D^{(\lambda)}(S)\,M = \left[\sum_R D^{(\lambda)}(S)\,D^{(\lambda)}(R) \times D^{(\lambda)}(R^{-1})\,D^{(\lambda)}(S^{-1})\right] D^{(\lambda)}(S)$$

$$= M\,D^{(\lambda)}(S) \quad \text{for all } S.$$

$$M = C\,I$$

$$c\,\delta_{\alpha\gamma} = M_{\alpha\gamma} = \sum_{R}\sum_{\bar\beta,\bar\delta} D^{(\lambda)}_{\alpha\bar\beta}(R)\,\underbrace{\delta_{\bar\beta\beta}\,\delta_{\bar\delta\delta}}_{\times}\,D^{(\lambda)}(R)^{+}_{\bar\delta\gamma}$$

$$= \sum_R D^{(\lambda)}_{\alpha\beta}(R)\; D^{(\lambda)}_{\gamma\delta}(R)^*$$

$$\xrightarrow{\alpha=\gamma} \sum_R D^{(\lambda)}_{\alpha\beta}(R)\, D^{(\lambda)}_{\delta\delta}(R)^*$$

$$l_\lambda c = \sum_{\alpha=1}^{l_\lambda} c(\chi)\,\delta_{\alpha\alpha} = \sum_R \sum_\alpha D^{(\lambda)}_{\alpha\beta}(R)\, D^{(\lambda)*}_{\alpha\delta}(R) = h\,\delta_{\beta\delta}$$

Thus we have proved the above orthogonality relations. Examine this relation in the t group:

	E	A	B	C	D	F
t_{11}	1	1	$-1/2$	$-1/2$	$-1/2$	$-1/2$
t_{22}	1	-1	$1/2$	$1/2$	$-1/2$	$-1/2$

$$\sum_R t_{11}(R)\, t_{11}^*(R) = 3 = \frac{6}{2}$$

Hence:

$$h \geq l_1^2 + l_2^2 + \cdots + l_c^2$$

Character

the character is defined by:

$$\chi(R) = \mathrm{Tr}\, D(R) = \sum_i D_{ii}(R)$$

The trace has the property of invariance under similitude transformations, so the character is the same for all elements in the same class.

The character has orthogonality relationships.

Construct the character table for t, det, and unit representation:

	E	A	B	C	D	F
t	2	0	0	0	-1	-1
det	1	-1	-1	-1	1	1
1	1	1	1	1	1	1

From the general orthogonality relation, we see:

$$\sum_R \chi^{(\alpha)}(R)\, \chi^{(\beta)*}(R) = h\, \delta_{\alpha\beta}$$

In terms of classes:

$$\sum_{\rho=1}^{k} g_\rho\, \chi^{(\alpha)}(C_\rho)\, \chi^{(\beta)*}(C_\rho) = h\, \delta_{\alpha\beta}$$

g_ρ ↑ number of elements in C_ρ

k = no. of classes

Since now we can have only k linearly independent character vectors, $k \geq C$ = no. of inequivalent, irreducible representations.

Recall the method of reducing representations:

$$\chi = \sum_i \chi^{(i)} = \sum_i a_i \chi^{(i)}$$

$$S^{-1} \left(\quad \right) S = \left(\quad \right) \qquad \text{all } R$$

$$\sum_R \chi(R)\, \chi^{(\alpha)*} = \sum_R \sum_\beta a_\beta \chi^{(\beta)}(R)\, \chi^{(\alpha)*}(R)$$

$$= a_\alpha h \; ; \quad a^\alpha = \frac{1}{h} \sum_R \chi(R)\, \chi^{(\alpha)*}$$

However, the character remains the same.

LECTURE 9: 2-27-62

Recall: Orthogonality relations between irreducible representations:

$$\sum_R D^{(\lambda)}_{\alpha\beta}(R)\, D^{(\gamma)*}_{\delta\delta}(R) = \frac{h}{l_\lambda}\,\delta_{\alpha\delta}\,\delta_{\beta\delta}\,\delta_{\lambda\gamma}$$

The same relation holds for characters:

$$\chi^{(\lambda)}(R) = \sum_\alpha D^{(\lambda)}_{\alpha\alpha}(R)$$

$$\sum_\rho g_\rho\, \chi^{(\lambda)}(C_\rho)\, \chi^{(\gamma)*}(C_\rho) = h\,\delta_{\lambda\gamma}$$

h = no. of classes

$$\sum_{\rho=1} g_\rho = h$$

For irreducible representations, we can write:

$$\chi(R) = \sum a_\lambda\, \chi^{(\lambda)}(R)$$

$$a_\lambda = \sum_{\text{group}} \chi(R)\, \chi^{(\lambda)*}(R)$$

Form: $\sum_R \chi(R)\,\chi^*(R) = \sum_R |\chi(R)|^2$

$$= \sum_{\lambda\gamma} a_\lambda\, \chi^{(\lambda)}(R)\; a_\gamma^*\, \chi^{(\gamma)*}(R) = h \sum_{\lambda\gamma} a_\lambda\, a_\gamma^*\, \delta_{\lambda\gamma}$$

$$= h \sum_\lambda a_\lambda^2$$

Thus, this is a way of telling whether or not the group is reduced.

χ	E	A	B	C	D	F
t	2	0	0	0	-1	-1
det	1	-1	-1	-1	1	1
unit	1	1	1	1	1	1
$t \times t$	4	0	0	0	1	1

We can also write the character table in terms of classes

χ	E	ABC	DF
$+$	2	0	-1
det	1	-1	1
unit	1	1	1

We now observe that $+ \times + = + + \det + \text{unit}$

That is,

look at: $\chi\left(D^{(+)}(B) \times D^{(+)}(B)\right)$

$$B \times B = \frac{1}{4}\left(\begin{array}{cc|cc} 1 & -\sqrt{3} & -\sqrt{3} & 3 \\ -\sqrt{3} & -1 & 3 & \sqrt{3} \\ \hline -\sqrt{3} & 3 & -1 & \sqrt{3} \\ 3 & \sqrt{3} & \sqrt{3} & 1 \end{array}\right)$$

and the above conclusion is immediate.

Examine more closely the importance of characters. The character is invariant under similitude transformations. However, also, if two representations have the same character, they are equivalent. This is obvious for irreducible representations.

The characters are unique for irreducible representations except for the ordering of the "blocks".

Digress for a while to symmetric direct products.

Example: $x_1 \cdots x_N$ times $x_1 \cdots x_N$

gives

x_1^2

$x_1 x_2$ as opposed to $x_1 \cdots x_N$ times $y_1 \cdots y_N$ where we would have to differentiate between $x_1 y_2$ and $y_1 x_2$

x_2^2

$x_1 x_3$

$x_2 x_3$

x_3^2

$\vdots$

Suppose:

$$D(R) = \begin{pmatrix} a_1^2 & & & \\ & a_1 a_2 & & \\ & & a_2^2 & \\ & & & \ddots \end{pmatrix}$$

$$\chi_{\text{sym}}(R) = a_1^2 + a_2^2 + \cdots + a_1 a_2 + a_1 a_3 + \cdots$$

$$\chi_{\text{total}}(R) = a_1^2 + a_2^2 + \cdots + 2\left(a_1 a_2 + a_1 a_3 + \cdots\right)$$

Then:

$$\chi_{\text{sym}}(R) = \frac{1}{2}\left[\chi(R)\right]^2 + \frac{1}{2}\chi(R^2)$$

$$\chi_{\text{anti}}(R) = \frac{1}{2}\left[\chi(R)\right]^2 - \frac{1}{2}\chi(R^2)$$

Excercise 3: Find $\chi_{\text{sym}}(l_1 \otimes l_2 \otimes l_3)$; χ_{anti} ; $\chi_{\text{left-over}}$

What irreducible representations are contained in the $t \otimes t \otimes t$ representation of the t group. Notice that the t group is isomorphic to the permutation group of 3 things. Find the irreducible representation of the t group contained in $t \times t \times t$ $\begin{pmatrix} x_1 & y_1 & z_1 \\ x_1 & y_2 & z_2 \\ \vdots & & \\ x_2 & y_2 & z_2 \end{pmatrix}$ permutations.

What are χ_{sym}, χ_{anti}, $\chi_{\text{left-over}}$ in this case?

The Regular Representation:

This is obtained when we write the group multiplication table in the following form:

A	E	A	B	C	D	F
E^{-1}	0	1	0	0	0	0
A^{-1}	1	0	0	0	0	0
B^{-1}	0	0	0	0	0	1
C^{-1}	0	0	0	0	1	0
D^{-1}	0	0	0	1	0	0
F^{-1}	0	0	1	0	0	0

LECTURE 10 : 3-1-62

We want to show $\sum_{\lambda=1}^{c} l_\lambda^2 = h$ and $c = h$,
That is, the number of classes = number of irreducibles.
We do this with the regular representation. The regular representation of B is:

	B	E	A	B	C	D	F
	E^{-1}	0	0	1	0	0	0
	A^{-1}	0	0	0	0	1	0
X^{-1}	B^{-1}	1	0	0	0	0	0
	C^{-1}	0	0	0	0	0	1
	D^{-1}	0	1	0	0	0	0
	F^{-1}	0	0	0	1	0	0

(Y)

The regular representation is a representation: Proof:

$B = X^{-1}Y \quad ; \quad C = Y^{-1}Z \quad ; \quad B_{X^{-1}Y} = 1$

$BC = X^{-1}YY^{-1}Z = X^{-1}Z \quad ; \quad (BC)_{X^{-1}Z} = \sum_Y B_{X^{-1}Y} C_{Y^{-1}Z} = 1$

What is $\chi^{reg}(E)$? $\chi^{reg}(E) = h \quad ; \quad \chi^{reg}(\text{not } E) = 0$

since χ is invariant: $\chi^{reg} = \sum_{\lambda=1}^{c} a^\lambda \chi^{(\lambda)}$

$a_\lambda = \frac{1}{h} \sum_R \chi^{reg}(R)\, \chi^{(\lambda)}(R) = \frac{1}{h}\, \chi^{reg}(E)\, \chi^{(\lambda)}(E) = l_\lambda$

Then $\chi^{reg} = \sum_{\lambda=1}^{c} l_\lambda \chi^{(\lambda)}$.

But: $h = \chi^{reg}(E) = \sum_{\lambda=1}^{c} l_\lambda \chi^{(\lambda)}(E) = \sum_{\lambda=1}^{c} l_\lambda^2$ QED

The elements of the regular representation are linearly independent.

Dirac's Approach to Characters

Form: $\Omega E = E \quad ; \quad \Omega_{ABC} = A+B+C \quad ; \quad \Omega_{DF} = D+F$

Then for any X in the group: $X\Omega = \Omega X$

or: $X\Omega X^{-1} = \Omega$

Then, within each group, $\Omega = C^{(\alpha)} I^{(l_\alpha \times l_\alpha)}$

The Ω's are all linearly independent.

$\Omega_E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_1$; $\Omega_{ABC} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}_{-3}$; $\Omega_{DF} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}_2$

Make an eigenvalue table:

	Ω_E	Ω_{ABC}	Ω_{DF}
+	1	0	-1
+	1	0	-1
det	1	-3	2
unit	1	3	2

Recall the character table:

χ	E	ABC	DF
+	2	0	-1
det	1	-1	1
unit	1	1	1

How are the Ω's and χ's related?

$$\chi^{(\alpha)}(R) = \frac{l_\alpha \Omega'(C_\rho)}{g_\rho}$$

g_ρ = no. of elements in class ρ.

Recall the orthogonality relations:

$$\sum_R \chi^{(\alpha)}(R) \chi^{(\beta)*}(R) = h\, \delta_{\alpha\beta}$$

$$\sum_\rho \chi^{(\alpha)}(C_\rho) \chi^{(\alpha)*}(C_\rho) \frac{g_\rho}{h} = \delta_{\alpha\beta}$$

or: $$\sum_\rho \sqrt{\frac{g_\rho}{h}}\, \chi^{(\alpha)}(C_\rho) \sqrt{\frac{g_\rho}{h}}\, \chi^{(\beta)*}(C_\rho) = \delta_{\alpha\beta}$$

But this is of the form:

$$\sum_{\rho=1}^{k} V_{i\rho}\, V^{+}_{j\rho} = \delta_{ij} = \sum_{\rho=1}^{n} V_{i\rho}\, (V^{\dagger})_{\rho j}$$

or $V V^{+} = 1$ which implies $V^{+} V = I$ or:

$$\sum_{j} V^{+}_{\rho j}\, V_{j\rho'} = \delta_{\rho\rho'}$$

$$\sum_{j} \sqrt{\frac{g_\rho}{h}}\, \chi^{(i)}(C_\rho) \sqrt{\frac{g_{\rho'}}{h}}\, \chi^{(i)}(C_{\rho'}) = \delta_{\rho\rho'}$$

or $$\sum_{j} \chi^{(i)}(C_\rho)\, \chi^{(i)}(C_{\rho'}) = \frac{h}{g_\rho}\, \delta_{\rho\rho'}$$

So if we normalize in this way, the character table forms a unitary matrix:

χ_{norm}	E	ABC	DF
+	2	0	$-\sqrt{2}$
det	1	$-\sqrt{3}$	$\sqrt{2}$
1	1	$\sqrt{3}$	$\sqrt{2}$

The Dirac approach is also useful for generating characters from the multiplication table.

We know: $\Omega_i \Omega_j = \sum_R a_R R$

Does: $\Omega_i \Omega_j = \sum_k b^{ij}_k \Omega_k$?

The b's are integers and positive.

We have: $\Omega_i \Omega_j = \Omega_j \Omega_i$ for all i, j, which means that Ω is diagonal and hence $\Omega_i \Omega_j$ is diagonal. But Ω's are linearly independent within R and hence $\Omega_i \Omega_j$ can be expressed as a linear combination of Ω's.

LECTURE 11 : 3-3-62

Recall: $\Omega_E = E$; $\Omega_{ABC} = A+B+C$; $\Omega_{DF} = D+F$

$\Omega_{DF}\,\Omega_{DF} = (D+F)(D+F) = F+2E+D = 2\Omega_E + \Omega_{DF}$

$\Omega_{DF}\,\Omega_{ABC} = (D+F)(A+B+C) = 2\Omega_{ABC}$

$\Omega_E\,\Omega_{ABC} = \Omega_{ABC}$

$\Omega_{ABC}\,\Omega_{ABC} = (A+B+C)(A+B+C) = A^2+AB+AC+BA+B^2+BC+CA+CB+C^2$

$= E+D+F+E+F+D+D+F+E = 3\Omega_E + 3\Omega_{DF}$

since Ω commutes with all group elements, then in the irreducible representation Ω's are diagonal. since in the regular representation, EABCDF are linearly independent, so are Ω_E, Ω_{ABC}, Ω_{DF} and they are also orthogonal. We can then say:

$\Omega_x \Omega_y = \sum a_k^{(xy)} \Omega_k$ where a is always an integer.

Since: $\Omega = \begin{pmatrix} \Omega' & & 0 \\ & \Omega' & \\ 0 & & \ddots \end{pmatrix}$ we can write:

$(\Omega'_{DF})^2 = 2\Omega'_E + \Omega'_{DF}$, $(\Omega'_{DF}-2)(\Omega'_{DF}+1) = 0$

so that $\Omega'_{DF} = 2, -1$

From $(\Omega'_{ABC})^2 = 3\Omega'_E + 3\Omega'_{DF}$, $\Omega'_{ABC} = \pm 3, 0$

Then the eigenvalue table looks like:

Ω'	E	ABC	DF
	1	0	-1
	1	-3	2
	1	3	2

Recall the Dirac character: $\chi'^{(\alpha)}(R) = \frac{\alpha'(R)}{g_p}$

χ'	E	ABC	DF
	1	0	$-1/2$
	1	-1	1
	1	1	1

The usual character is: $\chi^{(\alpha)}(R) = l^{(\alpha)} \chi'^{(\alpha)}(R)$

$$h = \sum_R \chi^{(\alpha)}(R)\, \chi^{(\alpha)*}(R) = l^{(\alpha)2} \sum_R \chi'^{(\alpha)}(R)\, \chi'^{(\alpha)*}(R)$$

from which we can find the orders of the representations:

χ			
+	2	0	-1
det	1	-1	1
unit	1	1	1

$$6 = l^{(\alpha)2}\, 3/2$$

$$l^{(\alpha)} = \sqrt{\frac{6}{3/2}} = 2$$

So we can construct the character Table from the abstract multiplication table by the Dirac method.

We will next consider physical applications.

LECTURE 12: 3-6-62

Exercise 4: Compute the character for the even permutation group in 4 variables by Dirac's method and some other method.

Exercise 5: Derive the "other" orthogonality relations from the Diracian relation $\Omega^{(A)}(A)\,\Omega^{(B)}(B) = \sum_C a_C^{(AB)}\,\Omega^{(B)}(C)$ and the properties of the regular representation. (Hint: consider $B = A^{-1}$).

Application: Lorentz Invariance of the Dirac Equation.

$$\sum_{\mu=1}^{4}\left(\gamma^\mu \frac{\partial}{\partial x^\mu} + \frac{mc}{\hbar}\right)\Psi = 0$$

where $\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2\delta_{\mu\nu}$

The γ^μ's can be represented by 4×4 matrices.
To put into Dirac form, multiply by $\hbar c\,\gamma^4$

$$\left\{\hbar c\,\frac{\partial}{\partial \imath ct} + \hbar c\,\gamma^4 \sum_{k=1}^{3}\gamma^k \frac{\partial}{\partial x_k} + mc^2\gamma^4\right\}\Psi = 0$$

Let: $\alpha^k = \imath\gamma^4\gamma^k$; $\beta = \gamma^4$

Then:

$$\left\{\frac{\hbar}{\imath}\frac{\partial}{\partial t} + \frac{\hbar}{\imath}c\sum_k \alpha^k \frac{\partial}{\partial x_k} + \beta mc^2\right\}\Psi = 0$$

One possible representation is:

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix};\quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix};\quad \alpha^k = \begin{pmatrix} 0 & \sigma^k \\ \sigma^k & 0 \end{pmatrix}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix};\quad \sigma_2 = \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix};\quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

LECTURE 13: 3-8-62

Recall: $$\left(\sum_{\mu=1}^{4} \gamma^\mu \frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar} \right) \Psi = 0$$

with $\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2\delta_{\mu\nu}$
and where the γ's are represented by 4×4 matrices and the Ψ's are column matrices.

We desire Lorentz invariance such that in the new coordinate system we have:

$$\left(\sum_{\mu=1}^{4} \gamma'^\mu \frac{\partial}{\partial x'_\mu} + \frac{mc}{\hbar} \right) \Psi' = 0$$

with the γ''s obeying the same commutation rules.
The LT is given by:

$$x_\mu = \sum_\nu a_{\mu\nu} x'_\nu$$

The principle of relativistic invariance states that:

$$x^T x = x'^T x'$$

Then $x^T x = x'^T x' = x'^T A^T A x'$

demands: $A^T A = 1 = A A^T$

Define: $\Psi = S \Psi'$ and form:

$$S^{-1} \left(\sum_{\mu,\nu=1}^{4} \gamma^\mu a_{\mu\nu} \frac{\partial}{\partial x'_\nu} + \frac{mc}{\hbar} \right) S \Psi' = 0$$

Now, if: $$\sum_{\mu=1}^{4} S^{-1} \gamma^\mu S a_{\mu\nu} = \gamma^{\nu\prime}$$

Then we get the desired Lorentz invariant form.

Also: $$S^{-1} \gamma^\mu S = \sum_{\nu=1}^{4} a_{\mu\nu} (\gamma^\nu)'$$

Consider: $$\gamma^\mu = \sum_{\nu'} a_{\mu\nu'} \gamma^{\nu'}$$

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = \sum_{\nu'\rho} a_{\mu\nu'} a_{\nu\rho} \underbrace{\left(\gamma^{\nu'} \gamma^\rho + \gamma^\rho \gamma^{\nu'} \right)}_{2\delta_{\nu'\rho}} = 2\delta_{\mu\nu}$$

This shows that $S^{-1}\gamma^\mu S$ has the same commutation rules as the γ's.

We now form a group of the γ's.

$$\gamma_1\gamma_1 = E \quad ; \quad \gamma_1\gamma_2\gamma_1\gamma_2 = -E$$

Right away, we have two groups, one + and one −. The distinct products are:

γ_1	$\gamma_1\gamma_2$	$\gamma_1\gamma_2\gamma_3$
γ_2	$\gamma_1\gamma_3$	$\gamma_1\gamma_2\gamma_4$
γ_3	$\gamma_1\gamma_4$	$\gamma_1\gamma_3\gamma_4$
γ_4	$\gamma_2\gamma_3$	$\gamma_2\gamma_3\gamma_4$
	$\gamma_2\gamma_4$	$\gamma_1\gamma_2\gamma_3\gamma_4$
	$\gamma_3\gamma_4$	

and their negatives. The above satisfy all the requirements for a group, having unit and inverse properties. The order $h = 32$ and $E, -E$ are invariant subgroups. There are 17 classes. How many elements has the factor group of the invariant subgroups? There are 16, and the factor group is Abelian. There are 16 irreducible representations of the factor group.

There are 16 representations of the whole group.

$$32 = h = \sum_{i=1}^{17} l_i^2 = 16 + l_{17}^2 \quad ; \quad l_{17} = 4$$

This shows that if the Dirac matrices are to be irreducible then they must be 4×4.

LECTURE 14: 3-10-62

We can find an S such that:

$$\gamma^\nu = S^{-1}\left(\sum_\mu \gamma^\mu a_{\mu\nu}\right) S$$

Now can write:

$$\left(\sum_{\mu,\nu} \frac{\partial}{\partial x_\nu} a_{\mu\nu}\gamma^\mu + \frac{mc}{\hbar}\right)\Psi'(x') = 0$$

as:

$$\left(\sum_\nu S\gamma^\nu S^{-1}\frac{\partial}{\partial x'_\nu} + \frac{mc}{\hbar}\right)\Psi'(x') = 0$$

or:

$$S\left(\sum_\nu \gamma^\nu \frac{\partial}{\partial x'_\nu} + \frac{mc}{\hbar}\right) S^{-1}\underbrace{\Psi'(x')}_{\Psi''(x')} = 0$$

The new 4 component wave function is: $\Psi''(x') = S^{-1}\Psi'(x')$

Now form the Hermitean conjugate:

$$\left(-\frac{\partial\psi^+}{i\partial ct}\gamma^4 + \sum_k \frac{\partial\psi^+}{\partial x_k}\gamma^k + \frac{mc}{\hbar}\psi^+\right) = 0 \qquad \Big\{\gamma^4$$

The γ's are Hermitean. We get:

$$\left(-\frac{\partial}{\partial x_\mu}\psi^+\gamma^4\gamma^\mu + \frac{mc}{\hbar}\psi^+\gamma^4\right) = 0$$

We define $\bar\psi = \psi^+\gamma^4$. We want $\bar\psi\psi$ to be invariant under Lorentz transformations. That is:

$$\bar\psi'\psi' = \bar\psi S^{-1}S\psi = \bar\psi\psi$$

This means that S is not unitary because since $\psi = S\psi'$, then $\psi^+ = \psi^+ S^+$. Now perform an LT on the adjoint equation:

$$S\left(-\sum_\nu a_{\mu\nu}\frac{\partial}{\partial x'_\nu}\bar\psi' S^{-1}\gamma^\mu + \frac{mc}{\hbar}\bar\psi' S^{-1}\right) = 0$$

or: $$\left(-\sum_\mu \frac{\partial}{\partial x'_\mu}\bar\psi''\gamma^\mu + \frac{mc}{\hbar}\bar\psi''\right) = 0$$

now look at the quantity: $s^\mu = \bar{\Psi} \gamma^\mu \Psi$

Under an LT: $\bar{\psi}'' S^{-1} \gamma^\mu S \psi' = \sum_\nu a_{\mu\nu} \bar{\psi}'' \gamma^\nu \psi''$

$= \sum_\nu a_{\mu\nu} s^\nu$

so that s^μ transforms as a 4-vector which satisfies the continuity equation:

$\sum_\mu \frac{\partial}{\partial x_\mu} S^\mu = 0$ as can be shown by considering the Dirac equation. We include external fields by writing:

$$\left(\sum_{\mu=1}^{4} \left(\frac{\partial}{\partial x_\mu} + \frac{ie A_\mu}{\hbar c} \right) \gamma^\mu + \frac{mc}{\hbar} \right) \bar{\Psi} = 0$$

and for the adjoint equation:

$$\left(\sum_{\mu=1}^{4} \left(-\frac{\partial}{\partial x_\mu} + \frac{ie A_\mu}{\hbar c} \right) \bar{\psi}'' \gamma^\mu + \frac{mc}{\hbar} \bar{\psi}'' \right) = 0$$

LECTURE 15: 3-13-62

what kind of representations can we have for the γ's?

$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$ } want γ's to mix only two components at a time. Also, γ's must obey commutation rule: $\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2\delta_{\mu\nu}$

Could take: $\gamma_4 = \begin{pmatrix} \sigma_2 & 0 \\ 0 & -\sigma_2 \end{pmatrix} = \sigma_2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$; $\gamma^4 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$

Exercise: show that for a suitable choice of γ matrices (or equivalently of the spinor representation) the spinor components scramble in pairs under space rotations. Show this choice for γ matrices is equivalent to the choice you are most familiar with.

Eigenfunctions and Representations:

Consider the following functions:

1	s state		
x, y, z	p states	$r\sin\theta\cos\varphi$, $r\sin\theta\sin\varphi$, $r\cos\theta$ $= r\sin\theta \begin{pmatrix} e^{i\varphi} \\ e^{-i\varphi} \end{pmatrix}$	All these functions form invariant subspaces under space rotations.
$x^2 - y^2$	d states	$r^2\sin^2\theta(\cos 2\varphi)$	
$x^2 + y^2 - 2z^2$		$r^2(1 - 3\cos^2\theta)$	
$x^2 + y^2 + z^2$			
xy		$r^2\sin^2\theta\sin^2\varphi$	
yz		$r^2\sin\theta\cos\theta\sin\varphi$	
zx		$r^2\cos\theta\sin\theta\cos\varphi$	

We note that these are just some of the spherical harmonics. Call the above functions:

$Y_{lm}(\theta, \varphi)$

We now rotate the coordinates system but still consider the same physical point.

$$\psi_{\ell m}(\theta,\varphi) = \psi_{\ell m}(\theta',\varphi') = \sum_{m'} \psi_{\ell m'}(\theta',\varphi')\, D^{(\ell)}_{m'm}(R)$$

and $\psi'_{\ell m}(\theta,\varphi) = \sum_{m'} \psi_{\ell m'}(\theta,\varphi)\, D^{(\ell)}_{m'm}(R) = \hat{R}\, \psi_{\ell m}(\theta,\varphi)$

What about consecutive operations?

$$R_1 \underline{\psi}^T = \underline{\psi}^T D_1$$

$$R_2 R_1 \underline{\psi}^T = R_2 \underline{\psi}^T D_1 = \underline{\psi}^T D_2 D_1$$

We see that the transformations are applied opposite to the operations.

LECTURE 16 : 3-15-62

Consider the general matrix elements:

$$\int \psi_i^* \mathcal{H} \psi_j \, dx = \int \psi_i^*(x)\, \mathcal{H}(x)\, \psi_j(x)\, dx$$

Make an operation on coordinates and form:

$$\int \psi_i^*(Rx)\, \mathcal{H}(Rx)\, \psi_j(Rx)\, dx = \int \psi^* \mathcal{H} \psi \, dx$$

We only consider R to be an orthogonal transformation. Assume that the ψ_j's can be represented by:

$$\psi_j(Rx) = \sum_{j'} \psi_{j'}(x)\, D^{(\ell)}_{j'j}(R) = \psi'_j(x)$$

Then the ME becomes:

$$\sum_{i'j'} D^{(\ell)}_{ii'}(R)^* \int \psi_{i'}^*(x)\, \mathcal{H}(Rx)\, \psi_{j'}(x)\, D^{(\ell)}_{j'j}(R)\, dx$$

Assume $D(R)$ is part of an irreducible representation.

suppose R is a symmetry operation of the Hamiltonian: $\mathcal{H}(Rx) = \mathcal{H}(x)$. Then:

$$ME = \sum_{i'j'} D^{(l)}_{ii'}(R)^* \, D^{(l')}_{j'j}(R) \int \psi_{i'}^*(x) \, \mathcal{H}(x) \, \psi_{j'}(x) \, dx$$

Perform all operations of the group:

$$h \int \psi_i^* \mathcal{H} \psi_j \, dx = \sum_R \sum_{i'j'} D^{(l)}_{ii'}(R)^* \, D^{(l'')}_{j'j}(R) \int \psi_{i'}^*(x) \, \mathcal{H}(x) \, \psi_{j'}(x) \, dx$$

Use orthogonality relations among group element representations:

$$h \int \psi_i^* \mathcal{H} \psi_j \, dx = \frac{h}{l} \sum_{i'j'} \delta_{ll'} \delta_{ij} \delta_{i'j'} \int \psi_{j'}^* \mathcal{H} \psi_{i'} \, dx$$

$$= \frac{h}{l} \delta_{ll'} \delta_{ij} \sum_{i'=1}^{l} \psi_{i'}^* \mathcal{H} \psi_{i'} \, dx$$

$$= h \, \delta_{ll'} \delta_{ij} \int \psi_i^* \mathcal{H} \psi_{i'} \, dx$$

Hence:

$$\int \psi_i^* \mathcal{H} \psi_j \, dx = \delta_{ll'} \delta_{ij} \int \psi_{i'}^* \mathcal{H} \psi_{i'} \, dx$$

Alternative Proof:

$$\langle \lambda_x | \mathcal{H}_x | \gamma_x \rangle = \int \langle \lambda | x \rangle \langle x | \mathcal{H} | x' \rangle \langle x' | \gamma \rangle \, dx \, dx'$$

$$= \langle \lambda_{Rx} | \mathcal{H}_{Rx} | \gamma_{Rx} \rangle = D^{(l)\dagger}(R) \langle \lambda_x | \mathcal{H}_x | \gamma_x \rangle D^{(l')}(R)$$

$$= D^{(l)\dagger}(R) \langle \lambda | \mathcal{H} | \gamma \rangle D^{(l')}(R) \quad \text{if } \mathcal{H} \text{ is invariant.}$$

Then we conclude:

$$D^{(l)}(R) \langle \lambda | \mathcal{H} | \gamma \rangle = \langle \lambda | \mathcal{H} | \gamma \rangle D^{(l')}(R)$$

which by Schur's Lemma means that $\langle \lambda | \mathcal{H} | \gamma \rangle$ is a constant times the unit matrix.

Consider the inversion group: $E: x \to x$

$I: x \to -x$

$$\int \psi_1^*(x)\, \psi_2(x)\, dx \longrightarrow \int \psi_1^*(-x)\, \psi_2(-x)\, dx = D^{(1)*} D^{(2)} \int \psi_1^*(x)\, \psi_2(x)\, dx$$

$$= \delta_{12} \int \psi_1^*(x)\, \psi_2(x)\, dx$$

Consider an matrix M form by the operation:

$$M(x) = \sum_R \psi(R^{-1}x)\, D^{(2)}(R)$$

We want to prove: $SM = M D^{(2)}(S)$, S in group.

$$SM = \sum_R \psi(SR^{-1}x)\, D^{(2)}(R)$$

$SR^{-1} = P^{-1}$ (member of group)

$$D^{\ell}(S)\, D^{\ell}(R^{-1}) = D^{\ell}(P^{-1})$$

$$D(S) = D(P^{-1})\, D(R) \quad ; \quad D(R) = D(P^{-1})\, D(S)$$

Then $$SM = \sum_R \psi(SR^{-1}x)\, D(SR^{-1})\, D(S)$$

$$= \sum_R \psi(R^{-1}x)\, D(R)\, D(S)$$

Exercise: Use this rule to reduce out the regular representation of the perm. group in these variables.

LECTURE 17 : 3-17-62

Crystal Point Groups:

Operations on a Triangle:

Consider the cyclic group:

$C_n, C_n^2, C_n^3, \cdots C_n^n = E$

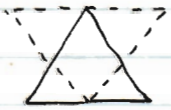
$$\varepsilon = e^{i\frac{2\pi}{n}}$$

The character table is:

C_n	E	C_1	C_2	$\cdots$	C_{n-1}
	1	1	1	$\cdots$	1
	1	ε	ε^2		ε^{n-1}
	1	ε^2	ε^4		ε^{2n-2}
	$\vdots$	$\vdots$			
	1	ε^{n-1}	ε^{2n-2}		

We also have reflections in the horizontal plane denoted by σ_h. Also have σ_v and i, inversion symmetry.

Consider:

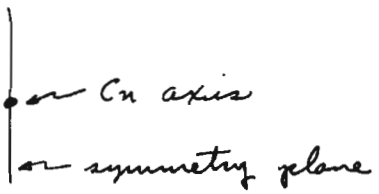


--- and — are equal distances below and above the paper.

The symmetry operation is given by $S_6 = C_6 \sigma_h$.

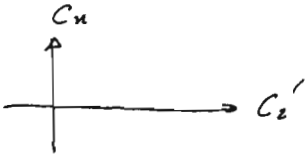
For the single triangle, we can write the group as $C_{nh} = C_n \times \sigma_h$ which gives an example of the direct product group.

Suppose we have a vertical symmetry plane:



The operations around C_n that involve symmetry planes are called C_{nv}.

If we have two symmetry axes:



The operations are called D_n

However, we see that there are really n two fold axis and the operations are C_n and C_2' about n two-fold axis. The triangle has D_3 symmetry. If we have a reflection plane in the plane formed by C_n, C_2', we call this D_{nh} symmetry. For diagonal planes, symmetry called D_{nd}.

Exercise: How many symmetry classes are there for D_{nd}? Derive the character table for D_{2d}.

Cubic Symmetry:

T, Td, Th, O, Oh

We will discuss the group O which is all the symmetry operations of the cube:

The operations are:

$E \quad 3(C_2, C_4^2) \quad 8(C_3, C_3^2) \quad 6\,C_2 \quad 6(C_4', C_4^3)$

We see we have 24 operations. This group is isomorphic with Td which are the permutations of the corners of a tetrahedron.

LECTURE 18: 3-20-62

T: rotations on tetrahedron, 24 elements, 4! even perm.
T_d: includes T with diagonal reflection plane, 24 elements, 4!
T_h: has reflection plane parallel to sides, 24 elements
O: isomorphic with T_d

Recall the operations:

$E \quad 3(C_2 C_4^2) \quad 8(C_3, C_3^2) \quad 6\,C_2 \quad 6(C_4 C_4^3)$

We see that there are 5 classes as can be seen from the fact that the irreducible representations are governed by:

$$h = \sum_i l_i^2$$

Here, for O: $24 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2$

Construct the character table:

O	E	$3C_4^2$	$8\,C_3, C_3^2$	$6\,C_2$	$6\,C_4, C_4^3$	
$x^2+y^2+z^2$	1	1	1	1	1	found from factor group
xyz	1	1	1	−1	−1	
x^2-y^2 $x^2+y^2-2z^2$	2	2	−1	0	0	
xy, yz, zx	3	−1	0	1	−1	found from ortho. relations
x, y, z	3	−1	0	−1	1	

To fill in, look for invariant subgroups. One is D_2 composed of $E, 3C_4^2$. We can form the factor group:

$(E, 3C_4^2)$	$(8C_3, C_3^2)$	$(6C_2, 6(C_4, C_4^3))$
1	1	1
1	1	−1
2	−1	0

One knows that there are 3 classes because:

$6 = 2^2 + 1^2 + 1^2$

We fill in the rest of the factor group character table by use of the orthogonality relations. We can now use this to fill in some of the main character table from $E=1$ to $E=2$. For $E=3$ twice, one can use the orthogonality relations to complete the table.

Let us look for basis functions for the O group: Consider x, y, z transformation:

$$\begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} ; \quad \chi(\theta) = 1 + 2\cos\theta = 1 + 2\cos\frac{2\pi}{n}$$

For x, y, z transformation, θ = multiples of 90°.
Find:

χ^{xyz} : 3 −1 0 −1 1

Similarly, we can find basis functions for the other representations. These are listed on the O character table.

For the group O_h, we have a horizontal reflection plane. This gives inversion symmetry. Then O_h is given by the direct product:

$$O \times I$$

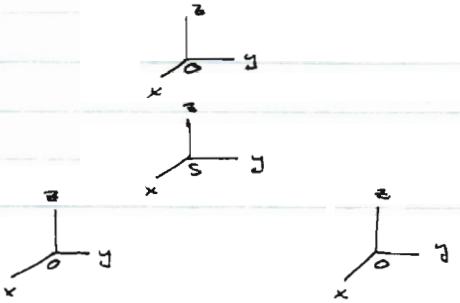
where

I	E	I
	1	1
	1	−1

giving 48 elements in O_h.

LECTURE 19: 3-22-62

Consider the vibrations of the SO_3 radical:



We write in normal mode formulation:

$$KE = \frac{1}{2}\sum_k m_k \dot{\vec{r}}_k^{\,2} \quad ; \quad PE = \text{constant} + \sum_k \frac{\partial V(0)}{\partial \vec{r}_k}\,\delta\vec{r}_k + \sum_{kl}\frac{\partial^2 V(0)}{\partial \vec{r}_k\,\partial \vec{r}_l}\,\frac{\delta\vec{r}_k\,\delta\vec{r}_l}{2} + \cdots$$

$$\frac{\partial V(0)}{\partial \vec{r}_k} = 0$$

Make a transformation to normal coordinates:

$$\vec{r}_k = f_k(q_1 \cdots q_N)$$

$$\dot{\vec{r}}_k = \sum_\alpha \frac{\partial f_k}{\partial q_\alpha}\dot{q}_\alpha$$

$$\delta\vec{r}_k = \sum_\alpha \frac{\partial f_k}{\partial q_\alpha} q_\alpha$$

$$KE = \frac{1}{2}\sum_{k,\alpha\beta}\left(m_k \frac{\partial f_k}{\partial q_\alpha}\frac{\partial f_k}{\partial q_\beta}\right)\dot{q}_\alpha \dot{q}_\beta = \sum_{\alpha\beta} \dot{q}_\alpha M_{\alpha\beta}\dot{q}_\beta$$

where:

$$M_{\alpha\beta} = \sum_k m_k \frac{\partial f_\alpha}{\partial q_\alpha}\frac{\partial f_\alpha}{\partial q_\beta}$$

Also: $PE = \frac{1}{2}\sum_{\alpha\beta} q_\alpha V_{\alpha\beta} q_\beta$

We form the Lagrangian and use Lagranges equation:

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha}\right) - \frac{\partial \mathcal{L}}{\partial q_\alpha} = 0$$

We obtain:

$$\sum_j (M_{ij}\ddot{q}_j + V_{ij} q_j) = 0$$

If we take a harmonic solution: $\ddot{q}_j = -\omega^2 q_j = \lambda q_j$
we have a secular equation:

$$\sum_j (M_{ij}\lambda + V_{ij}) q_j = 0 \quad ; \quad |M_{ij}\lambda + V_{ij}| = 0$$

Write $W = KE + PE$ in matrix form:

$$W = \tfrac{1}{2}\dot{q}^T M \dot{q} + \tfrac{1}{2} q^T V q$$

Make the transformation: $q_\beta = S^T \lambda^{-1/2} q'_\beta$

$$W = \tfrac{1}{2}\dot{q}'^T \lambda^{1/2} \underbrace{S M S^T}_{\lambda} \lambda^{-1/2}\dot{q}' + PE$$

$$= \tfrac{1}{2}\dot{q}'^T \dot{q}' I + \tfrac{1}{2} q'^T \lambda^{1/2} S V S^T \lambda^{-1/2}$$

Now make transformation that diagonalizes PE term and obtain finally:

$$W = \tfrac{1}{2}\dot{Q}^T\dot{Q} + \tfrac{1}{2} Q^T \Lambda Q \quad , \text{ where } \Lambda \text{ is diagonal}$$

$$\ddot{Q} + \Lambda Q = 0 \quad ; \quad \ddot{Q} = -\Lambda Q$$

$$\ddot{Q} = \begin{pmatrix} \omega_1^2 & & 0 \\ & \omega_2^2 & \\ 0 & & \ddots \end{pmatrix} Q$$

Now, SO_3 has symmetry of C_{3v}. Then we can write:

$$(q)' = D(R)(q) \quad ; \quad D = \begin{pmatrix} D^{(1)} & & 0 \\ & D^{(2)} & \\ 0 & & D^{(3)} \end{pmatrix}$$

This gives symmetry coordinates.

Now: $PE = \frac{1}{2} q^T V q = \frac{1}{2} q'^T V q' = \frac{1}{2} q^T \underbrace{D^T V D}_{V} q$

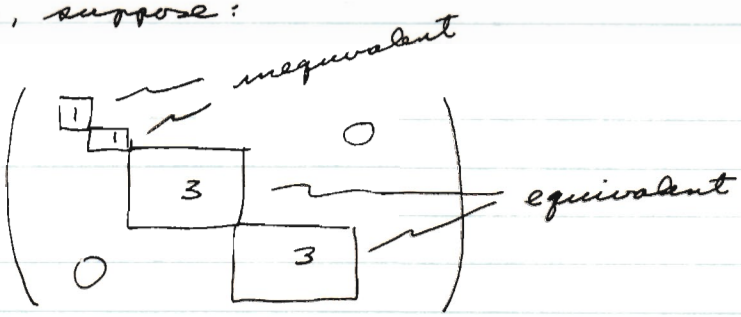
and: $D^T V D = V$ or $VD = DV$ for all operations of the group. Use Shur's Lemma:

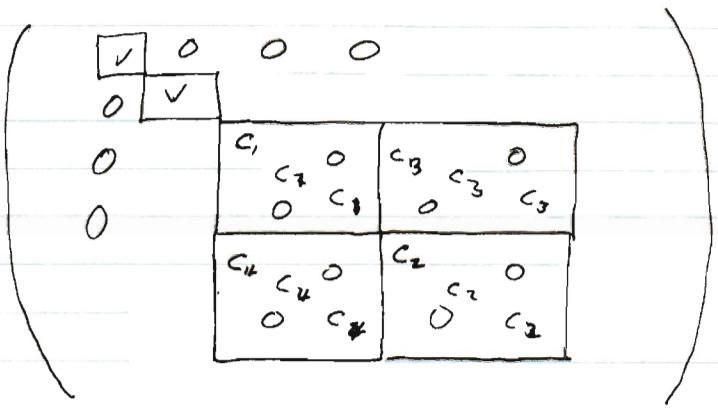
$V = \left(\begin{array}{|c|} \hline \\ \hline \end{array} \right)$; $D^{(i)}(R) V_{ij} = V_{ij} D^{(j)}(R)$

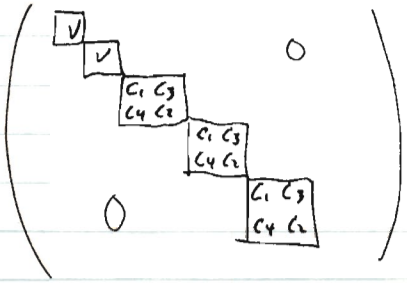
Hence: $V_{ij} = 0$ if $D^{(i)}$, $D^{(j)}$ are inequivalent

$V_{ij} = cI$ if " " " equivalent

For example, suppose:

$D(R) =$ 

$V =$ 

→ 

LECTURE 20: 3-24-62

Recall CO_3 model with D_{3h} symmetry. In generalized coordinates, there will be 12 coordinates. We now construct the character table using $\chi(\theta) = 1 + 2\cos\theta$:

	E	$2C_3$	$3C_2$	σ_h	$2\sigma_h C_3$	$3\sigma_v$	
χ^{CO_3}	12	0	−2	4	−2	2	
Polar vector translation	3	0	−1	1	−2	1	$A_2'' + E'$
rigid rotation	3	0	−1	−1	2	−1	$A_2' + E''$
$\chi^{internal}$	6	0	0	4	−2	2	$A_1' + A_2'' + 2E'$

In finding χ^{CO_3}, must remember to include each molecule once. We now consider the irreducible representation: $12 = 1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2$

		E	$2C_3$	$3C_2$	σ_h	$2\sigma_h C_3$	$3\sigma_v$
	A_1'	1	1	1	1	1	1
	A_2'	1	1	−1	1	1	−1
	A_1''	1	1	1	−1	−1	−1
z	A_2''	1	1	−1	−1	−1	1
x, y	E'	2	−1	0	2	−1	0
	E''	2	−1	0	−2	1	0

LECTURE 21: 3-31-62

Continuation of the Normal Mode Vibration of a Molecule with D_{3h} Symmetry.

The characters of the internal vibration are:

	E	$2C_3$	$3C_2$	σ_h	$2C_3\sigma_h$	$3\sigma_v$
χ^{internal}	6	0	0	4	-2	2

This is composed of the irreducible representation $A_1' + A_2'' + 2E'$. Hence there is the possibility of a two-fold degeneracy.

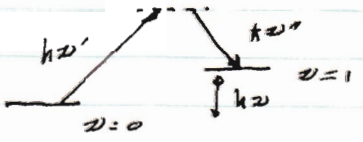
Consider the matrix element due to an applied electric field and the transition from a ground state ψ_{sym} (A_1') to some excited state:

$$\left| \int d\vec{r}\ \psi^*_{sym}\, e\vec{r}\cdot\vec{E}\ \psi_{exc} \right|^2$$

ψ_{sym} is invariant under operations of the group. $\vec{r}\cdot\vec{E}$ transforms as a polar vector or as $A_2'' + E'$. Now, the matrix element will vanish unless ψ_{exc} contains A_2'' or E'. In molecules, these representation are called infra-red active.

Raman Effect

Here we have the interplay of some intermediate state:



$$h\nu = h(\nu' - \nu'')$$

Here the interaction is a dyadic: $\vec{r}_1\vec{r}_2$

This has components:

$x_1x_2 + y_1y_2 + z_1z_2$ (A_1')

$x_1y_2 - x_2y_1$	$x_1x_2 + y_1y_2 - 2z_1z_2$	axial vector
$y_1z_2 - y_2z_1$	$x_1x_2 - y_1y_2$	
$z_1x_2 - z_2x_1$	3 asymmetric	

We now figure the character table for the interaction $\vec{r}_1 \vec{r}_2$:

$$\chi_{sym}(R) = \frac{1}{2}\left\{[\chi(R)]^2 + \chi(R^2)\right\} - 1$$

$$\chi(R_\theta) = 1 + 2\cos\theta$$
$$\chi(R_\theta^2) = 1 + 2\cos 2\theta$$

$$\chi_{sym}(R_\theta) = 1 + 2\cos\theta + 2\cos 2\theta$$

	E	$2C_3$	$3C_2$	σ_h	$2C_3\sigma_h$	$3\sigma_v$
$\chi_{tot\ sym}$	1	1	1	1	1	1
χ_{sym}	5	-1	1	1	1	1

$\chi_{sym} \rightarrow A_1' + E' + E''$

We are using for the interaction :

$$\langle 1|\vec{r}\vec{r}|1\rangle \approx \sum_n \frac{\langle 1|\vec{r}|n\rangle\langle n|\vec{r}|1\rangle}{E - E_n}$$

Start from a symmetric ground state, and find that A_1' and E'' are Raman active.

LECTURE 22 : 4-10-62

Continuous Groups

Consider the 2-D Unitary transformation with determinant 1:

$$\begin{pmatrix} \xi' \\ \eta' \end{pmatrix} = \underbrace{\begin{pmatrix} a & b \\ c & d \end{pmatrix}}_{U} \begin{pmatrix} \xi \\ \eta \end{pmatrix} \quad ; \quad \det U = 1$$

We must have:

$$\begin{aligned} a a^* + b b^* &= 1 \\ c c^* + d d^* &= 1 \\ a c^* + b d^* &= 0 \\ a b^* + c d^* &= 0 \end{aligned}$$

We find:

$$\begin{aligned} d d^* &= 1 - b b^* = a a^* \\ c c^* &= b b^* \end{aligned}$$

Hence we can construct:

$$\begin{pmatrix} a & b \\ \underline{b} & \underline{a} \end{pmatrix} \rightarrow \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$$

This satisfies $\det U = 1$ if we take:

$$\begin{aligned} a &= e^{-\frac{1}{2}(\alpha+\gamma)} \cos\frac{\beta}{2} \\ b &= -e^{-\frac{1}{2}(\alpha-\gamma)} \sin\frac{\beta}{2} \end{aligned}$$

Then we can write U as the product of:

$$U = \underbrace{\begin{pmatrix} e^{-\frac{1}{2}\alpha} & 0 \\ 0 & e^{\frac{1}{2}\alpha} \end{pmatrix}}_{\text{rotation about } z \text{ thru } \alpha} \underbrace{\begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix}}_{\text{rotation about } y} \underbrace{\begin{pmatrix} e^{-\frac{1}{2}\gamma} & 0 \\ 0 & e^{\frac{1}{2}\gamma} \end{pmatrix}}_{\text{rotation about } z \text{ thru } \gamma}$$

We see that this is isomorphic with rotations involving the Euler angles. We can form a unitary group from the product of unitary matrices.

What functions transform according to this group? Take:

$$\mathcal{U}^{\ell}_{m} = \frac{\xi^{\ell+m}\,\eta^{\ell-m}}{\sqrt{(\ell-m)!\,(\ell+m)!}} \quad ; \quad m = -\ell, \ldots, \ell$$

Form:

$$\sum_m |\mathcal{U}^{\ell}_{m}|^2 = \frac{1}{(2\ell)!}\left[(\xi\xi^*)^{2\ell} + 2\ell\,(\xi\xi^*)^{2\ell-1}\eta\eta^* + \cdots\right]$$

$$= \frac{(\xi\xi^* + \eta\eta^*)^{2\ell}}{(2\ell)!}$$

We see that the length of a vector is left invariant under unitary transformations for ℓ an integer or half-integer.

Consider $\ell = 1$:

$$\begin{pmatrix} \xi' \\ \eta' \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} \xi \\ \eta \end{pmatrix}$$

$m=1$: $$\frac{\xi'^2}{\sqrt{2}} = \frac{(a\xi + b\eta)^2}{\sqrt{2}} = \frac{a^2\xi^2 + 2ab\,\xi\eta + b^2\eta^2}{\sqrt{2}}$$

$m=0$: $$\xi'\eta' = (a\xi + b\eta)(-b^*\xi + a^*\eta) = -ab^*\xi^2 + (aa^* - bb^*)\xi\eta + ba^*\eta^2$$

$m=-1$: $$\frac{\eta'^2}{\sqrt{2}} = \frac{(-b^*\xi + a^*\eta)^2}{\sqrt{2}} = \frac{b^{*2}\xi^2 - 2b^*a^*\xi\eta + a^{*2}\eta^2}{\sqrt{2}}$$

Construct the transformation matrix for $\ell = 1$:

$$\begin{pmatrix} \frac{\xi'^2}{\sqrt{2}} & \xi'\eta' & \frac{\eta'^2}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{\xi^2}{\sqrt{2}} & \xi\eta & \frac{\eta^2}{\sqrt{2}} \end{pmatrix}\begin{pmatrix} a^2 & -ab^*\sqrt{2} & b^{*2} \\ ab\sqrt{2} & aa^* - bb^* & -\sqrt{2}\,b^*a^* \\ b^2 & ba^*\sqrt{2} & a^{*2} \end{pmatrix}$$

We can throw this into the form of the Euler angles. (see Wigner).

What we now want to show is that $\frac{\xi^2}{\sqrt{2}}$, $\xi\eta$, $\frac{\eta^2}{\sqrt{2}}$

transforms like $\frac{x+iy}{\sqrt{2}}$, z, $\frac{x-iy}{\sqrt{2}}$

<u>Exercise</u>: Write the transformation as:

$$u_m^{l'} = \sum_{m'} D^{(l)}_{mm'}(\alpha\beta\gamma)\, u_{m'}^{l}$$

Show that $D^{(1)}(\alpha\beta\gamma)$ transforms $\frac{x+iy}{\sqrt{2}}$, z, $\frac{x-iy}{\sqrt{2}}$

corresponding to the rotations γ about z, β about y, α about z.

Consider the Pauli spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These, with the unit matrix, form a complete set, and their trace $= 0$.

Form:

$$h = x\sigma_x + y\sigma_y + z\sigma_z = \begin{pmatrix} z & x-iy \\ x+iy & -z \end{pmatrix}$$

The trace is still zero. Form:

$$\bar{h} = UhU^{\dagger} = x'\sigma_x + y'\sigma_y + z'\sigma_z = \begin{pmatrix} z' & x'-iy' \\ x'+iy' & -z' \end{pmatrix}$$

using the fact that the Hermiticity is preserved under U. We can relate U now to the Euler angle rotation. Thus with each U there is associated a real orthogonal transformation on $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$. However, the association is double valued because $-U$ also leads to the same orthogonal transformation.

LECTURE 23: 4-12-62

Recall: $\bar{h} = U h U^+$; $h = x\sigma_x + y\sigma_y + z\sigma_z = \begin{pmatrix} z & x+iy \\ x-iy & -z \end{pmatrix}$

Now: $x'^2 + y'^2 + z'^2 = \det \bar{h} = \det h = x^2 + y^2 + z^2$

Hence, the transformation is length-preserving. To every such unitary transformation, there corresponds a rotational transformation, hence the groups of the transformations are homomorphic.

How many U's correspond to a single rotation? Consider; the unit transformation that takes h into itself.

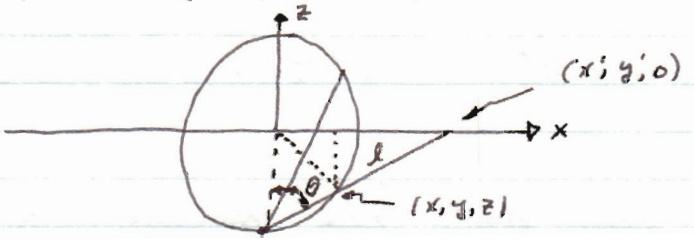
$$h = U h U^+ \; ; \quad hU = Uh$$

U must be diagonal, and furthermore, is a constant times the unit matrix. By requiring unimodularity, this constant is ± 1, hence:

$$U(1) = \pm \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Thus we have a two to one isomorphism between the unitary group and the rotational group.

It can be shown that the unitary group contains all rotations of the rotational group so that the isomorphism is complete. Consider the stereographic projection:



Define: $J = x' + iy'$

Then: $iy + x = \dfrac{2J}{1 + JJ^*}$

$$z = \frac{1 - JJ^*}{1 + JJ^*}$$

Because:

$$|J| = l \sin\theta$$
$$1 = l \cos\theta$$

$$\therefore \quad |J| = \frac{\sin\theta}{\cos\theta}$$

$$X + iy = \frac{2\,\frac{\sin\theta}{\cos\theta}\,e^{i\varphi}}{1 + \frac{\sin^2\theta}{\cos^2\theta}} = \sin 2\theta\, e^{i\varphi}$$

$$Z = \frac{1 - \frac{\sin^2\theta}{\cos^2\theta}}{1 + \frac{\sin^2\theta}{\cos^2\theta}} = \cos^2\theta - \sin^2\theta = \cos 2\theta$$

If we include the position of the south pole, we can write:

$$J = \frac{\xi}{\eta}$$

Then:

$$X + iy = \frac{2\eta\xi^*}{\xi\xi^* + \eta\eta^*}$$

$$-Z = \frac{\xi\xi^* - \eta\eta^*}{\xi\xi^* + \eta\eta^*}$$

We can fix $\xi\xi^* + \eta\eta^*$ by choosing the size of the projection sphere. Take $\xi\xi^* + \eta\eta^* = 1$. All points on the sphere are given by the ratios of ξ/η and then re-orientate the sphere by unitary transformations hence generating all the orthogonal rotational transformations by products of these unitary transformations. By removing the unitary requirement we can also represent the Lorentz groups.

LECTURE 24 : 4-14-62

References : Weyl, Ch 3, #8 (b)
Eckart, Rev. Mod. Phys. 2

We have from last lecture, with corrections :

$$z = \frac{1 - JJ^*}{1 + JJ^*} \quad ; \quad J = \frac{\eta}{\xi} \quad ; \quad z = \frac{\xi\xi^* - \eta\eta^*}{\xi\xi^* + \eta\eta^*}$$

$$x + iy = \frac{2J}{1 + JJ^*} = \frac{2\eta\xi^*}{\xi\xi^* + \eta\eta^*}$$

$$x - iy = \frac{2\xi\eta^*}{\xi\xi^* + \eta\eta^*}$$

We are interested in the transformation isomorphic to rotational transformations; given by the unitary transformation:

$$\begin{pmatrix} \xi \\ \eta \end{pmatrix}' = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \begin{pmatrix} \xi \\ \eta \end{pmatrix}$$

including an arbitrary phase factor.

The basis functions of the group of rotational transformations are :

$$u_m^l = \frac{\xi^{l+m}\,\eta^{l-m}}{[(l+m)!\,(l-m)!]^{1/2}} \quad ; \quad m = -l, \cdots, l$$

The representation $D^{(l)}_{mm'}(\alpha\beta\delta)$ is single-valued for l an integer and double-valued for l = half integer.

Note the effect of the group on the spherical harmonics and its connection with infinitesimal transformations.

Now examine if $D^{(l)}_{mm'}(\alpha\beta\delta)$ is irreducible.

$$a = e^{-i/2(\alpha+\delta)} \cos\beta/2 \quad ; \quad b = -e^{\frac{i}{2}(\alpha-\delta)} \sin\frac{\beta}{2}$$

Choose $\beta = 0$, $\alpha + \gamma = \varphi$, Then:

$$\frac{\xi'^{l+m}\,\eta'^{l-m}}{\sqrt{(l+m)!\,(l-m)!}} = \frac{a^{l+m}\,a^{*\,l-m}\,\xi^{l+m}\,\eta^{l-m}}{\sqrt{\quad}} = e^{-im\varphi}\,u^{l}_{lm}$$

$$= u'^{l}_{m}$$

Hence: $u'^{l}_{m} = D^{(l)}_{mm'}\,u^{l}_{m'}$

$$D^{(l)}(\alpha 0 \gamma) = \begin{pmatrix} e^{-il\varphi} & & & \\ & \cdot & & \\ & & \cdot & \\ & & & e^{il\varphi} \end{pmatrix}$$

If there is an M such that $MD = DM$, then M is diagonal.

Consider $\beta \neq 0$, $\alpha = \gamma = 0$ and:

$$u'^{l}_{l} = \frac{\xi'^{2l}}{\sqrt{(2l)!}} = \frac{\left(\cos\frac{\beta}{2}\,\xi - \sin\frac{\beta}{2}\,\eta\right)^{2l}}{\sqrt{(2l)!}}$$

Hence our D is of the form:

$$\begin{pmatrix} \checkmark & & & & \\ & \checkmark & & & \\ & & \checkmark & & \\ & & & \checkmark & \\ & & & & \checkmark \end{pmatrix}$$

so that M must be diagonal and a constant times the unit matrix and hence D is irreducible.

Orthogonality Relation for Continuous Groups:

$$\int_{\text{group}} D^{(l)*}_{\alpha\beta}(R)\; D^{(l')}_{\alpha'\beta'}(R)\, dR = \frac{\delta_{ll'}\,\delta_{\alpha\alpha'}\,\delta_{\beta\beta'}\int dR}{l \to \text{dimension of } D}$$

Also:

$$\int_{\text{group}} \chi^{(l)*}(R)\;\chi^{(l')}(R)\, dR = \delta_{ll'}\int dR$$

$$\int_{\text{class}} \chi^{(l)*}(\omega)\, \chi^{(l')}(\omega)\, \rho_\omega\, d\omega \Longrightarrow \delta_{ll'} \int d\omega\, \rho_\omega$$

Now:

$$\chi(\varphi) = \mathrm{Tr} \begin{pmatrix} e^{-il\varphi} & & \\ & \ddots & \\ & & e^{il\varphi} \end{pmatrix}$$

$$\boxed{\chi(\varphi) = \frac{\sin\left(l+\frac{1}{2}\right)\varphi}{\sin\frac{1}{2}\varphi}}$$

Then: $\rho_\omega = \frac{1}{\pi}\sin^2\frac{1}{2}\varphi = \frac{1-\cos\varphi}{2\pi}$

and:

$$\int_{\text{class}} \chi^{(l)*}(\omega)\, \chi^{(l')}(\omega)\, \rho_\omega\, d\omega = \delta_{ll'}$$

LECTURE 25: 4-19-62

Consider:

$$\psi^{l_1}_{m_1} = u^{l_1}_{m_1} = \frac{\xi_1^{l_1+m_1}\,\eta_1^{l_1-m_1}}{\sqrt{(l_1+m_1)!\,(l_1-m_1)!}} \quad : D^{(l_1)}$$

$$\psi^{l_2}_{m_2} = u^{l_2}_{m_2} = \frac{\xi_2^{l_2+m_2}\,\eta_2^{l_2-m_2}}{\sqrt{(l_2+m_2)!\,(l_2-m_2)!}} \quad : D^{(l_2)}$$

$$\Gamma^{(l_1)}(\omega) = \mathrm{Tr}\, D^{(l_1)}(\omega) = \mathrm{Tr} \begin{pmatrix} e^{-i l_1 \omega} & & \\ & \ddots & \\ & & e^{i l_1 \omega} \end{pmatrix} = \sum_{m_1=-l_1}^{l_1} e^{i m_1 \omega}$$

$$\Gamma^{(l_1)}(\omega) \otimes \Gamma^{(l_2)}(\omega) = \sum_k C_k \Gamma^{(k)}(\omega)$$

$$\sum_{m_1=-l_1}^{l_1} e^{i m_1 \omega} \sum_{m_2=-l_2}^{l_2} e^{i m_2 \omega} = \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{M=-L}^{L} e^{i M \omega}$$

Note that the angular momentum functions transform according to:

0	3	5	7	...
S	P	D	F	...
$D^{(0)}$	$D^{(1)}$	$D^{(2)}$	$D^{(3)}$	...

Also:

$$\sum_k C_k \Gamma^{(k)}(\omega) = \Gamma^{|l_1-l_2|}(\omega) + \Gamma^{|l_1-l_2|+1}(\omega) + \cdots + \Gamma^{l_1+l_2}(\omega)$$

This is the Clebsch-Gordon theorem.

We now want to find:

$$\psi^{(L)}_M = \sum_{m_1} A^{L\, l_1 l_2}_{M\, m_1 m_2}\, \psi^{(l_1)}_{m_1} \psi^{(l_2)}_{m_2} \quad ; \quad M = m_1 + m_2$$

A are the Wigner or Clebsch-Gordon coefficients where the ψ's are consistently normalized.

Now $\psi_M^{(L)}$ transforms like u_M^L. Write $\psi_M^{(L)} = w_M^{(L)}$. We form:

$$w_M^{(L)} = \frac{(\xi_1 + x\xi_2)^{L+M}(\eta_1 + x\eta_2)^{L-M}}{\sqrt{(L+M)!\,(L-M)!}}$$

where x is arbitrary

Now $(\xi_1\eta_2 - \xi_2\eta_1)$ is invariant because it is antisymmetric. Also any power is invariant.

Now, since x is arbitrary, every coefficient of x transformed as $w_M^{(L)}$.

$$w_M^{(L)} = C(\xi_1\eta_2 - \xi_2\eta_1)^q \frac{(\xi_1 + x\xi_2)^{L+M}(\eta_1 + x\eta_2)^{L-M}}{\sqrt{(L+M)!\,(L-M)!}}$$

We claim that A is an appropriate coefficient of x:

$$\sum_{m_1} A^{L l_1 l_2}_{M m_1 m_2} \frac{\xi_1^{l_1+m_1}\eta_1^{l_1-m_1}\xi_2^{l_2+m_2}\eta_2^{l_2-m_2}}{\left[(l_1+m_1)!\,(l_1-m_1)!\,(l_2+m_2)!\,(l_2-m_2)!\right]^{1/2}}$$

We take coefficients of x^p and we find the rules:

$$2L - p + q = 2l_1 \quad ; \quad p + q = 2l_2$$

We determine C by imposing:

$$\sum_{m_1} \left(A^{L l_1 l_2}_{M m_1 m_2}\right)^2 = 1$$

Exercise: Ground out a few Wigner coefficients by the $\xi'\eta$ calculus and also from a general formula and compare with values in tables (eg Condon and Shortley).

LECTURE 26 : 4-21-62

Recall the Wigner coefficients :

$$\psi_M^L = \sum_{m_1} A^{L\, l_1, l_2}_{M m_1, m_2}\ \psi^{l_1}_{m_1}(\theta\phi)\ \psi^{l_2}_{m_2}(\theta\phi)$$

$m = -l, \ldots, l$

$L = |l_1 - l_2|, \ldots, l_1 + l_2$

$M = m_1 + m_2$

References :

Wigner, Ch. 24, 27
Rose
Edmonds
Lomont

Fundamentals : Eckart, Rev. Mod. Phys.

Relative Intensities of Zeeman Components :

$$\int \psi^{l_1 *}_{m_1}\, O\, \psi^{l_2}_{m_2}\, d\tau$$

where O goes as $L = 1$:

$$\frac{x + iy}{\sqrt{2}} \to \frac{\eta^2}{\sqrt{2}}$$

$$z \to \xi\eta$$

$$\frac{x - iy}{\sqrt{2}} \to -\xi^2/\sqrt{2}$$

These transform by the representation $D^{(1)}_{m m'}$

By the CG theorem, $O\, \psi^{l_2}_{m_2}$ has components $l_2 - 1$, l_2, $l_2 + 1$.

Consider :

$$M_{m' m_1} = \int \psi^{l_1 *}_{m_1}\, \psi^{l'}_{m'}\, d\tau = \text{constant}\ \delta^{l_1}_{l'}\, \delta^{m_1}_{m'}$$

But M transforms as :

$(M_{m m'}) = D^{(l_1)\dagger}_{(\alpha\beta\delta)}\, M\, D^{(l')}_{(\alpha\beta\delta)}$ which gives the above result by Schur's Lemma.

We see immediately that the selection rules are:

$$l_1 = \begin{cases} l_2 \pm 1 \\ l_2 \end{cases}$$

We can write the CG theorem in terms of matrices:

$$\psi_{LM} = \sum_{m_1, m_2} A_{LM, m_1 m_2} \psi^{l_1}_{m_1} \psi^{l_2}_{m_2}$$

and: $$\psi^{l_1}_{m_1} \psi^{l_2}_{m_2} = \sum_{LM} (A_{LM, m_1 m_2})^T \psi_{LM}$$

We can then write:

$$H_{m_1 m_2} = \int \psi^{l_1 *}_{m_1} O^{\lambda}_{\mu} \psi^{l_2}_{m_2} d\tau$$

$$= C^{\lambda\, l_1 l_2} A^{L\, l_1 \lambda}_{M m_1 \mu}$$

For $\lambda = 1$; $\mu = \{ \underline{+}, 0 \}$

Note that we can only compare intensities within the manifold of $l_1 l_2$.

LECTURE 27: 4-26-62

Recall; for integer l:

$$P_l(\cos\theta) = P_l(\cos\theta')P_l(\cos\theta'') + 2\sum_{m=1}^{l} P_l^m(\cos\theta')P_l^m(\cos\theta'')\cos(\phi''-\phi')$$

$$D^{(l)}_{m\,m''}(\alpha\beta\gamma) = \sum_{m'} D^{(l)}_{m\,m'}(\alpha\beta\gamma)\, D^{(l)}_{m'\,m''}(\alpha\beta\gamma)$$

$$D^{(l)}_{m\,m'}(\alpha\beta\gamma) = e^{im\alpha} F_{m\,m'}(\beta)\, e^{im'\gamma}$$

If m or $m' = 0$, we have tesseral harmonics
If m and $m' = 0$, we have legendre polynomials

$$D^{(l)}_{0\,0}(0\,0\,0) = \sum_{\substack{m'\\ =-l}}^{l} D^{(l)}_{0\,m'}(0\,\theta'(\phi''-\phi'))\, D^{(l)}_{m'\,0}(0\,\theta''\,0)$$

as long as the D's obey the legendre polynomial addition rule. Furthermore:

$$\int_{-1}^{1} |P_l^m(u)|^2\, du = \frac{2}{2l+1}\,\frac{(l+m)!}{(l-m)!}$$

Consider:

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma\, |D^{(l)}_{m\,m'}(\alpha\beta\gamma)|^2 = \frac{8\pi^2}{2l+1}$$

Hence:

$$\int_0^{\pi} \sin\beta\, d\beta\, |F^{(l)}_{m\,m'}(\beta)|^2 = \frac{2}{2l+1}$$

Exercise: Grind out a few $F^{(l)}_{0m}(\theta)$ by the $\xi\eta$ calculus and show these are except for normalization $P_l^m(\theta)$'s.

All the above is for integer l because the development is based on the P_l^m sum rule.

Consider: Let $\begin{pmatrix}0\\1\\0\end{pmatrix}$ represent $m=0$. Then a coordinate transformation looks like: $\begin{pmatrix}\psi_m\end{pmatrix} = (\,)' = D^{(l)}(\alpha\beta\gamma)\begin{pmatrix}0\\1\\0\end{pmatrix}$

or:

$$\psi_m = D^{(l)}_{m0}(\alpha\beta\gamma)$$

Generally, if the ψ_m form a complete set:

$$\psi_m(\theta,\varphi) = \sum \underbrace{\psi_{m'}(\theta,\varphi)}_{P_\ell^m(\cos\theta)} D^{(\ell)}_{m m'}(\alpha\beta\gamma)$$

Here we consider $P_\ell^0(0) = 1$, or: $\psi_{m'} = \delta_{m'0}$.

If we know the basis in one direction for a specific α,β,γ, then we can generate the basis for any α,β,γ, and we can also find the α,β,γ dependence of $D^{(\ell)}(\alpha\beta\gamma)$ and hence the tesseral harmonics.

Consider: $M = \int \psi^{\ell *}_m \, \mathcal{H} \, \psi^{\ell'}_{m'} \, d\tau = \delta_{\ell\ell'}\delta_{mm'}$ constant

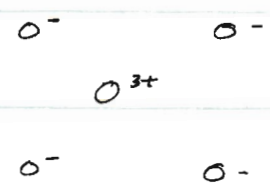
($\mathcal{H}$: invariant; $\psi^{\ell *}_m \to D^{\ell *}_{m m''}(\alpha\beta\gamma)$; $\psi^{\ell'}_{m'} \to D^{\ell'}_{m' m''}(\alpha\beta\gamma)$)

Then $D^{(\ell)} M = M D^{(\ell')}$

LECTURE 28 : 4-28-62

Crystal Field Theory

Consider a 3+ ion in a cubic field:



Ordinarily, we have spherical symmetry:

$L, l = 0, 1, 2, 3$
s p d f
S P D F

We search for linear combinations of the spherical degenerate wave functions that transform according to the cubic group.
We need to find:

$$\chi^{(l)}(R) = Tr\ D^{(l)}(R)$$

We consider only l = integer

$$\chi(\omega) = 1 + 2\cos\omega + 2\cos 2\omega + \cdots + 2\cos l\omega$$

For inversion: $\chi(I\omega) = \underbrace{\pm 1}_{\text{parity}}\ \chi(\omega)$

The parity for a single orbital is $(-1)^l$.
Forming terms from the orbitals:

pd → ^1D : odd
pp → ^1D : even

We see that term wave function parity follows a "multiplicative" rule of the orbital parities.

Once we obtain the $\chi^{(l)}(R)$ we can determine how it is contained in the cubic group. Recall:

$\Gamma_1 \rightarrow x^2+y^2+z^2$

$\Gamma_2 \rightarrow xyz$

$\Gamma_3 \rightarrow x^2+y^2-2z^2 \;;\; x^2-y^2$

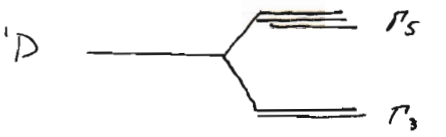
$\Gamma_4 \rightarrow x, y, z$

$\Gamma_5 \rightarrow xy, yz, zx$

We see: $S \rightarrow \Gamma_1$

$P \rightarrow \Gamma_4$

$D \rightarrow \Gamma_3, \Gamma_5$



In general: $\int \Gamma_k^{(l)} \mathcal{H} \Gamma_\ell^{(l')} = \text{constant } \delta_{ll'} \delta_{k\ell}$ ← invariant under O_h

An electric dipole transition between Γ_3 and Γ_5 is forbidden because of parity. Also the direct product $\Gamma_3 \times \Gamma_4 \times \Gamma_5$ does not contain Γ_1.
The magnetic dipole is allowed from parity considerations. Take $\Gamma_3 \times \Gamma_4 \times \Gamma_5$. Use:

$\Gamma_4 \times \Gamma_4 = \Gamma_5 \times \Gamma_5 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$

$\Gamma_4 \times \Gamma_5 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$

$\Gamma_2 \times \Gamma_5 = \Gamma_4$

$\Gamma_2 \times \Gamma_4 = \Gamma_5$

We see from $\Gamma_4 \times \Gamma_5$ that magnetic dipole is allowed. For electric quadropole, $l=2$, Γ_3, Γ_5 parity is ok and is allowed on a direct product basis.

Excercise: Examine the decomposition of $3d4s \rightarrow {}^1G$ and $3d^2 \rightarrow {}^1G$ states in fields of cubic symmetry, then in a field which is distorted into trigonal symmetry by stretching along cube diagonal, then totally asymmetric, and which transitions are allowed? (md, eq in O_h field and within Γ_5).

LECTURE 29: 5-1-62

Complex Conjugate Representations:

If $D(R)\,D(S) = D(RS)$, then $D^*(R)\,D^*(S) = D^*(RS)$. If D is irreducible, would D^* to be also. There are three cases:

1) $D^* = U D U^\dagger$: equivalent to real representation
2) $D^* = U D U^\dagger$: not " " " "
3) D^* and D not equivalent

Cases 1 and 2 have equal and real characters:

$$\chi^*(R) = \mathrm{Tr}\, D^*(R) = \mathrm{Tr}\, D(R) = \chi(R)$$

Case 3 has complex characters.

If $D^* = UDU^\dagger$: $\quad D = D^{**} = U^* D^* U^T$

or: $\quad D = U^* U D U^\dagger U^T$

or: $\quad D\,U^*U = U^*U\,D$

Then by Schur's Lemma: $U^*U = c\,I$.

Now $U = c\,U^T = c^2 U$, hence $c = \pm 1$

Now, $\chi^*(R) = \mathrm{Tr}\, D^*(R) = \mathrm{Tr}\, D^\dagger(R) = \mathrm{Tr}\, D(R^{-1}) = \chi(R^{-1})$

If the character of an operation is equal to its inverse, then the operations are in the same class. This is another test to distinguish 1, 2 from 3.

For a representation where D and D^* are inequivalent in the crystal group C_3:

C_3	E	C_3	C_3^2
identity	1	1	1
E_1	1	ε	ε^2
E_2	1	ε^2	ε

$$\varepsilon = e^{\frac{2\pi i}{3}}$$

A rule to tell 1, 2, 3 apart is:

$$\frac{1}{h}\sum_R \chi^\lambda(R^2) = \begin{cases} 1 & \text{case 1} \\ -1 & \text{case 2} \\ 0 & \text{case 3} \end{cases} \quad ; \quad D(R^2) = D(R)\,D(R)$$

Proof:

$$\frac{1}{h}\sum_R \sum_{rs} D^\lambda_{rs}(R)\, D^\lambda_{sr}(R) = 0 \quad \text{if } D^1(R) = D^2(R)^* \text{ inequivalent to } D^\lambda(R)$$

$$\frac{1}{h}\sum_R \sum_{t,u,s} U^*_{tr} D^{\lambda *}_{tu}(R)\, U_{us}\, D^\lambda_{sr}(R) = \frac{1}{h}\sum_{t,u,s} U^*_{tr} U_{us} \frac{h}{l_\lambda}\delta_{ts}\delta_{ur}$$

$$= \frac{1}{l_\lambda}\sum_{rs} U^*_{sr} U_{rs} = \frac{1}{l_\lambda} Tr\, U^* U = \frac{l_\lambda c}{d_\lambda} = c$$

$$= \pm 1$$

If D is real, then $\sum_R \chi^\lambda(R^2) = +1$. Also $U^* U = I$.
Define B, such that $B^2 = d$; $BB^* = I$,
Now $D^* = U D U^\dagger = BBDB^\dagger B^\dagger = BB\,D\,B^* B^\dagger$;
$B^* D^* B = (BDB^\dagger)^\dagger = BDB^* =$ real
So if we can find B we can bring D into real form.
B can be found from bringing U into diagonal form with another unitary matrix V:

$$VUV^\dagger = d \quad ; \quad B = V^\dagger d^{1/2} V \quad ; \quad B^2 = V^\dagger \underbrace{d^{1/2} V V^\dagger d^{1/2}}_{d} V$$

$$= V^\dagger d V = U \quad ; \quad BB^* = I \; ; \; BB^\dagger = 1 \text{, then } B = B^T \text{ and is symmetric.}$$

Finally -1 can only correspond to case 2. If we have case 2, it is claimed that the dimensionality of D must be even, because $\det U = \det U^T = (-1)^{l_\lambda} \det U$ so l_λ must be even. We can see that all the representations of the $+$ group are of type 1.

For C_3:

identity → type 1
E_1 → type 3
E_2 → type 3

The physical significance of U may be that of a time reversal operation.

Recall:

$$D^{1/2}(\alpha\beta\gamma) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$$

$$a = e^{-\frac{i}{2}(\alpha+\gamma)} \cos \beta/2$$
$$b = -e^{-\frac{i}{2}(\alpha-\gamma)} \sin \beta/2$$

Consider operation on a spinor: $\begin{pmatrix} u_+ \\ u_- \end{pmatrix}$

$$(\,)^{*\prime} = D^{*1/2} (\,)^*$$

Form:

$$i\sigma_y (\,)' = i\sigma_y D^{1/2} - i\sigma_y \, i\sigma_y (\,)$$

where $i\sigma_y = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$. $i\sigma_y$ is unitary and has the place of U in the above development.

Note that $i\sigma_y D^{1/2} - i\sigma_y = B^{1/2*}$

hence the spinor:

$i\sigma_y (\,)$ is transform by the complex conjugate operation.

$$\begin{pmatrix} u_- \\ -u_+ \end{pmatrix} = i\sigma_y \begin{pmatrix} u_+ \\ u_- \end{pmatrix}$$

$$i\sigma_y \, i\sigma_y \begin{pmatrix} u_+ \\ u_- \end{pmatrix} = - \begin{pmatrix} u_+ \\ u_- \end{pmatrix}$$

LECTURE 30 : 5-3-62

Time Reversal:

$$\mathcal{H}\psi = E\psi$$

Apply a unitary operator:

$$O H O^{\dagger} O\psi = E O\psi$$

If $OHO^{\dagger} = H$, then $O\psi$ is another eigenfunction. Now if H is real, then ψ^* gives the same energy. If H is an imaginary operator:

$$L_z^* \psi^* = m\psi^* \; ; \; -L_z\psi^* = m\psi^* \; ; \; L_z\psi^* = -m\psi^*$$

Hence complex conjugation reverses the motion of the system.

Consider:

$$i\sigma_y \, D^{1/2}(\alpha\beta\gamma)\,(-i)\sigma_y = D^{1/2*}(\alpha\beta\gamma)$$

$$i\sigma_y = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

$$i\sigma_y \begin{pmatrix} u_+ \\ u_- \end{pmatrix} = \begin{pmatrix} -u_- \\ u_+ \end{pmatrix} \; ; \; i\sigma_y \, i\sigma_y \begin{pmatrix} u_+ \\ u_- \end{pmatrix} = -\begin{pmatrix} u_+ \\ u_- \end{pmatrix}$$

Kramers found the following operation preserves the symmetry of a one-electron Hamiltonian:

$$K_1 = i\sigma_y K_0 \; ; \; K_0 \text{ means complex conjugation}$$

For many electrons: $K_{(n)} = i^n \sigma_{y_1} \cdots \sigma_{y_n} K_0$

Consider:

$$K \vec{r} K^{-1} = i\sigma_y K_0 \vec{r} (-i\sigma_y) K_0 = \vec{r}$$

$$K \vec{p} K^{-1} = -\vec{p}$$

$$K \vec{\sigma} K^{-1} = -\vec{\sigma}$$

Therefore: $K\,H(\vec{r},\vec{p},\vec{\sigma})\,K^{-1} = H(\vec{r},-\vec{p},-\vec{\sigma})$

H is invariant unless a magnetic field can be applied because this gives terms like $\mu_0 \vec{L}\cdot\vec{H}$; $\mu_0 \vec{\sigma}\cdot\vec{H}$. However $e\vec{r}\cdot\vec{E}$ is invariant.

Assume that H is invariant. Now $O\psi$ could be a degenerate wave function or a simple multiple of ψ.

Assume: $K\psi = a\psi$; $KK\psi = K(a\psi) = a^* K\psi = a^* a\psi$
$= (-1)^n \psi$

Hence for n odd we have a degeneracy present. For even number of electrons $\langle\psi|l_z|\psi\rangle = 0$ because the net moment vanishes.

The group theoretical treatment of Time reversal is complicated by the anti-linear nature of K. It was treated by Wigner:

Wegner: Ges. Gott. Math. Phys. K. Nachr. (1932)
(In MIT library: 510.63 G38)

see also: Johnston PRS A243, 546 (1958)
Heine

Suppose H is invariant under some group (not including K) and then also K. Consider one electron:
Consider K operating on a space $S(\Gamma^\alpha)$ that transforms by like Γ^α. We have:

Case a) $K\,S(\Gamma^\alpha) = S(\Gamma^\alpha)$
Case b) $K\,S(\Gamma^\alpha) = S'(\Gamma^\alpha)$
Case c) $K\,S(\Gamma^\alpha) = S(\Gamma^\beta)$

} These cases do not correspond to the previous cases 1, 2, 3. S' is orthogonal to S.

However, case 3 above does correspond to the previous case 3. For one electron:

$K\,S(\Gamma^\alpha) = S(\Gamma^\alpha) \Rightarrow U = -U^T$ → { For n even, have case 1, non-degeneracy case 2, even dimension.

$K\,S(\Gamma^\alpha) = S'(\Gamma^\alpha) \Rightarrow$ degeneracy → either case 1 or case 2.

LECTURE 31 : 5-8-62

Permutation Groups Consistent with Pauli Principle.

The associated irreducible representations of the permutation group = the irreducible representation with the sign reversed for odd permutations.
For 3 permutations, use the + groups.

For spin included:

$$D^{+}_{\text{orb}}(P) \times D^{+}_{\text{spin}}(P) = D^{\text{det}} + D^{2} + D^{3}$$

↑ determinantal representation

The determinantal representations is always included at least once in the reduction of the direct product. For + groups:

$$D^{+} \times D^{+} = D^{\text{det}} + D^{\text{unit}} + D^{+}$$

Time Reversal:

Recall:

$$K = i^{n} \sigma_{y_1} \cdots \sigma_{y_n} K_0$$

$$K \vec{\sigma} K = -\vec{\sigma}$$
$$K \vec{p} K = -\vec{p}$$
$$K \vec{r} K = \vec{r}$$

$$K H(\vec{r}\,\vec{p}\,\vec{\sigma}) K = H(\vec{r}, -\vec{p}, -\vec{\sigma})$$

If $\underbrace{OHO^{-1}}_{H} O\psi = E O\psi$

$$H\, O\psi = E O\psi$$

so that $O\psi$ is an eigenfunction.

Recall $K^2\psi = (-1)^n \psi$

For one electron:

$$K_0\, i\sigma_y\, K_0\, i\sigma_y \begin{pmatrix} u_+ \\ u_- \end{pmatrix} = -\begin{pmatrix} u_+ \\ u_- \end{pmatrix}$$

This leads to Kramers degeneracy, since $K\psi = a\psi$ and $K^2\psi = a^* a \psi$ and $a^* a > 0$

To express TR group theoretically, we admit three possibilities:

1) $D^*(R) = U D(R) U^\dagger$, equivalent and real, $U^T = U$, $\sum_R \chi(R) = 1$

2) $D^*(R) = U D(R) U^\dagger$, not equivalent and real, $U^T = -U$, $\sum_R \chi(R) = -1$

3) $D^*(R)$, $D(R)$ inequivalent, $U = 0$, $\sum_R \chi(R) = 0$

Does TR introduce further degeneracy? Define the operation $O = G \oplus K$ where G is the original group of operations. The possibilities are: (S = space)

(a) $K S(\Gamma^\alpha) = S(\Gamma^\alpha)$

(b) $K S(\Gamma^\alpha) = S'(\Gamma^\alpha)$

(c) $K S(\Gamma^\alpha) = S'(\Gamma^\beta)$; $\alpha \neq \beta$

(a) $K \psi_r = \sum_s \psi_s U_{sr}$

$$(-)^n \psi_r = K K \psi_r = K \sum_s \psi U_{sr} = \sum_s (K\psi_s) U^*_{sr}$$

Form: $(-)^n \boxed{\psi} U^T = \boxed{K\psi} U^* U^T = \boxed{K\psi}$

$U = (-)^n U^T$

Hence for n odd: $U = -U^T$: at least 2 fold degenerate (2)

for n even: $U = U^T$: not necessarily degenerate (1)

(b) n odd : either (1) or (2) : (2) → no additional degeneracy, (1) → degeneracy

n even : either (1) or (2) : additional degeneracy.

(c) n odd : (3) , have additional degeneracy

n even : (3) " " "

END OF COURSE

CHAPTER X

GROUP THEORY

The Schrödinger equation can be solved exactly in only a very few simple cases; in general, we are limited to the approximate methods of solution discussed in Chapter VII. There exists, however, a large class of results which depend only on the symmetry properties of the system under consideration; these results can be obtained exactly by use of the branch of mathematics known as group theory. We present in this chapter an elementary treatment of group theory, although we make no claim to completeness. Several of the important theorems are presented without proof; the interested reader may refer to one of the complete expositions of the field (see General References). Group theory, in the form which will be of interest to us, makes considerable use of matrix notation, so that we shall first present the elements of matrix algebra, with particular reference to the matrices involved in linear transformations of coordinates.

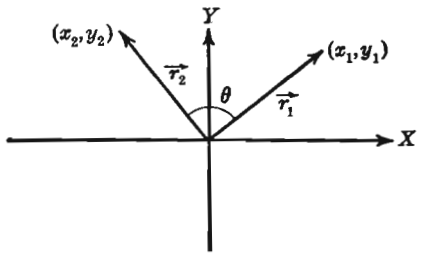


FIG. 10·1.

10a. Matrices. Let us consider a point in the xy plane, this point being specified by the coordinates (x_1, y_1) (Figure 10·1). These two numbers may also be thought of as defining the vector $\mathbf{r}_1$. A rotation of this vector through an angle θ will transform it into the new vector $\mathbf{r}_2$, defined by the numbers x_2 and y_2. The relation between (x_2, y_2) and (x_1, y_1) and the angle of rotation θ is given by the set of linear equations

$$x_2 = x_1 \cos\theta - y_1 \sin\theta$$

$$y_2 = x_1 \sin\theta + y_1 \cos\theta \qquad 10\cdot1$$

The reverse transformation is

$$x_1 = x_2 \frac{\cos\theta}{\Delta} + y_2 \frac{\sin\theta}{\Delta}$$

$$y_1 = -x_2 \frac{\sin\theta}{\Delta} + y_2 \frac{\cos\theta}{\Delta} \qquad 10\cdot2$$

where Δ is the determinant of the coefficients in 10·1:

$$\Delta = \begin{vmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{vmatrix} = \cos^2\theta + \sin^2\theta = 1$$

The set of equations 10·1 can be written as

$$\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} \qquad 10\cdot3$$

where

$$\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \qquad 10\cdot4$$

is the matrix of the transformation which takes $\mathbf{r}_1$ into $\mathbf{r}_2$. The corresponding matrix for the reverse transformation is

$$\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \qquad 10\cdot5$$

In the n-dimensional case, we have the corresponding set of equations

$$\begin{aligned} x_1' &= a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n \\ x_2' &= a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ x_n' &= a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n \end{aligned} \qquad 10\cdot6$$

where the x_i''s are the new coordinates and where the a's satisfy the relations

$$\begin{aligned} &\sum_{j=1}^{n} a_{jk}^2 = 1 && k = 1, 2, \cdots n \\ &\sum_{j=1}^{n} a_{kj}^2 = 1 && k = 1, 2, \cdots n \\ &\sum_{j=1}^{n} a_{jk}a_{jl} = 0 && k, l = 1, 2, \cdots n;\ k \neq l \\ &\sum_{j=1}^{n} a_{kj}a_{lj} = 0 && k, l = 1, 2, \cdots n;\ k \neq l \end{aligned} \qquad 10\cdot7$$

In addition, the determinant of the a's is unity. The matrix formed by a set of a's which satisfy the relations 10·7 is said to be a unitary matrix; the matrices representing rotations, reflections, and inversions are unitary. It will be noted that the matrices 10·3 and 10·4 satisfy the relations 10·7. The transformation which is the reverse of 10·6 is given by the set of equations

$$\begin{aligned} x_1 &= a_{11}x_1' + a_{21}x_2' + \cdots + a_{n1}x_n' \\ x_2 &= a_{12}x_1' + a_{22}x_2' + \cdots + a_{n2}x_n' \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ x_n &= a_{1n}x_1' + a_{2n}x_2' + \cdots + a_{nn}x_n' \end{aligned} \qquad 10\cdot8$$

The matrix of the reverse transformation is thus obtained from the matrix for the original transformation merely by changing columns into rows.

The set of equations in 10·6 can be written in the compact form

$$x_j' = \sum_k a_{jk}x_k \qquad k, j = 1, 2, \cdots n \qquad 10\cdot9$$

An even simpler notation which expresses the same thing is obtained if we write

$$x' = \mathbf{a}x \qquad 10\cdot10$$

where $\mathbf{a}$ is the matrix

$$\mathbf{a} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix}$$

of the transformation from the unprimed to the primed coordinates. A second transformation could be written as

$$x'' = \mathbf{b}x'; \quad \text{or} \quad x_i'' = \sum_j b_{ij}x_j' \qquad 10\cdot11$$

These two successive transformations are equivalent to some one transformation

$$x'' = \mathbf{c}x; \quad \text{or} \quad x_i'' = \sum_k c_{ik}x_k \qquad 10\cdot12$$

Combining the above equations, we have

$$x_i'' = \sum_j b_{ij}x_j' = \sum_j \sum_k b_{ij}a_{jk}x_k = \sum_k c_{ik}x_k \qquad 10\cdot13$$

The components of the product matrix $\mathbf{c} = \mathbf{ba}$ are thus given by the relation

$$c_{ik} = \sum_j b_{ij}a_{jk} \qquad 10\cdot14$$

which is the rule for matrix multiplication. The product of the matrices of the transformations 10·6 and 10·8 must be a matrix which represents no transformation of coordinates at all, that is

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \begin{pmatrix} a_{11} & a_{21} & \cdots & a_{n1} \\ a_{12} & a_{22} & \cdots & a_{n2} \\ \cdots & \cdots & \cdots & \cdots \\ a_{1n} & a_{2n} & \cdots & a_{nn} \end{pmatrix} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} \qquad 10\cdot15$$

From the rule for matrix multiplication, and the relations in 10·7, we see that the matrix equation 10·15 is indeed true.

Before proceeding with the formulation of group theory, we need certain general concepts concerning vectors. In three-dimensional space, any three numbers may be thought of as defining a vector, the vector from the origin of coordinates to the point specified by the three numbers. If we have the two vectors $\mathbf{A}$ and $\mathbf{B}$, defined by the numbers (A_1, A_2, A_3) and (B_1, B_2, B_3), the vectors are said to be orthogonal if

$$A_1B_1 + A_2B_2 + A_3B_3 = 0$$

In the three-dimensional case, this means that vectors are perpendicular, or, in the notation outlined in Appendix II, the scalar product $\mathbf{A} \cdot \mathbf{B}$ is zero. In more general terms, we may consider n numbers $(A_1, A_2 \cdots A_n)$ as defining a vector $\mathbf{A}_n$ in n-dimensional space. If $\mathbf{B}_n$ is another n-dimensional vector, the two vectors are said to be orthogonal if their scalar product

$$\mathbf{A}_n \cdot \mathbf{B}_n = A_1B_1 + A_2B_2 + \cdots + A_nB_n$$

is equal to zero. If the numbers which define the vectors are complex, the vectors are said to be orthogonal if the Hermitian scalar product

$$(\mathbf{A}_n \cdot \mathbf{B}_n) = A_1^*B_1 + A_2^*B_2 + \cdots + A_n^*B_n$$

is zero.

In three dimensions any arbitrary vector can be expressed in terms of a linear combination of three orthogonal vectors, for example, the three unit vectors along the coordinate axes. In other words, it is possible to construct only three independent orthogonal vectors in three-dimensional space. Analogously, in n-dimensional space, it is possible to construct only n independent vectors. This concept of a set of numbers defining a vector will prove useful later.

10b. The General Principles of Group Theory. The set of operations which send a symmetrical figure into itself are said to form a

group. Let us consider the symmetrical figure formed by three points at the corners of an equilateral triangle, as in Figure 10·2. The operations which send this figure into itself are:

1. The identity operation E, which leaves each point unchanged.
2. Operation A, which is a reflection in the yz plane.
3. B — reflection in the plane passing through the point b and perpendicular to the line joining a and c.
4. C — reflection in the plane passing through c and perpendicular to the line joining a and b.
5. D — clockwise rotation through 120°.
6. F — counterclockwise rotation through 120°.

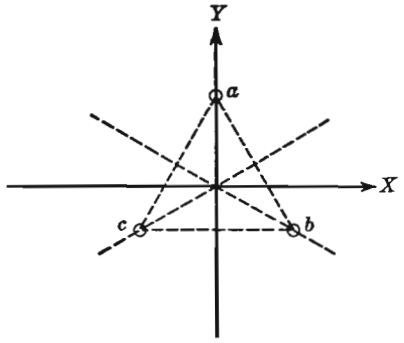


FIG. 10·2.

Other symmetry operations are possible, but they are all equivalent to one of the operations given above. For example, a clockwise rotation through 240° is a symmetry operation, but it is identical with operation F; a rotation through 180° about the y axis is identical with operation A.

The successive application of any two of the operations listed above will be equivalent to some single operation. Rotation in the clockwise direction through 240° is obtained by applying operation D twice; this is equivalent to the single operation F — we denote this fact by the equation $DD = F$. Operation A interchanges points b and c; if operation D is applied to the resulting figure, c is returned to its original position, b goes to the position originally occupied by a, and a goes to that originally occupied by b. Operation A followed by operation D is thus equivalent to operation C, or $DA = C$. If we work out all possible products of two operations, we obtain the following multiplication table, Table 10·1, where the operation which is to be applied to the figure first is written across the top of the table. The set of operations E, A, B, C, D, F forms a group, and Table 10·1 is known as the multiplication table for this group. The number of operations in the group is called the order h of the group; here the order of the group is 6.

TABLE 10·1

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

More generally, any set of elements P, Q, R, $S \cdots$ is said to form a group if the following conditions are satisfied:

1. The product of any two elements in the set is another element in the set.
2. The set must contain the identity operation E which satisfies the relation $ER = RE = R$, where R is any element of the set.
3. The associative law of multiplication, $P(QR) = (PQ)R$, must hold; that is, P times the product of Q and R must be equal to the product of P and Q times R.
4. Every element must have a reciprocal such that, if R is the reciprocal of S, then $RS = SR = E$.

That all these conditions are satisfied by the group given above is easily verified. The commutative law of multiplication does not necessarily hold. From Table 10·1 we see that $AB = D$; $BA = F$, so that $AB \neq BA$. If $PQ = QP$ for all elements of the group, the group is said to be Abelian.

In the group of symmetry operations on three points as given above, we have three distinct types of operations: the identity operation E; the reflections A, B, and C; and the rotations D and F. We say that each of these sets of elements forms a class; that is, E forms a class by itself, A, B, and C form a class, and D and F form a class. Usually the geometric considerations will enable us to pick out the classes; more precisely, two elements P and Q which satisfy the relation $X^{-1}PX = P$ or Q, where X is any element of the group and X^{-1} is its reciprocal, are said to belong to the same class. From the multi-

plication table, we have

$$EDE = D \qquad EFE = F$$
$$ADA = F \qquad AFA = D$$
$$BDB = F \qquad BFB = D$$
$$CDC = F \qquad CFC = D$$
$$FDD = D \qquad FFD = F$$
$$DDF = D \qquad DFF = F$$

The elements D and F therefore form a class; in the same way it is found that A, B, and C form a class, and that E forms a class. If the group is Abelian, then $X^{-1}PX = X^{-1}XP = P$ for all X's and P's. Each element of the group then forms a class by itself, and the number of classes is equal to the number of elements. The concept of a class of operations has the following geometric meaning. If two operations belong to the same class, it is possible to pick out a new coordinate system in which one operation is replaced by the other. For example, in the group given above, we could equally well have taken our y axis through the point b and perpendicular to the line joining a and c. The operation A in the new coordinate system is the same as the operation B in the old coordinate system, since A has been defined to be a reflection in the yz plane.

Any set of elements which multiply according to the group multiplication table is said to form a representation Γ of the group. For the group given above, we immediately see that the sets of numbers assigned to the various elements in the following way form representations of the group:

E	A	B	C	D	F
1	1	1	1	1	1
1	−1	−1	−1	1	1

The corresponding matrices will also form a representation of the group if we replace ordinary multiplication by matrix multiplication. If we denote by **e**, **a**, **b**, **c**, **d**, **f** the matrices of the transformations of coordinates associated with the corresponding operations, we see that these matrices form a representation of the group. That is, the product of, say, A and B is $AB = D$; the product of the matrices **a** and **b** must

therefore be **ab** = **d**, so that the matrices multiply according to the group multiplication table. We have therefore found three matrix representations:

	E	A	B	C	D	F
Γ_1	(1)	(1)	(1)	(1)	(1)	(1)
Γ_2	(1)	(−1)	(−1)	(−1)	(1)	(1)
Γ_3	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&+1\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&-\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$

In Γ_3, the matrices **e** and **a** can be written down immediately. **d** and **f** are obtained from 10·4 by inserting the proper value of θ; **b** and **c** can then be found by means of the group multiplication table and the rule for matrix multiplication.

It is possible to find other representations of the group. For example, if we assign to the points, a, b, and c the coordinates (x_a, y_a), etc., the matrices of the transformations would be of dimension 6 (six-row matrices) and would form a representation of the group. Let us suppose that we have found some such representation, and let us call the corresponding matrices **e**′, **a**′, **b**′, **c**′, **d**′, **f**′. The new set of matrices $\mathbf{e}'' = \boldsymbol{\beta}^{-1}\mathbf{e}'\boldsymbol{\beta}$; $\mathbf{a}'' = \boldsymbol{\beta}^{-1}\mathbf{a}'\boldsymbol{\beta}'$; $\mathbf{b}'' = \boldsymbol{\beta}^{-1}\mathbf{b}'\boldsymbol{\beta}$, etc., also form a representation of the group, as may be seen as follows. Assume that

$$\mathbf{a}''\mathbf{b}'' = \mathbf{d}'' \qquad 10\cdot16$$

Then $\boldsymbol{\beta}^{-1}\mathbf{a}'\boldsymbol{\beta}\boldsymbol{\beta}^{-1}\mathbf{b}'\boldsymbol{\beta} = \boldsymbol{\beta}^{-1}\mathbf{d}'\boldsymbol{\beta}$. From the associative law of multiplication, we have

$$\boldsymbol{\beta}^{-1}\mathbf{a}'\mathbf{b}'\boldsymbol{\beta} = \boldsymbol{\beta}^{-1}\mathbf{d}'\boldsymbol{\beta}$$

If we now multiply from the left by $\boldsymbol{\beta}$ and from the right by $\boldsymbol{\beta}^{-1}$ we have

$$\mathbf{a}'\mathbf{b}' = \mathbf{d}' \qquad 10\cdot17$$

Since 10·17 is true, 10.16 must also be true; the transformed matrices **e**″, etc., therefore also form a representation of the group. The transformations of the type $\mathbf{a}'' = \boldsymbol{\beta}^{-1}\mathbf{a}'\boldsymbol{\beta}$ are called similarity transformations. Let us now suppose that it is possible to find a similarity transformation which will transform *all* the matrices **e**′, **a**′ · · · into

the form

$$\mathbf{a}'' = \boldsymbol{\beta}^{-1}\mathbf{a}'\boldsymbol{\beta} = \begin{pmatrix} \mathbf{a}_1'' & 0 & 0 & \vdots \\ 0 & \mathbf{a}_2'' & 0 & \vdots \\ 0 & 0 & \mathbf{a}_3'' & \vdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \qquad 10\text{-}18$$

where $\mathbf{a}_1''$ is a square matrix which has the same dimension as $\mathbf{b}_1''$, $\mathbf{c}_1'' \cdots$, and where there are only zeros outside the squares. Since $\mathbf{a}''\mathbf{b}'' = \mathbf{d}'' \cdots$, we have from the law of matrix multiplication the relations

$$\begin{aligned} \mathbf{a}_1''\mathbf{b}_1'' &= \mathbf{d}_1'' \\ \mathbf{a}_2''\mathbf{b}_2'' &= \mathbf{d}_2'' \\ &\cdots\cdots \end{aligned} \qquad 10\text{-}19$$

The sets of matrices $\mathbf{e}_1''$, $\mathbf{a}_1''$, $\mathbf{b}_1'' \cdots$; $\mathbf{e}_2''$, $\mathbf{a}_2''$, $\mathbf{b}_2'' \cdots$; etc., therefore form representations of the group. The matrix representation $\mathbf{e}'$, $\mathbf{a}'$, $\mathbf{b}' \cdots$ is said to be reducible and to have been reduced by the similarity transformation with the matrix $\boldsymbol{\beta}$. If it is not possible to find a similarity transformation which will further reduce all the matrices of a given representation, the representation is said to be irreducible.

The representations Γ_1, Γ_2, Γ_3 given above are all irreducible. Since matrices representing transformations of interest to us are unitary, we may restrict ourselves to representations which involve only unitary matrices and to similarity transformations with unitary matrices. Two irreducible representations which differ only by a similarity transformation are said to be equivalent. We shall now show that the non-equivalent irreducible representations Γ_1, Γ_2, Γ_3 given above are the only non-equivalent irreducible representations of the corresponding group, and we shall then state, without proof, certain general theorems regarding irreducible representations.

We denote by $\Gamma_i(R)$ the matrix corresponding to the operation R of the ith irreducible representation, and by $\Gamma_i(R)_{mn}$ the mnth component of this matrix. For the above representations, we therefore

have the relations:[1]

$$\begin{aligned} \sum_R \Gamma_1(R)_{11}\Gamma_1(R)_{11} &= 6 \\ \sum_R \Gamma_2(R)_{11}\Gamma_2(R)_{11} &= 6 \\ \sum_R \Gamma_3(R)_{11}\Gamma_3(R)_{11} &= \sum_R \Gamma_3(R)_{12}\Gamma_3(R)_{12} \\ = \sum_R \Gamma_3(R)_{21}\Gamma_3(R)_{21} &= \sum_R \Gamma_3(R)_{22}\Gamma_3(R)_{22} = 3 \end{aligned} \qquad 10\text{-}20$$

In addition, we note that

$$\begin{aligned} \sum_R \Gamma_1(R)_{11}\Gamma_2(R)_{11} &= 0 \\ \sum_R \Gamma_1(R)_{11}\Gamma_3(R)_{11} &= 0 \\ \sum_R \Gamma_1(R)_{11}\Gamma_3(R)_{12} &= 0 \\ \sum_R \Gamma_3(R)_{11}\Gamma_3(R)_{12} &= 0, \text{ etc.} \end{aligned} \qquad 10\text{-}21$$

All the relations of the type 10·21 can be expressed by the equations

$$\begin{aligned} \sum_R \Gamma_i(R)_{mn}\Gamma_j(R)_{m'n'} &= 0; \quad i \neq j \\ \sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{m'n'} &= 0; \quad m \neq m'; \quad n \neq n' \end{aligned} \qquad 10\text{-}22$$

while the relations 10·20 can be written as

$$\sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{mn} = \frac{h}{l_i} \qquad 10\text{-}23$$

where h is the order of the group and l_i is the dimension of the ith representation. Equations 10·22 and 10·23 can be combined into the general relation (see Appendix VI)

$$\sum_R \Gamma_i(R)_{mn}\sqrt{\frac{l_i}{h}}\,\Gamma_j(R)^*_{m'n'}\sqrt{\frac{l_j}{h}} = \delta_{ij}\,\delta_{mm'}\,\delta_{nn'} \qquad 10\text{-}24$$

where $\delta_{ij} = 1$ if $i = j$; $\delta_{ij} = 0$ otherwise. *Equation 10·24 may be shown to be true for the non-equivalent irreducible representations of any group.*

From equation 10·22 we see that the matrix components $\Gamma_i(R_1)_{mn}$, $\Gamma_i(R_2)_{mn} \cdots \Gamma_i(R_h)_{mn}$ of the h elements of the group can be regarded as the components of an h-dimensional vector which is orthogonal to any one of the vectors obtained by a different choice of the subscripts

[1] To be more general, these expressions should be replaced by $\sum_R [\Gamma_1(R)]^*_{11}\Gamma_1(R)_{11}$, etc., but this form of the equations will be sufficiently general for our purposes.

m and n, as well as being orthogonal to any of the similar vectors obtained from a different irreducible representation. If there are c such irreducible representations, each of dimension l_i, there are $l_1^2 + l_2^2 + \cdots + l_c^2$ such orthogonal vectors. But it is possible to construct only h orthogonal h-dimensional vectors. Actually,

$$l_1^2 + l_2^2 + \cdots + l_c^2 = h \qquad 10\cdot25$$

This result is perfectly general and follows directly from 10·24. The representations Γ_1, Γ_2, and Γ_3 are therefore the only non-equivalent irreducible representations of the symmetric group of three points.

The sum of the diagonal elements of a matrix is known as the character of the matrix. We denote by $\chi_i(R)$ the character of the matrix of the operation R belonging to the ith irreducible representation of the group, that is

$$\chi_i(R) = \sum_m \Gamma_i(R)_{mm} \qquad 10\cdot26$$

The characters of the representations Γ_1, Γ_2, Γ_3 of the group which we have been discussing are

	E	A	B	C	D	F
χ_1	1	1	1	1	1	1
χ_2	1	−1	−1	−1	1	1
χ_3	2	0	0	0	−1	−1

The character of a matrix is unchanged by a similarity transformation. The character of a matrix P is $\chi_P = \sum_j P_{jj}$. The character of $Q = X^{-1}PX$ is

$$\chi_Q = \sum_i Q_{ii} = \sum_i \sum_j \sum_k X_{ij}^{-1} P_{jk} X_{ki} = \sum_j \sum_k \sum_i X_{ki} X_{ij}^{-1} P_{jk}$$
$$= \sum_j \sum_k \delta_{kj} P_{jk} = \sum_j P_{jj} = \chi_P$$

If two operations belong to the same class, the corresponding matrices for a given representation have the same character, as may also be verified from the character table above.

From 10·24, we have the result

$$\sum_R \Gamma_i(R)_{mm} \Gamma_j(R)_{m'm'} = \frac{h}{l_j} \delta_{ij}\, \delta_{mm'}$$

Summing over m from 1 to l_i and over m' from 1 to l_j gives

$$\sum \chi_i(R)\chi_j(R) = \frac{h}{l_j} \delta_{ij} \sum_{m=1}^{l_i} \sum_{m'=1}^{l_j} \delta_{mm'} = \frac{h}{l_j} \delta_{ij} \sum_{m'=1}^{l_j} 1 = h\, \delta_{ij} \qquad 10\cdot27$$

We see, therefore, that the characters of the matrices of the irreducible representations form sets of orthogonal vectors. Since the character is unchanged by a similarity transformation, we see that two non-equivalent representations have different character systems and that two irreducible representations with the same character system are equivalent.

Since the characters of all matrices of a given representation which correspond to operations in the same class are equal, 10·27 can be written as

$$\sum_{\rho=1}^{k} \chi_i(R_\rho)\chi_j(R_\rho) g_\rho = h\, \delta_{ij}$$

or

$$\sum_{\rho=1}^{k} \chi_i(R_\rho) \sqrt{\frac{g_\rho}{h}}\, \chi_j(R_\rho) \sqrt{\frac{g_\rho}{h}} = \delta_{ij} \qquad 10\cdot28$$

where g_ρ is the number of elements in class ρ, R_ρ is any one of the operations in this class, $\chi(R_\rho)$ is the corresponding character, and k is the number of classes. The normalized characters $\chi_i(R_\rho)\sqrt{\frac{g_\rho}{h}}$ are therefore the components of a set of orthogonal vectors in k-dimensional space. Since there can be k such vectors, we see that the number of irreducible representations is equal to the number of classes.

From the relations already developed it is possible to obtain further interesting results. Any matrix representation of a group must be some one of the irreducible representations or some combination of them; otherwise it would be an additional irreducible representation, but the number of irreducible representations is limited to the number of classes. Any reducible representation can be reduced to its irreducible representations by a similarity transformation which leaves the character unchanged. Thus we can write for the character of a matrix R of the reducible representation the expression

$$\chi(R) = \sum_{j=1}^{k} a_j \chi_j(R) \qquad 10\cdot29$$

where a_j is the number of times the jth irreducible representation occurs in the reducible representation. From 10·24 we have

$$\sum_R \chi(R)\chi_i(R) = \sum_R \sum_j a_j \chi_j(R)\chi_i(R) = h a_i \qquad 10\cdot30$$

so that the number of times the irreducible representation Γ_i occurs

in the reducible representation is

$$a_i = \frac{1}{h}\sum_R \chi(R)\chi_i(R) \qquad 10\text{·}31$$

Since there is a one-to-one correspondence between the character systems of a group and the irreducible representations of the group, we will usually find it sufficient to deal with the characters themselves rather than with the irreducible representations. For any group, the character table can be built up by means of the relations already derived. We here summarize these rules in a convenient form.

RULE 1. The number of irreducible representations is equal to the number of classes of the group.

RULE 2. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, that is,

$$l_1^2 + l_2^2 + \cdots + l_k^2 = h$$

Since $l_j = \chi_j(E)$, this is equivalent to the relation

$$\sum_j [\chi_j(E)]^2 = h \qquad 10\text{·}32$$

RULE 3. The character systems of non-equivalent irreducible representations form orthogonal vectors; that is

$$\sum_R \chi_i(R)\chi_j(R) = 0; \quad i \neq j \qquad 10\text{·}33$$

RULE 4. The sum of the squares of the characters of a given irreducible representation is equal to the order of the group; that is

$$\sum_R [\chi_i(R)]^2 = h \qquad 10\text{·}34$$

10c. Group Theory and Quantum Mechanics. We consider now the Schrödinger equation

$$\mathbf{H}\psi_i = E_i\psi_i$$

for some atomic or molecular system. Suppose that R is some transformation of coordinates which has the effect of interchanging like particles in the system. For example, in helium, R could be the transformation which interchanges the two electrons; in H_2O, R could be the transformation which interchanges the hydrogen atoms. We subject both sides of the Schrödinger equation to the transformation R, obtaining $R\mathbf{H}\psi_i = RE_i\psi_i$. Since R interchanges only like particles, it can have no effect on the Hamiltonian, so that $R\mathbf{H} = \mathbf{H}R$. R, of course, commutes with the constant E_i, so that we have

$$\mathbf{H}R\psi_i = E_iR\psi_i \qquad 10\text{·}35$$

that is, the function $R\psi_i$ is a solution of the Schrödinger equation with the eigenvalue E_i. If E_i is a non-degenerate eigenvalue, then ψ_i or constant multiples of ψ_i are the only eigenfunctions satisfying 10·35, so that for this case we have $R\psi_i = c\psi_i$; in order that $R\psi_i$ be normalized, $c = \pm 1$. If E_i is k-fold degenerate, then any linear combination of the functions $\psi_{i1}, \psi_{i2}, \cdots \psi_{ik}$ will be a solution of 10·35, so that in this case we have

$$R\psi_{il} = \sum_{j=1}^{k} a_{jl}\psi_{ij} \qquad 10\text{·}36$$

where the a_{il}'s must satisfy the relation

$$\sum_{j=1}^{k} a_{jl}^2 = 1$$

If S is another operation which interchanges like particles, we also have

$$S\psi_{ij} = \sum_{m=1}^{k} b_{mj}\psi_{im} \qquad 10\text{·}37$$

Applying operation S to 10·36 gives

$$SR\psi_{il} = \sum_{j=1}^{k} a_{jl}S\psi_{ij} = \sum_{j=1}^{k}\sum_{m=1}^{k} a_{jl}b_{mj}\psi_{im} \qquad 10\text{·}38$$

Now the product of S and R, which we may denote by $SR = T$, is likewise an operation which interchanges like particles, so that

$$T\psi_{il} = \sum_{m=1}^{k} c_{ml}\psi_{im} \qquad 10\text{·}39$$

Comparing 10·38 and 10·39, we see that

$$c_{ml} = \sum_{j=1}^{k} b_{mj}a_{jl} \qquad 10\text{·}40$$

If we now form the matrix **a** from the coefficients a_{jl}, and the matrix **b** from the coefficients b_{mj}, we see that the product of these two matrices is equal to the matrix **c** formed from the coefficient c_{ml}; moreover, all the matrices are unitary. In other words, the matrices obtained from the coefficients in the expansion of $R\psi_{il}$, etc., form a representation of the group of operations which leave the Hamiltonian unchanged. The set of eigenfunctions $\psi_{i1}, \cdots \psi_{ik}$ is said to form a basis for a representation of the group, since the representation is generated by the application of operations R, S, etc. The dimension

of the representation is equal to the degeneracy of the corresponding eigenvalue. The representations generated by the eigenfunctions corresponding to a single eigenvalue are irreducible representations, as otherwise it would be possible to form sets of linear combinations

$$\psi'_{i1}, \psi'_{i2} \cdots; \quad \psi'_{is}, \psi'_{i,s+1} \cdots; \quad \cdots; \quad \cdots \psi'_{ik}$$

of the original eigenfunctions such that operations of the group would send one of the new eigenfunctions into a linear combination involving only members of the same set. But, if this were possible, the eigenvalues corresponding to the new sets could be different, which would contradict our original assumption, except for the extremely rare case of "accidental degeneracy" (where two eigenvalues are the same even though the corresponding eigenfunctions behave differently under the operations of the group). We may therefore in general assume that sets of eigenfunctions with the same eigenvalue form a basis for an irreducible representation of the group of operations which leave the Hamiltonian unchanged. Returning to our original notation, if Γ_j is an irreducible representation of dimension k, and if $\psi_1^j, \psi_2^j \cdots \psi_k^j$ is a set of degenerate eigenfunctions which form the basis for the jth irreducible representation of the group of symmetry operations, these eigenfunctions transform according to the relation

$$R\psi_i^j = \sum_{l=1}^{k} \Gamma_j(R)_{li} \psi_l^j \qquad 10\text{·}41$$

If we are dealing with a symmetrical atomic or molecular system, these considerations place a severe restriction on the possible eigenfunctions of the system. All possible eigenfunctions must form bases for some irreducible representation of the group of symmetry operations. From a knowledge of the irreducible representations of the group, we therefore know immediately what degrees of degeneracy are possible. The form of the possible eigenfunctions is also determined to a large extent, since they must transform in a quite definite way under the operations of the group. For example, if our system had the symmetry of the group of three points which we have discussed in detail in this chapter, our eigenfunctions would be of the following types. There would be a set of eigenfunctions which would form bases for the representation Γ_1. These eigenfunctions would be non-degenerate and would remain unchanged if subjected to any of the operations of the group. There would be another set of non-degenerate eigenfunctions which form bases for the representation Γ_2; these would remain unchanged if subjected to operations E, D, and F, but would change sign if subjected to operations A, B, or C. Finally, there would be a set of doubly

degenerate eigenvalues; two eigenfunctions with the same eigenvalue would behave in the manner determined by the matrices for the irreducible representation Γ_3 and equation 10·41. No other types of eigenfunctions would be possible; for example, there would be no triply degenerate eigenvalues, nor would there be any non-degenerate eigenfunctions which changed sign when subjected to operations D or F.

10d. The Direct Product. Let us suppose that R is some operation of a group, and that $A_1, A_2 \cdots A_m$; $B_1, B_2 \cdots B_n$ are two sets of functions which form bases for representations of the group. Then

$$RA_i = \sum_{j=1}^{m} a_{ji} A_j$$

$$RB_k = \sum_{l=1}^{n} b_{lk} B_l$$

and

$$RA_iB_k = \sum_{j=1}^{m} \sum_{l=1}^{n} a_{ji} b_{lk} A_j B_l = \sum_j \sum_l c_{jl,\ ik}\, A_j B_l$$

The set of functions A_iB_k forms a basis for a representation of the group of dimension mn. The matrix $\mathbf{c}$ of this representation has the character

$$\chi(c) = \sum_j \sum_l c_{jl,\ jl} = \sum_{j=1}^{m} \sum_{l=1}^{n} a_{jj} b_{ll} = \chi(a)\chi(b) \qquad 10\text{·}42$$

The set of functions A_iB_k is called the direct product of the sets of functions A_i and B_k. Equation 10·42 then tells us that the character of the representation of the direct product is equal to the product of the characters of the individual representations. The representation of the direct product of two irreducible representations will in general be a reducible representation but may be expressed in terms of the irreducible representations by means of equation 10·31. For example, for the direct products of the irreducible representations Γ_1, Γ_2, Γ_3 of the symmetric group of three points, we have

$$\Gamma_1\Gamma_1 = \Gamma_1 \qquad \Gamma_1\Gamma_2 = \Gamma_2$$
$$\Gamma_2\Gamma_2 = \Gamma_1 \qquad \Gamma_1\Gamma_3 = \Gamma_3$$
$$\Gamma_3\Gamma_3 = \Gamma_1 + \Gamma_2 + \Gamma_3 \qquad \Gamma_2\Gamma_3 = \Gamma_3$$

The importance of the direct product appears when we wish to evaluate integrals involving functions which are bases for representations of the group. If we have an integral $\int \varphi_A \varphi_B \, d\tau$, this integral will be different from zero only if the integrand is invariant under all the operations of the group or may be expressed as a sum of terms of which

at least one is invariant. The integrand belongs to the representation $\Gamma_{\text{int}} = \Gamma_A\Gamma_B$ where $\Gamma_A\Gamma_B$ is the direct product of the representations of φ_A and φ_B. In general, $\Gamma_A\Gamma_B$ will be reducible, that is, will be expressible as

$$\Gamma_A\Gamma_B = \sum_i a_i\Gamma_i$$

where the Γ_i's are irreducible representations of the group. The integral will be different from zero only if $\Gamma_A\Gamma_B$ contains the totally symmetrical representation Γ_1. It may readily be verified from the tables in Appendix VII that, if the characters of the representation are real, as they will be in all cases of interest to us, then $\Gamma_A\Gamma_B$ contains Γ_1 only if $\Gamma_A = \Gamma_B$. For our purposes, therefore, we may state the following corollary to this theorem: The integral $\int \varphi_A f \varphi_B \, d\tau$ is different from zero only if $\Gamma_A\Gamma_B = \Gamma_f$. Moreover, since the Hamiltonian operator belongs to the totally symmetrical representation Γ_1, the integral $\int \varphi_A \mathbf{H} \varphi_B \, d\tau$ is different from zero only if $\Gamma_A = \Gamma_B$. In the secular determinant of the type

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & \cdots & H_{1n} - S_{1n}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E & \cdots & H_{2n} - S_{2n}E \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ H_{n1} - S_{n1}E & H_{n2} - S_{n2}E & \cdots & H_{nn} - S_{nn}E \end{vmatrix} = 0$$

the terms H_{ij} and S_{ij} will be different from zero only if φ_i and φ_j belong to the same irreducible representation. By classifying the eigenfunctions φ according to the representation to which they belong, it is often possible to reduce the order of the secular equation.

It may happen that in certain problems we start a perturbation calculation with zero-order eigenfunctions which do not themselves form bases for irreducible representations of a group. If we take the proper linear combinations of these eigenfunctions so that the new eigenfunctions form bases for irreducible representations, the secular equation will be simplified. These linear combinations can be found by the following procedure. Denote the original eigenfunctions by φ' and the new by φ, where φ^i_{km} is the eigenfunction belonging to the ith irreducible representation of dimension l_i with the eigenvalue E_{ik}. Suppose further that there are s_i eigenvalues corresponding to the representation Γ_i; that is, the representation Γ_i occurs s_i times in the reducible representation to which the φ''s belong. Then any of the

φ''s may be expressed in terms of the φ's by

$$\varphi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{l_i} c_{ikm}\varphi^i_{km} \qquad 10\cdot43$$

If R is any operation of the group, then by 10·41

$$R\varphi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{l_i} c_{ikm} \sum_{n=1}^{l_i} \Gamma_i(R)_{nm}\varphi^i_{kn} \qquad 10\cdot44$$

If we now multiply by $\chi_j(R) = \sum_{t=1}^{l_j} \Gamma_j(R)_{tt}$ and sum over all operations of the group, we have

$$\sum_R \chi_j(R)R\varphi' = \sum_i \sum_{k=1}^{s_i} \sum_{m=1}^{l_i} c_{ikm} \sum_{n=1}^{l_i} \sum_{t=1}^{l_j} \sum_R \Gamma_j(R)_{tt}\Gamma_i(R)_{nm}\varphi^i_{kn} \qquad 10\cdot45$$

From 10·24, we see that this expression reduces to

$$\sum_R \chi_j(R)R\varphi' = \sum_{k=1}^{s_j} \sum_{m=1}^{l_j} c_{jkm} \frac{h}{l_j} \sum_{n=1}^{l_j} \sum_{t=1}^{l_j} \delta_{tn}\delta_{tm}\varphi^j_{kn} \qquad 10\cdot46$$

$$= \sum_{k=1}^{s_j} \sum_{t=1}^{l_j} \frac{h}{l_j} c_{jkt}\varphi^j_{kt} \qquad 10\cdot47$$

Equation 10·47 has the following meaning. If both s_j and l_j are unity, then $\sum_R \chi_j(R)R\varphi'$ will give a constant times φ^j_{11}, regardless of which φ' we use. If l_j is unity, but s_j is, say, two, then $\sum_R \chi_j(R)R\varphi'$ will give expressions of the form $a\varphi^j_{11} + b\varphi^j_{21}$. There will be two linearly independent expressions of this form; the combinations of those which correspond to the two eigenvalues are determined in the usual way after the corresponding two-row determinant has been solved. For s_j equal to unity, l_j equal to 2, we obtain two independent linear combinations which have the same eigenvalue. For s_j and l_j equal to 2, we obtain four independent linear combinations, the solution of the corresponding secular determinant will then enable us to form two sets of two combinations each, one set for each of the two eigenvalues. The other cases are analogous.

A description of the various symmetry groups of interest in the theory of molecular structure has been included in Appendix VII. Appendix VII also contains the character tables for these groups, as well as the transformation properties of certain quantities which will be of interest in our later work. We shall make considerable use of group theory in later chapters; the actual applications are much easier to perform than might be expected from some of the rather complicated equations which appear above.

ACKNOWLEDGMENTS

I wish to express my appreciation to Professor Lloyd P. Smith, under whose direction this work was carried out, for his constant advice and encouragement.

I also wish to express my gratitude to Dr. V. K. Zworykin, of the Electronic Research Laboratory of the RCA Manufacturing Company, for extending to me the facilities of the laboratories for this work, as well as to express my appreciation for his constant advice and encouragement.

I am particularly indebted to Dr. E. G. Ramberg for many valuable discussions and for his contributions to the explanation of the phenomenon.

I wish to express my thanks to Messrs. H. W. Leverenz and H. W. Rhoades for the care in preparing the various oxidizing baths employed.

JULY 1, 1936 PHYSICAL REVIEW VOLUME 50

Theory of Brillouin Zones and Symmetry Properties of Wave Functions in Crystals

L. P. BOUCKAERT,* R. SMOLUCHOWSKI AND E. WIGNER, *The Institute for Advanced Study Princeton University, Princeton, New Jersey and the University of Wisconsin*

(Received April 13, 1936)

It is well known that if the interaction between electrons in a metal is neglected, the energy spectrum has a zonal structure. The problem of these "Brillouin zones" is treated here from the point of view of group theory. In this theory, a representation of the symmetry group of the underlying problem is associated with every energy value. The symmetry, in the present case, is the space group, and the main difference as compared with ordinary problems is that while in the latter the representations form a discrete manifold and can be characterized by integers (as e.g., the azimuthal quantum number), the representations of a space group form a continuous manifold, and must be characterized by continuously varying parameters. It can be shown that in the neighborhood of an energy value with a certain representation, there will be energy values with all the representations the parameters of which are close to the parameters of the original representation. This leads to the well-known result that the energy is a continuous function of the reduced wave vector (the components of which are parameters of the above-mentioned kind), but allows in addition to this a systematic treatment of the "sticking" together of Brillouin zones. The treatment is carried out for the simple cubic and the body-centered and face-centered cubic lattices, showing the different possible types of zones.

I.

INVESTIGATIONS of the electronic structure of crystal lattices in particular in metals, made on the basis of Bloch's theory, led to the conception of the so-called Brillouin zones.[1] In spite of these investigations, which cover a large part of the field, it seems desirable to develop the theory from a unique point of view. It appears that taking into account special symmetry properties of different lattices brings out interesting features of the constitution of the B-Z which are not evident from the existing general theory. These features can be dealt with

* C. R. B. Fellow.

[1] The existence of these zones was first noticed by M. J. O. Strutt, Ann. d. Physik **85**, 129 (1928); **86**, 319 (1929); and then, independently, by F. Bloch, Zeits. f. Physik **52**, 555 (1928); cf. also P. M. Morse, Phys. Rev. **35**, 1310 (1930). From another point of view, they were discussed by R. Peierls, Ann. d. Physik **4**, 121 (1930). Their connection with x-ray reflection was first pointed out by L. Brillouin (cf. e.g., *Die Quantenstatistik* (Berlin, 1931)). Important physical applications were given by H. Jones, Proc. Roy. Soc. **A144**, 225 (1934); **147**, 396 (1934); H. Jones, N. F. Mott and H. W. B. Skinner, Phys. Rev. **45**, 379 (1934); J. C. Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 209 (1934); F. Hund and B. Mrowka, Ber. Sachs. Akad. D. Wiss. **87**, 185, 325 (1935). Compare also F. Hund, Zeits. f. tech. Physik **16**, 331, 494 (1935); Zeits. f. Physik **99**, 119 (1936). Hund's work deals with those properties of the Brillouin zones which are common to all zones of the same lattice (as matter of fact he does not discriminate between different types of zones at all). We consider here the different types of zone separately. The differences between the different types are of the same kind as e.g. the difference between even and odd terms in atomic spectra. It is surprising that there are at all common properties of all zones but Hund has shown that this is the case for the more complicated crystal structures.

uniformly by the methods of group theory,[2] and we propose to take up the subject here from this point of view. The first start in this direction has been made by F. Seitz,[3] and we shall use his results extensively, though a knowledge of his work should not be necessary for the understanding of this paper.

In the theory of Bloch, every electron has a separate wave function. This assumption is identical with the Hartree-Fock approximation method and amounts to neglecting the statistical correlations between electrons. If we neglect these correlations, every electron obeys a separate Schrödinger equation of the type

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+V\psi=E\psi \qquad (1)$$

in which V contains the ordinary and exchange potentials of the ions and electrons.[4] The potential V has the whole symmetry of the lattice, that is, the group of our Schrödinger equation (1) is the space group of the lattice.

It is clear from the ordinary group theory[2] that every characteristic value of (1) belongs to a certain representation of the space group and the dimension of the representation is equal to the number of characteristic functions belonging to this characteristic value.[5] Thus far the group theory of the B-Z is not different from the group theory of any other system. But while in atoms, molecules, etc., the characteristic values of (1) are well separated, the characteristic values of (1) for a crystal form a continuous manifold. There will be several characteristic values in the neighborhood of any one E and the representations of these characteristic values will be said to form the neighborhood of the representation of E for this B-Z. Thus a certain topology for the representations must exist and it will be shown that part of this topology is independent of the special B-Z. Even if E, E', $\cdots$ be in different B-Z but have the same representation, there will be energy values neighboring E (with a few exceptions) with the same representations as those of energy values neighboring E', etc. The investigation of the "topology" of representations will be essentially the subject of this paper, from the mathematical point of view.

II.

We must review next, the theory of representations of space groups. F. Seitz[3] has shown that all space groups are soluble groups and their representations can be obtained according to the general theory for these.[3, 6] Seitz first considers the invariant subgroup formed by the translations. Since these commute, the corresponding matrices in the representation can be assumed to have the diagonal form. This means that we shall consider such linear combinations ψ_μ ($\mu=1, 2, \cdots n$, where n is the dimension of the representation) of the wave functions, which are merely multiplied by constant factors ("multipliers") $\omega_{\mu 1}$, $\omega_{\mu 2}$, $\omega_{\mu 3}$ if a displacement by the three elementary identity periods is made. In other words, the matrix corresponding to the displacement by the first elementary identity period is a diagonal matrix with the diagonal elements ω_{11}, ω_{21}, $\cdots$, ω_{n1}, with similar matrices for the representatives of the other displacements. Since all matrices must be unitary, $|\omega_{\mu 1}|=|\omega_{\mu 2}|=|\omega_{\mu 3}|=1$; and if one writes

$$\begin{aligned}\omega_{\mu 1}&=e^{i(k_x x_1+k_y y_1+k_z z_1)}\\ \omega_{\mu 2}&=e^{i(k_x x_2+k_y y_2+k_z z_2)}\\ \omega_{\mu 3}&=e^{i(k_x x_3+k_y y_3+k_z z_3)}\end{aligned} \qquad (2)$$

with x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, the x, y, z components of the first, second and third identity periods, the vector $\mathbf{k}$ is called[7] "the reduced wave number vector." Of course, $\mathbf{k}$ will be, in general, different for the different wave functions ψ_1, ψ_2, $\cdots$, ψ_n. It must be remembered, how-

[2] Cf. e.g., E. Wigner, *Die Gruppentheorie und ihre Anwendungen* (Braunschweig, 1931). The first application of group theory to crystal lattices has been given by H. Bethe, Ann. d. Physik 3, 133 (1929).

[3] F. Seitz, Ann. of Math. 37, 17 (1936).

[4] L. Brillouin, *Actualités Scientifiques et Industrielles* (Paris, 1933).

[5] To the symmetry operations of the space group, the "reversal of time" (cf. E. Wigner, Gott. Nachr. 546 (1932)) should be added. It has been remarked by F. Hund (reference 1) that this will often be of great importance. It can be omitted, however, in the case of the cubic lattices investigated here.

[6] G. Frobenius, Berl. Ber. 337 (1893); I. Schur, Berl. Ber. 164 (1906).

[7] Cf. A. Sommerfeld and H. Bethe's article in *Handbuch der Physik*, Vol. 24 (Berlin, 1933), chapter 3. Also J. C. Slater, Rev. Mod. Phys. 6, 209 (1934). For a simple cubic lattice $x_1=y_2=z_3=d$; $y_1=z_1=x_2=z_2=x_3=y_3=0$. For a face centered lattice $y_1=z_1=x_2=z_2=x_3=y_3=d/2$; $x_1=y_2=z_3=0$, etc.

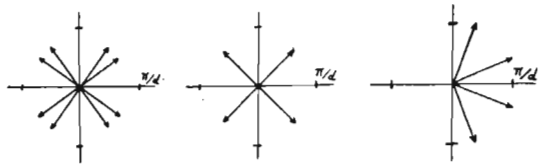
ever, that the reduced wave vector $\mathbf{k}$ is defined by (2) only up to an integer multiple of a vector $\mathbf{r}$ of the reciprocal lattice, i.e., a vector $\mathbf{r}$, for which

$$\begin{aligned} r_x x_1 + r_y y_1 + r_z z_1 &= 2\pi n_1 \\ r_x x_2 + r_y y_2 + r_z z_2 &= 2\pi n_2 \\ r_x x_3 + r_y y_3 + r_z z_3 &= 2\pi n_3 \end{aligned} \tag{2a}$$

always can be added to $\mathbf{k}$, without changing its meaning. The space of $\mathbf{k}$ is periodic with all the periods $\mathbf{r}$, satisfying (2a); two reduced wave vectors differing by such an $\mathbf{r}$ are considered identical. If there are no essential gliding planes and screw axes in the space group,[8] one needs to consider, in addition to the above translations, rotations and reflections only. If such a transformation is applied to ψ_μ, it will be transformed into a wave function, say ψ_λ, the reduced wave vector of which arises from that of ψ_μ by just the rotation or reflection considered. Thus the reduced wave vectors of the wave functions of one representation all arise from one another by the pure rotations and reflections of the group, i.e., the elements of the crystal class. If the reduced wave vector of one ψ_μ is transformed by every element of the crystal class into a different vector, this will be true for all of them, and we shall have as many wave functions $\psi_1, \cdots, \psi_n$ as the crystal class has elements. The matrices of the representation corresponding to rotations and reflections will merely interchange the different ψ_μ. If there are symmetry elements which leave a wave vector invariant, they form a group which we shall call *the group of the wave vector*. So, for example, if the wave vector lies in the x direction, its group will contain all rotations around x and all reflections in planes through x.

A wave function ψ_μ with a wave vector $\mathbf{k}$ either is left invariant under the transformations of the group of $\mathbf{k}$, or else transformed into a new ψ_λ with the same wave vector, $\mathbf{k}$, however. In the first case there will be only one wave function with the wave vector $\mathbf{k}$. In the second case there will be several of them and they will transform under the transformations of the group of $\mathbf{k}$ by an irreducible representation of this group, which we shall call the *small representation*. These are the results of Seitz.

Hence the representations of the space group must be characterized by two symbols. The first gives the reduced wave vectors (or set of ω) which occur in the representation; the figure of all these wave vectors forms a "star" with all the rotational and reflection symmetries of the lattice. Three such stars are given in Fig. 1 for



a b c

FIG. 1.

a two-dimensional quadratic lattice. The second symbol characterizes the small representation, which is an irreducible representation of the group of one wave vector (the groups of all wave vectors of a star are holomorphic). If the wave vectors lie in general positions (Fig. 1a) their group will contain the unit element only. In this case the second symbol may be omitted. It may be emphasized again that two wave vectors must be considered identical, if the corresponding set of ω's is the same. Thus for example, if the three $k_x x_i + k_y y_i + k_z z_i$ are all integer multiples of π (not necessarily of 2π) the wave vector k_x, k_y, k_z is identical with the wave vector $-k_x$, $-k_y$, $-k_z$ and the inversion ($x \to -x$, $y \to -y$, $z \to -z$) always belongs to the group of the wave vector.[9]

III.

We now consider an energy value E with a certain representation D and the wave functions $\psi_1, \cdots, \psi_n$. If we multiply one of these by $e^{i(\kappa_x x + \kappa_y y + \kappa_z z)}$ where κ_x, κ_y, κ_z, are the components

[8] We mean by this that all symmetry elements can be considered as products of two symmetry elements, the one of which is a pure translation, the other a pure rotation or reflection. This is the case in the most important space groups.

[9] It is in this connection that the time reversal is important (cf. F. Hund, reference 1). If the crystal class does not contain the inversion, k_x, k_y, k_z will still be carried over into $-k_x$, $-k_y$, $-k_z$ by the "time reversal." Since, as we shall see, the above consideration determines the surface of the B-Z, this will be fundamentally affected by the operation of time reversal.

of a very small vector, it will have the wave vector $\mathbf{k}+\kappa$ and belong to a new representation D'. The set of new representations obtained in such a way will be called the neighborhood of D. It is clear that there will be near E, an E' with a representation D'. For if ψ_1 satisfies (1), $\psi_1 e^{i(\kappa_x x+\kappa_y y+\kappa_z z)}=\psi_1'$ satisfies

$$\left(-\frac{\hbar^2}{2m}\Delta+V\right)\psi_1'+\frac{\hbar^2 i}{m}\left(\kappa_x\frac{\partial}{\partial x}+\kappa_y\frac{\partial}{\partial y}+\kappa_z\frac{\partial}{\partial z}\right)\psi_1'$$
$$=\left(E+\frac{\hbar^2}{2m}(\kappa_x^2+\kappa_y^2+\kappa_z^2)\right)\psi_1'. \quad (3)$$

In this equation the second term is small, and its negative value may be treated as a perturbation. Performing the perturbation calculation, we shall obtain a characteristic value E' of (1) which is near E and the wave function of which will have the same translational symmetry as ψ_1', since both the original operator in (3), and the perturbation

$$-\frac{\hbar^2 i}{m}\left(\kappa_x\frac{\partial}{\partial x}+\kappa_y\frac{\partial}{\partial y}+\kappa_z\frac{\partial}{\partial z}\right) \quad (3a)$$

have the whole translational symmetry of the lattice.

This is all the general theory we need. If E had a star of the general type, the star of E' also will be of the general type and our result merely states the well-known fact, that the energy is a continuous (and even differentiable) function of the components of the wave vector. The set of all energies and wave functions which may be obtained from one single energy level continuously by this operation, never touching a point in which the star degenerates, is properly defined as one Brillouin zone. The restriction to such representations, the stars of which are of the general type, is necessary for the definition of a Brillouin zone, since, as we shall see, two or more Brillouin zones may stick together for degenerated stars (as those in Figs. 1b and 1c).

If we consider an energy value, the wave vectors of which are left invariant by some of the rotation or reflection operations, the situation still will be left essentially unchanged, if no two wave functions have the same reduced wave vector (the same multipliers). If, however, two or more (say s) wave functions have the same wave vector, and we choose κ_x, κ_y, κ_z in such a way that the new wave vector $(\mathbf{k}+\kappa)$ has the general position, there will be s orthogonal wave functions, with the wave vector $\mathbf{k}+\kappa$ and with energies near E. Since for general wave vectors it never happens that two wave functions with the same wave vector belong to the same energy value, we must conclude that they all belong to different B-Z which are very close for small κ and that for the original energy value E these s B-Z "stick together." The sticking together will, therefore, always occur for such wave vectors which are left invariant by some symmetry operations.[10]

We must investigate two more cases. First let κ be such a vector that $\mathbf{k}+\kappa$ still has the group of $\mathbf{k}$. In this case, the small representation of E is equivalent to the small representation of E'. Otherwise the wave functions would have to change abruptly even for a small change of $\mathbf{k}$. The sticking together will be the same along symmetry elements.

In the second case, the group of $\mathbf{k}+\kappa$ is only a subgroup of $\mathbf{k}$, but still contains more than the identity. This case occurs, for instance, if we pass from a symmetry axis to a symmetry plane through this axis, or from the vector $\mathbf{k}=0$ to a symmetry axis. The small representations of E' will be irreducible representations of the subgroup, and if the small representation of E is not irreducible as representation of the group of $\mathbf{k}+\kappa$, the B-Z which stuck together for $\mathbf{k}$ will be partly separated for $\mathbf{k}+\kappa$. The small representations in these B-Z will be, for $\mathbf{k}+\kappa$, the irreducible parts of the small representation of the group of $\mathbf{k}$.

The proposed characterization of a B-Z is given, hence, by the small representations of the groups of all wave vectors, which have a group greater than unity. For wave vectors lying in equivalent symmetry elements, the small representations are equivalent, and for a symmetry element which is a subgroup of another, the small representation must be contained in the small representation of the latter. Wherever the small representation is s dimensional, we have a sticking together of s B-Z, all of them having this same small representation for the

[10] Including the time reversal.

symmetry element under consideration. Again, it is important to remember that the group of the wave vector for which

$$k_x x_i + k_y y_i + k_z z_i = n_i \pi \quad (\text{for } i = i_1) \qquad (4)$$

holds for one i, say $i = i_1$, contains all elements which transform $\mathbf{k}$ in such a way, that $(k_x x_i + k_y y_i + k_z z_i)/\pi$ remains an integer for $i = i_1$ and is unchanged for the two other i, since the corresponding wave vectors are all the same.

The argument which shows that the small representation will be the same all along a symmetry element, breaks down for such points in which two B-Z touch each other, if no such touching is required by symmetry considerations. In the case that the energy for a certain value of $\mathbf{k}$ is the same in two B-Z, without this being the result of the symmetry, we speak of an accidental degeneracy.[10a] In points of accidental degeneracy, the small representations of the two B-Z may be interchanged, but the case of such an accidental degeneracy is explicitly excluded from the following considerations. One can see that it does not occur for very large lattice constants, though it may occur for the actual ones.

In the following sections, these results will be applied to the three most important cubic lattices, the simple, the face-centered, and the body-centered cubic lattices. Since, for instance all small representations of wave vectors in the fourfold axes are the same, this small representation will be called "the representation along the fourfold axis" and a similar notation will be used for the other symmetry elements.

It has been pointed out by J. C. Slater[1] that the energy as function of $\mathbf{k}$ should be considered as a periodic, multivalued function, the periods being the vectors of the reciprocal lattice. The "discontinuities" then arise from considering for some $\mathbf{k}$ one, for other $\mathbf{k}$ other branches of this multivalued function. In our way of talking, the periodicity is expressed by the fact that two wave vectors differing by a vector $\mathbf{r}$ of the reciprocal lattice, are considered identical. It is convenient to single out from all sets of "identical" vectors one (generally the shortest), and not to consider the rest at all. The manifold of these "reduced wave vectors" forms the inner of the B-Z, their boundary in the $k_x k_y k_z$ space (where the discontinuities are assumed ordinarily) forms the surface of the B-Z.

The energy as function of $\mathbf{k}$ has, furthermore, all the symmetry of the (reciprocal) lattice. This is clear, since wave functions with all the $\mathbf{k}$ of a star belong to the same representation, and have the same energy, hence.

IV.

We want to consider the effect of the time reversal, first. This transforms $\mathbf{k}$ into $-\mathbf{k}$. Thus $-\mathbf{k}$ is always in the star of $\mathbf{k}$, even if there is no inversion center present: the energy as function of $\mathbf{k}$ is always equal for $\mathbf{k}$ and $-\mathbf{k}$. Just as for x-ray reflection, the inversion is always added to the symmetry of the problem.[11]

For a triclinic lattice, for instance, this means that the derivative of energy with respect to $\mathbf{k}$ is zero in the middle of the faces, edges and at the corner points of the B-Z, i.e., for

$$k_x x_i + k_y y_i + k_z z_i = n_i \pi \quad (i = 1, 2, 3). \qquad (5)$$

One can see directly also, that the group of these $\mathbf{k}$ contains the time reversal and the wave functions are real, hence. Thus the average value of the perturbation operator (3a) vanishes for these wave functions and the energy change goes with κ^2.

This cannot be claimed, however, for all the surface of the B-Z, i.e., for points for which only one of Eq. (5) is satisfied. The derivative of energy with respect to $\mathbf{k}$ will not vanish in these points and they will not really form the surface of the Brillouin zone.[12]

According to the program of section III, we shall determine now the small representations and their connections in the different types of B-Z for the simple cubic body-centered, and face-centered cubic lattice. We shall begin with the simple cubic lattice, although no metal with this structure is known.

[10a] The case of an accidental degeneracy will be treated in a paper by C. Herring, to appear shortly. We wish to thank Mr. Herring for interesting discussions on this subject.

[11] Cf. G. Friedel, Comptes rendus 157, 1533 (1913). For a more critical discussion of Friedel's rule, cf., however, e.g., P. P. Ewald's article in *Handbuch der Physik*, Vol. 23/2 (Berlin, 1933).

[12] It is not always true, thus, that the k for which $\partial E/\partial k = 0$, are those for which the Bragg conditions are satisfied.

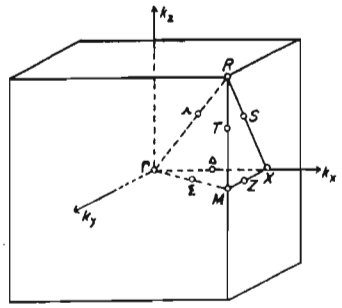


FIG. 2.

V.

Simple cubic lattice. Here the surface of the B-Z is a cube as represented in Fig. 2, with the cube edge $2\pi/d$. The inner symmetry elements are: the center Γ, the threefold axis Λ, the fourfold axis Δ, the twofold axis Σ, the symmetry planes $\Delta\Sigma$, $\Sigma\Lambda$ and $\Lambda\Delta$. The simplest way to obtain the group of a wave vector ending on the surface is to draw in all equally long wave vectors which are "identical" with it. The group of the figure constructed in this way is the group of the wave vector. For the arbitrary vector of the surface π/d, k_y, k_z, for instance, the figure contains the vector $-\pi/d$, k_y, k_z, and the group of the wave vector is, hence, the symmetry plane k_yk_z. Similarly, for the point T, there are four vectors $\pm\pi/d$, $\pm\pi/d$, k_z, and the group contains the fourfold axis k_z and all the symmetry planes through it. It is holomorphic with the group of the wave vector ending at Δ which contains the fourfold axis k_x and the symmetry planes through this. The group of S is holomorphic with that of Σ; that of Z contains the symmetry planes k_xk_y and k_yk_z and the rotation by π about k_y. R has the full cubic group like Γ; M has the group of T and, in addition, the symmetry plane k_xk_y. X has the same symmetry.

The tables[13] give the characters of the irreducible representations for the groups of the wave vectors designated in the upper left corner. The corresponding representations will be the "small representations" characterizing the B-Z. The upper right corner contains the group elements. E is the identity, its character will be the dimension of the representation. C_3 is the threefold axis; C_4, the rotation by $\pm\pi/2$ about the fourfold axis; C_4^2, the rotation by π about the same axis; and C_2 is the rotation about the twofold axis; J is the inversion. JC_4 is the product of J and C_4, etc. JC_2 and JC_4^2 are the reflections in the symmetry planes perpendicular to the twofold and fourfold axes, respectively. The figures before the symbols of group elements denote how many group elements of that kind are present in the group. The lower left corner gives the notation to be used to designate the small representation in question; it is always given for one of the wave vectors only, as, for instance, for Γ in Table I. The small representation of the wave vector R which has the same character as Γ_{12}' will be designated by R_{12}', etc. The lower right corner contains the character of the group element above it, for the representation to the left.

In order to save space we have included in the

[13] The representations of most crystallographic groups were given already by H. Bethe, loc. cit., reference 2. All of them are given in E. Wigner, Gött. Nachr. (1930), p. 133.

TABLE I. *Characters of small representations of* Γ, R, H.

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	−1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0

TABLE II. *Characters for the small representations of* Δ, T.

Δ, T	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
Δ_1	1	1	1	1	1
Δ_2	1	1	−1	1	−1
Δ_2'	1	1	−1	−1	1
Δ_1'	1	1	1	−1	−1
Δ_5	2	−2	0	0	0

TABLE III. *Characters for the small representations of* Λ, F.

Λ, F	E	$2C_3$	$3JC_2$
Λ_1	1	1	1
Λ_2	1	1	−1
Λ_3	2	−1	0

TABLE IV. *Characters for the small representations of* Σ, S.

Σ, S	E	C_2	JC_4^2	JC_2
Σ_1	1	1	1	1
Σ_2	1	1	−1	−1
Σ_3	1	−1	−1	1
Σ_4	1	−1	1	−1

tables some wave vectors (H and F) important for the body-centered lattice only.

For the points dealt with so far, it was sufficient to denote the group elements by the symbols C_2, C_3, etc., all the rotations about twofold axes being in the same class and having the same character in all representations. But for the point M, the rotation by π about the fourfold axes k_x, k_y is not equivalent to the rotation about the fourfold axis, k_z, which is perpendicular to the wave vector. The latter will be denoted by $C_4^2\perp$. Although the groups of the wave vectors ending at M and at X are holomorphic, the element in the second group which corresponds to $C_4^2\perp$ of the first is the rotation by π about k_x, which is the axis parallel to the wave vector ΓX. It will be denoted by $C_4^2\parallel$.

TABLE V. *Characters of small representations of* M, X.

M / X	E / E	$2C_4^2$ / $2C_4^2\perp$	$C_4^2\perp$ / $C_4^2\parallel$	$2C_{4\perp}$ / $2C_{4\parallel}$	$2C_2$ / $2C_2$	J / J	$2JC_4^2$ / $2JC_4^2\perp$	$JC_4^2\perp$ / $JC_4^2\parallel$	$2JC_{4\perp}$ / $2JC_{4\parallel}$	$2JC_2$ / $2JC_2$
M_1	1	1	1	1	1	1	1	1	1	1
M_2	1	1	1	−1	−1	1	1	1	−1	−1
M_3	1	−1	1	−1	1	1	−1	1	−1	1
M_4	1	−1	1	1	−1	1	−1	1	1	−1
M_1'	1	1	1	1	1	−1	−1	−1	−1	−1
M_2'	1	1	1	−1	−1	−1	−1	−1	1	1
M_3'	1	−1	1	−1	1	−1	1	−1	1	−1
M_4'	1	−1	1	1	−1	−1	1	−1	−1	1
M_5	2	0	−2	0	0	2	0	−2	0	0
M_5'	2	0	−2	0	0	−2	0	2	0	0

TABLE VI. *Characters of small representations of* Z, G, K, U, D.

Z / G, K, U / D	E / E / E	C_4^2 / C_2 / C_2	JC_4^2 / JC_4^2 / JC_2	$JC_4^2\perp$ / JC_2 / $JC_2\perp$
Z_1	1	1	1	1
Z_2	1	1	−1	−1
Z_3	1	−1	−1	1
Z_4	1	−1	1	−1

This finishes the investigation of the symmetry axes in Fig. 2, and there remain only the symmetry planes. A somewhat closer inspection will show, however, that the small representations

TABLE VII. *Compatibility relations between* Γ *and* Δ, Λ, Σ.

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'
Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$
Λ_1	Λ_2	Λ_3	$\Lambda_2\Lambda_3$	$\Lambda_1\Lambda_3$
Σ_1	Σ_4	$\Sigma_1\Sigma_4$	$\Sigma_2\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_3$
Γ_1'	Γ_2'	Γ_{12}'	Γ_{15}	Γ_{25}
Δ_1'	Δ_2'	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_2\Delta_5$
Λ_2	Λ_1	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$
Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_4$

TABLE VIII. *Compatibility relations between* M *and* Σ, Z, T.

M_1	M_2	M_3	M_4	M_1'	M_2'	M_3'	M_4'	M_5	M_5'
Σ_1	Σ_4	Σ_1	Σ_4	Σ_2	Σ_3	Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_4$
Z_1	Z_1	Z_3	Z_3	Z_2	Z_2	Z_4	Z_4	Z_2Z_4	Z_1Z_3
T_1	T_2	T_2'	T_1'	T_1'	T_2'	T_2	T_1	T_5	T_5

TABLE IX. *Compatibility relations between* X *and* Δ, Z, S.

X_1	X_2	X_3	X_4	X_1'	X_2'	X_3'	X_4'	X_5	X_5'
Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_1'	Δ_2'	Δ_2	Δ_1	Δ_5	Δ_5
Z_1	Z_1	Z_4	Z_4	Z_2	Z_2	Z_3	Z_3	Z_2Z_2	Z_1Z_4
S_1	S_4	S_1	S_4	S_2	S_3	S_2	S_3	S_2S_3	S_1S_4

prevailing on the symmetry axes already determine the representations for the symmetry planes, i.e., they determine whether the wave function will remain unchanged or assume the negative value, if reflected in one of the symmetry planes.

A B-Z must be characterized by one each of the following 10 symbols: Γ, Δ, Λ, Σ, R, T, M, S, X and Z. If there is an accidental degeneracy, however, the representation may change on an axis, etc. Not all the combinations of symbols correspond to possible B-Z. The small representation Δ on the fourfold axis must be contained in the representation Γ of the center, if this is considered as a representation of the group of Δ, and similar conditions exist between all pairs of adjoining symmetry elements. Table VII shows with which Δ, Λ, Σ, a certain Γ can be combined in the symbol of a possible B-Z. The compatibility relations between R and T, Λ, S, are the same as those between Γ and Δ, Λ, Σ. (Table VII.) These compatibility relations reduce considerably the number of possible types of B-Z. In addition to these compatibility relations, there are others originating from the four sets of wave vectors characterized by $k_z=0$; $k_z=k_y$; $k_y=k_z$; $k_z=\pi/d$. Every wave

vector satisfying one of these equations, has a group consisting of a symmetry plane, and the corresponding wave function will belong either to the symmetric, or to the antisymmetric representation of this group. This representation must be contained in the small representations of the axes lying in this plane. Table X gives, under +,

TABLE X. *Compatibility relations on symmetry planes.*

SYMMETRY PLANE	+	−
$k_z=0$	$\Sigma_1\Sigma_4$ $\Delta_1\Delta_2\Delta_5$ Z_1Z_3	$\Sigma_2\Sigma_3$ $\Delta_1'\Delta_2'\Delta_5$ Z_2Z_4
$k_x=k_y>k_z$	$\Sigma_1\Sigma_3$ $\Lambda_1\Lambda_3$ $T_1T_2'T_5$	$\Sigma_2\Sigma_4$ $\Lambda_2\Lambda_3$ $T_2T_1'T_5$
$k_y=k_z<k_x$	$\Lambda_1\Lambda_3$ S_1S_3 $\Delta_1\Delta_2'\Delta_5$	$\Lambda_2\Lambda_3$ S_2S_4 $\Delta_2\Delta_1'\Delta_5$
$k_x=\pi/d$	S_1S_4 $T_1T_2T_5$ Z_1Z_4	S_2S_3 $T_1'T_2'T_5$ Z_2Z_3

those representations along the axes, which are compatible with the symmetric representation in the plane, and under − those which are compatible with the antisymmetric representation. It shows that, for instance, Σ_1 is incompatible with Δ_1', Δ_2', Z_2, Z_4, Λ_2, T_2, T_1'.

As an example, we may consider the three B-Z which stick together at $k_x=k_y=k_z=0$ having for this wave vector the representation Γ_{25}. These three B-Z will be separated along the twofold axis, having there the small representations Σ_1, Σ_2, Σ_4, respectively (Table VII). We may consider the one with Σ_2. This necessarily goes with Δ_5 along the fourfold axis (Tables VII and X), and sticks together with one of the other zones there. Along the threefold axis it may have one of the two representations Λ_2 or Λ_3. We shall assume that it has Λ_2. For R, we still have the choice of R_2, R_{15}', R_1' or R_{25}. We shall choose R_2. This requires, then, S_4 and T_2, and hence Z_4. According to Table VIII, it will have M_3' and according to Table IX, X_5'. Its whole symbol will be $\Gamma_{25}\Sigma_2\Delta_5\Lambda_2R_{15}T_2S_4Z_4M_3'X_5'$ and we see that most small representations were uniquely given by the compatibility tables and the previous choices.

We believe that the above description of B-Z for the simple cubic lattice is complete from the point of view of symmetry. We are well aware, of course, that many of the types which are possible geometrically will not be important physically, since they have, for example, too high energies. It appeared to us, however, that for the sake of clarity a complete geometric discussion should be given once for a simple case.

The construction of the compatibility tables is very easy. If one is interested, e.g., in the compatibilities between Σ and M, one considers for M the characters corresponding to elements which are contained in Σ. These elements are E, C_2, $JC_4^2\perp$, JC_2 (one must take $JC_4^2\perp$, not JC_4^2, since the latter are the symmetry planes k_xk_z, k_yk_z which do not occur in the group of Σ). The corresponding characters in M_5, for instance, are 2, 0, −2, 0. One sees that this is the sum of the characters of Σ_2 and Σ_3 and these are, consequently, compatible with M_5. Thus it will not be necessary to give the compatibility relations for the other lattices explicitly.

VI. BODY-CENTERED CUBIC LATTICE

The shape of the surface of the B-Z is self-evident in the simple cubic lattice but not in the body-centered lattice. The identity periods can be taken as three space diagonals, with coordinates $1/2d$, $\pm1/2d$, $\pm1/2d$. The shortest vectors of the reciprocal lattice are the face diagonals, with coordinates 0, $\pm2\pi/d$, $\pm2\pi/d$; $\pm2\pi/d$, 0, $\pm2\pi/d$; $\pm2\pi/d$, $\pm2\pi/d$, 0. Since the inner of the B-Z should contain only different vectors $\mathbf{k}$, the addition of a vector of the reciprocal lattice to a $\mathbf{k}$ lying inside the B-Z must lead to a vector in the outside. This is most simply accomplished by choosing the rhombododecahedron of Fig. 3 as the surface, in which

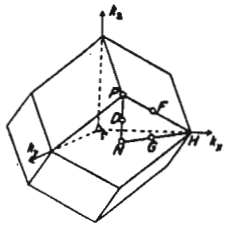


FIG. 3.

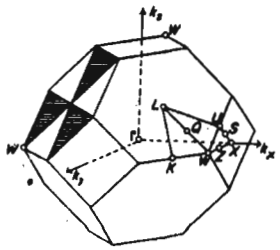


FIG. 4.

opposite faces just differ by a vector of the reciprocal lattice. The distance ΓH is $2\pi/d$.[14]

The symmetry elements in the inside of the B-Z are the same as in the simple cubic lattice, Γ, Δ, Λ, Σ, and the compatibility relations between these are also maintained. The point H has, however, the full cubic symmetry, since the vectors of the reciprocal lattice transfer it to all the end points of the coordinate axes. The point P is identical with three similar vertices, forming a tetrahedron.

TABLE XI. *Characters for the small representations of P.*

P	E	$3C_4^2$	$8C_3$	$6JC_4$	$6JC_2$
P_1	1	1	1	1	1
P_2	1	1	1	−1	−1
P_3	2	2	−1	0	0
P_4	3	−1	0	−1	1
P_5	3	−1	0	1	−1

TABLE XII. *Characters for the small representations of N.*

N	E	C_4^2	$C_2\|\|$	$C_2\perp$	J	JC_4^2	$JC_2\perp$	$JC_2\|\|$
N_1	1	1	1	1	1	1	1	1
N_2	1	−1	1	−1	1	−1	−1	1
N_3	1	−1	−1	1	1	−1	1	−1
N_4	1	1	−1	−1	1	1	−1	−1
N_1'	1	−1	1	−1	−1	1	1	−1
N_2'	1	1	1	1	−1	−1	−1	−1
N_3'	1	1	−1	−1	−1	−1	1	1
N_4'	1	−1	−1	1	−1	1	−1	1

The small representations for the other points were already given in the previous tables. We shall not give the compatibility relations between axes and points, since they are easily obtained by the method outlined in the previous section. It may be mentioned that the group of the vectors ending in a general point of the surface is the symmetry plane JC_2. The following relations are analogous to those of Table X.

TABLE XIII. *Compatibility relations for symmetry planes.*

SYMMETRY PLANE	+	−
$k_z=0$	$\Sigma_1\Sigma_4$, $\Delta_1\Delta_2\Delta_5$, G_1G_4	$\Sigma_1\Sigma_2$, $\Delta_1'\Delta_2'\Delta_5$, G_2G_3
$k_x=k_y>k_z$	$\Sigma_1\Sigma_3$, $\Lambda_1\Lambda_3$, D_1D_3	$\Sigma_2\Sigma_4$, $\Lambda_2\Lambda_3$, D_2D_4
$k_y=k_z<k_x$	$\Lambda_1\Lambda_3$, $\Delta_1\Delta_2'\Delta_5$, F_1F_3	$\Lambda_2\Lambda_3$, $\Delta_2\Delta_1'\Delta_5$, F_2F_3
$k_x+k_y=2\pi$	D_1D_4, F_1F_3, G_1G_3	D_2D_3, F_2F_3, G_2G_4

[14] The vectors $\mathbf{k}$ in the inside of the *B-Z* are transformed under this choice again into vectors in the inside by every symmetry element.

Since the surface of the B-Z is a symmetry plane, the derivative of the energy perpendicular to this plane is zero on the surface.

VII. FACE-CENTERED CUBIC LATTICE

The B-Z of the face-centered cubic lattice have a rather complicated structure. The reciprocal lattice is the body-centered lattice, the shortest vectors of which are the space diagonals with components $\pm 2\pi/d$, $\pm 2\pi/d$, $\pm 2\pi/d$. If we assume the inner of the B-Z to be bounded by the octahedron with the 8 planes $\pm x \pm y \pm z = 3\pi/d$, then no wave vectors of the inside will differ by one such vector. Nevertheless, some of them will be equivalent, differing by the sum of two shortest vectors of the reciprocal lattice, $\pm 4\pi/d, 0, 0; 0, \pm 4\pi/d, 0; 0, 0, \pm 4\pi/d$. In order to exclude these, one must cut off the corners of the octahedron by planes parallel to the coordinate planes at the distance $\pm 2\pi/d$ from these. The resulting figure is the well-known truncated octahedron of Fig. 4. With this choice of the surface of the B-Z, every wave vector of the inside will go over into a wave vector of the inside by all the symmetry operations. This requirement, however, which determines the whole shape of the surface for the simple cubic and body centered cases, fixes the surface here only at the truncating planes, but not at the octahedral planes. One could, for instance, bulge out in all octahedral planes the part which is shaded on one of the planes in Fig. 4 and bulge in by an equal amount the unshaded regions. The resulting surface would still satisfy all requirements. The truncating planes, on the other hand, cannot be deformed. If we pushed out a point on the $k_x = 2\pi/d$ plane, we would have to push in the corresponding point on the $k_x = -2\pi/d$ plane. After this, however, the reflection on the $k_y k_z$ plane would carry over wave vectors of the inside to the outside of the surface of the B-Z.

The B-Z is always uniquely determined if there is a symmetry plane perpendicular to the vector $\mathbf{r}$ of the reciprocal lattice,[15] which generates that part of the surface. In this case the surface lies at the distance $r/2$ on both sides of the symmetry plane. This was true for the vectors parallel to the coordinate axes which generated the surface

[15] Cf. Eq. (2a).

for the simple cubic lattice, it was true for the vectors parallel to the face diagonals in the body-centered structure and it is true for the vectors generating the truncating planes in Fig. 4. The situation for the octahedral plane of Fig. 4, however, is similar to that for the triclinic lattice and will be shown to have similar consequences.

Although the surface of the B-Z is thus left undetermined by general requirements, it is certainly allowable to assume it to have the shape of Fig. 4.

In the inside of the B-Z we have again the same situation as for the simple cubic lattice with the same compatibility relations holding between the small representations of Γ and the two-, three- and fourfold axes. This also applies to the points X, S and Z on the cubic plane. The point W is identical with three other points of the surface, two of which are shown on the figure, while one at the bottom is hidden. The small

TABLE XIV. *Characters of small representations of W.*

W	E	C_4^2	$2C_2$	$2JC_4$	$2JC_4^3$
W_1	1	1	1	1	1
W_1'	1	1	1	−1	−1
W_2	1	1	−1	1	−1
W_2'	1	1	−1	−1	1
W_3	2	−2	0	0	0

TABLE XV. *Characters of small representations of L.*

L	E	$2C_3$	$3C_2$	J	$2JC_3$	$3JC_2$
L_1	1	1	1	1	1	1
L_2	1	1	−1	1	1	−1
L_3	2	−1	0	2	−1	0
L_1'	1	1	1	−1	−1	−1
L_2'	1	1	−1	−1	−1	1
L_3'	2	−1	0	−2	1	0

representations for the points K and U were given in Table VI. L is identical with its antipode. The points Q on the line LW cannot be moved in or out. They belong to the surface, since they are carried over into themselves (i.e., into the "identical" point on the opposite face) by the twofold axis bisecting the Z and $-X$ axes. The wave function of the wave vector ending at Q will be either symmetric or antisymmetric with respect to this rotation. In the former case it is compatible with L_1, L_1', L_3, L_3' on one side and with $W_1W_1'W_3$ on the other. If it is antisymmetric, it is compatible with L_2, L_2', L_3, L_3' and W_2, W_2' and W_3.

The group of the points on the lines LK, KW, LU, UW contains only the symmetry plane on which they lie, they have no additional symmetry owing to their position on the surface. This is natural, since the surface can be shifted away from them. The Compatibility Table X holds for $k_x=k_y>k_z$ between Σ and Λ, but there is nothing to replace T, and T must be omitted also from the last section of ($k_x=\pi/d$) of this table. The rest of the table remains valid, however, and should be supplemented by the compatibilities just given, owing to the symmetry of the point Q.

The surface of the B-Z at the octahedral planes cannot be chosen in such a way that the "identical" point $k_x-2\pi/d$, $k_y-2\pi/d$, $k_z-2\pi/d$ to every point of the surface could be reached by a symmetry operation also. This has the consequence that the derivative of the energy perpendicular to the somewhat arbitrarily chosen plane octahedral face will only vanish on the diagonals (LW) corresponding to the separating lines between shaded and unshaded regions. On the other hand, it will have the consequence also that the energy for $k_x=\pi/d+\mu$, $k_y=\pi/d-\mu-v$, $k_z=\pi/d+v$ will be equal to the energy for $-\pi/d+\mu$, $-\pi/d-\mu-v$, $-\pi/d+v$ and, because of the twofold axis, also equal to the energy for $\pi/d-v$, $\pi/d+\mu+v$, $\pi/d-\mu$. The energy as function of $\mathbf{k}$ will be symmetric with respect to the line LW on the surface and, hence, will have on the octahedral *surface*, a sixfold rotational symmetry.

Crystallographic Groups

Schoenflies Classification for Point Groups

References

Schoenflies, Theorie der Kristallstruktur, Berlin, 1923.
Placek, in Marx, Handbuch der Radiologie, 2nd ed., VI, p. 279.
Seitz, Z. Krist. 88, 433; 90, 289, and perhaps later papers.
Bethe, Ann. der Physik. 3, 133 (1929).
Nice pictures in Ewald, Handbuch der Physik XXIV, p. 208.
R. S. Mulliken, Phys. Rev. 43, 279 (1933).
Rosenthal and Murphy, Rev. Mod. Phys. vol. 8.
E. Wigner, Gott. Nac. 1930; E. B. Wilson, Phys. Rev. 45, 706 (1934), and J. Chem. Phys. 2, 432 (1934). (Application to Molecular Vibrations.)
Eyring, et al., Quantum Chemistry.

Schoenflies Notation

i = inversion center, σ = symmetry plane, C_p = symmetry axis, pericd $2\pi/p$.

S_p = reflection rotation. Some authors define as rotation followed by reflection in a plane perpendicular to axis of rotation--some as rotation followed by reflection in the center of inversion. Wigner uses the latter convention.

Note that

$$(S_p)^2 = C_{p/2};\ (S_p)^{p/2} = C_2 \ (p/2 \text{ even}),$$

$$C_2 \cdot \sigma_h = \sigma_h \cdot C_2 = i,$$

$$C_2 \cdot i = i \cdot C_2 = \sigma_h.$$

In general σ_h denotes a symmetry plane perpendicular to axis of symmetry, while σ_v means one containing the axis of symmetry.

There are 32 different crystallographic groups, but this listing involves numerous redundancies due to isomorphisms. In all there are 14 really different kinds of so-called point groups, but two of these involve icosahedron structures which cannot be extended into space groups so as to build crystals. The so-called space groups involve translation as well as just symmetry operations with respect to a point. It can be shown that there are 230 different space groups.

Point Groups

1. C_p. 2. S_p.

3. C_{pv}. Here C_{pv} means that besides the symmetry C_p, there is a symmetry plane σ_v containing the rotation axis. The existence of the symmetry C_p implies that there are p-1 other such planes.

Note that the leaves of the planes come at intervals π/p, not $2\pi/p$.

4. D_p--dihedral group. C_p and a thereto perpendicular twofold axis determine p-1 further twofold axes, that intersect in a point and make angles π/p with each other.

5. C_{ph} C_p and a thereto perpendicular plane σ_h.

6. D_{pd}. If in D_p we introduce a vertical plane that halves the angle between the two axes, then there are p-1 further such planes, and there is thus a rotation reflection axis S_{2p} determined.

7. D_{ph}. If besides C_{pv}, there is a plane σ_h perpendicular to the axis, then the intersection of σ_v and σ_h determine a twofold axis C_2.

Special Cases

$V = D_2$ = four group

$V_h = D_{2h}$. Equivalent to V and a symmetry center. Three symmetry planes through the three axes are determined.

$V_d = D_{2d}$. Equivalent to V and vertical plane that halves the two axes. The symmetry requires that there be another such plane, and a fourfold rotation reflection axis S_4.

8-12 Cubic Groups

These are best understood by means of a cube, whose surfaces are intersected at their midpoints by the twofold axes of the four group V.

8. T = tetrahedral group. If one puts a threefold axis along a cube body diagonal, then three further threefold axes are determined in virtue of the symmetry, along remaining body diagonals.

9. T_d. One of the twofold axes of T becomes a fourfold rotation-reflection axis. The same holds for the other twofold axes. There are then planes of of symmetry through each two body diagonals--six such planes in all. Note that T_d represents the symmetry that one has in connection with an ordinary model of a tetrahedron, whereas T represents the symmetry of a model that it would not be legitimate to turn inside out.

10. O = Octahedron group (or cubic group). One of the twofold axes of T becomes a fourfold axis. Same applied to others. There are then six twofold axes not found in T (surface diagonals).

11. T_h = T and a symmetry center at cube center.

12. O_h = O and a symmetry center at the cube center.

13. I. Simple icosahedron group. Group of the spacial rotations of an icosahedron (20 equilateral triangles) or a pentagon dodecahedron (12 pentagons). There are six fivefold, ten threefold, and fifteen twofold axes.

14. I_h. Complete icosahedron group with center of symmetry included.

Number of elements

p for C_p, S_p,	2p for C_{pv}, D_p, C_{ph},	4p for D_{ph}, D_{pv},
12 for T,	24 for T_d, O, T_h,	48 for O_h,
60 for I,	120 for I_h.	

CHARACTER TABLES FOR THE 32 CRYSTALLOGRAPHIC POINT GROUPS

Triclinic

C_1	E
A	1

Also $C_{1i} = C_1 \times i$

Monoclinic

C_2; Co		E	C_2
	C_s	E	$iC_2 = \sigma$
A; z	A'	1	1
B; x or y	A''	1	-1

Also $C_{2h} = C_2 \times i$

Orthorhombic

$V \equiv D_2$; Co		E	$C_2(z)$	$C_2(y)$	$C_2(x)$
	C_{2v}	E	$C_2(z)$	$iC_2(y) = \sigma_v$	$iC_2(x) = \sigma_v$
A_1	A_1	1	1	1	1
B_1; z	A_2	1	1	-1	-1
B_2; y	B_1	1	-1	1	-1
B3; x	B_2	1	-1	-1	1

Also $V_h \equiv D_{2h} = V \times r$

Tetragonal

D_4; Co	E	C_2	$2C_4$	$2C_2$	$2C_2'$
C_{4v}	E	C_2	$2C_4$	$2iC_2 = \sigma_v$	$2iC_2' = \sigma_d$
$V_d \equiv D_{2d}$	E	C_2	$2iC_4 = 2S_4$	$2C_2$	$2iC_2' = \sigma_d$
A_1	1	1	1	1	1
A_2; z	1	1	1	-1	-1
B_1	1	1	-1	1	-1
B_2	1	1	-1	-1	1
E; x±iy	2	-2	0	0	0

C_4; Co	E	C_2	C_4	C_4^3
S_4	E	C_2	S_4	S_4^3
A; z	1	1	1	1
B	1	1	-1	-1
E;	1	-1	-i	i
x ±iy	1	-1	i	-i

Also $D_{4h} = D_4 \times i$, and

$C_{4h} = C_4 \times i$

Hexagonal

D_6; Co			E	C_2	$2C_3$	$2C_6$	$3C_2$	$3C_2'$
	C_{6v}		E	C_2	$2C_3$	$2C_6$	$3iC_2=3\sigma_v$	$3iC_2'=3\sigma_v$
		D_{3h}	E	$iC_3=\sigma_h$	$2C_3$	$2iC_6=2S_6$	$3C_2$	$3iC_2'=3\sigma_v$
A_1	A_1	A_1'	1	1	1	1	1	1
A_2; z	A_2	A_2'	1	1	1	1	-1	-1
B_1	B_2	A_1''	1	-1	1	-1	1	-1
B_2	B_1	A_2''	1	-1	1	-1	-1	1
E*	E*	E'	2	2	-1	-1	0	0
E*; x±iy	E*	E''	2	-2	-1	1	0	0

Also $D_{6h} = D_6 \times i$

C_6; Co	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	-1	1	-1	1	-1
E*	1	ω^2	$-\omega$	1	ω^2	$-\omega$
	1	$-\omega$	ω^2	1	$-\omega$	ω^2
E*	1	ω	ω^2	-1	$-\omega^2$	$-\omega$
	1	$-\omega^2$	$-\omega$	-1	ω^2	ω

Note: $\omega = \epsilon^{2\pi i/6} = -\omega^4$

Also $C_{6h} = C_3 \times i$; also $C_{3h} = C_3 \times \sigma_h$, with states A', A'', E', E''

Rhombohedral

D_3; Co	E	$2C_3$	$3C_2'$
C_{3v}	E	$2C_3$	$3iC_2'=3\sigma_v$
A_1	1	1	1
A_2; z	1	1	-1
E; x±iy	2	-1	0

C_3	E	C_3	C_3^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

Note: $\omega = \epsilon^{2\pi i/3}$

Also $D_{3d} = D_3 \times i$; $C_{3i} = S_6 = C_3 \times i$

Cubic

C; Co	E	$3C_2$ (x,y,z)	$4C_4$	$6C_2$	$8C_3$
Td	E	$3C_2$	$3iC_4=S_4$	$6iC_2=3\sigma_d$	$8C_3$
A_1	1	1	1	1	1
A_2	1	1	-1	-1	1
E	2	2	0	0	-1
T_1; (x,y,z)	3	-1	1	-1	0
T_2	3	-1	-1	1	0

T	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E	1	1	ω^2	ω
	1	1	ω	ω^2
T	3	-1	0	0

Note: $\omega = \epsilon^{2\pi i/3}$

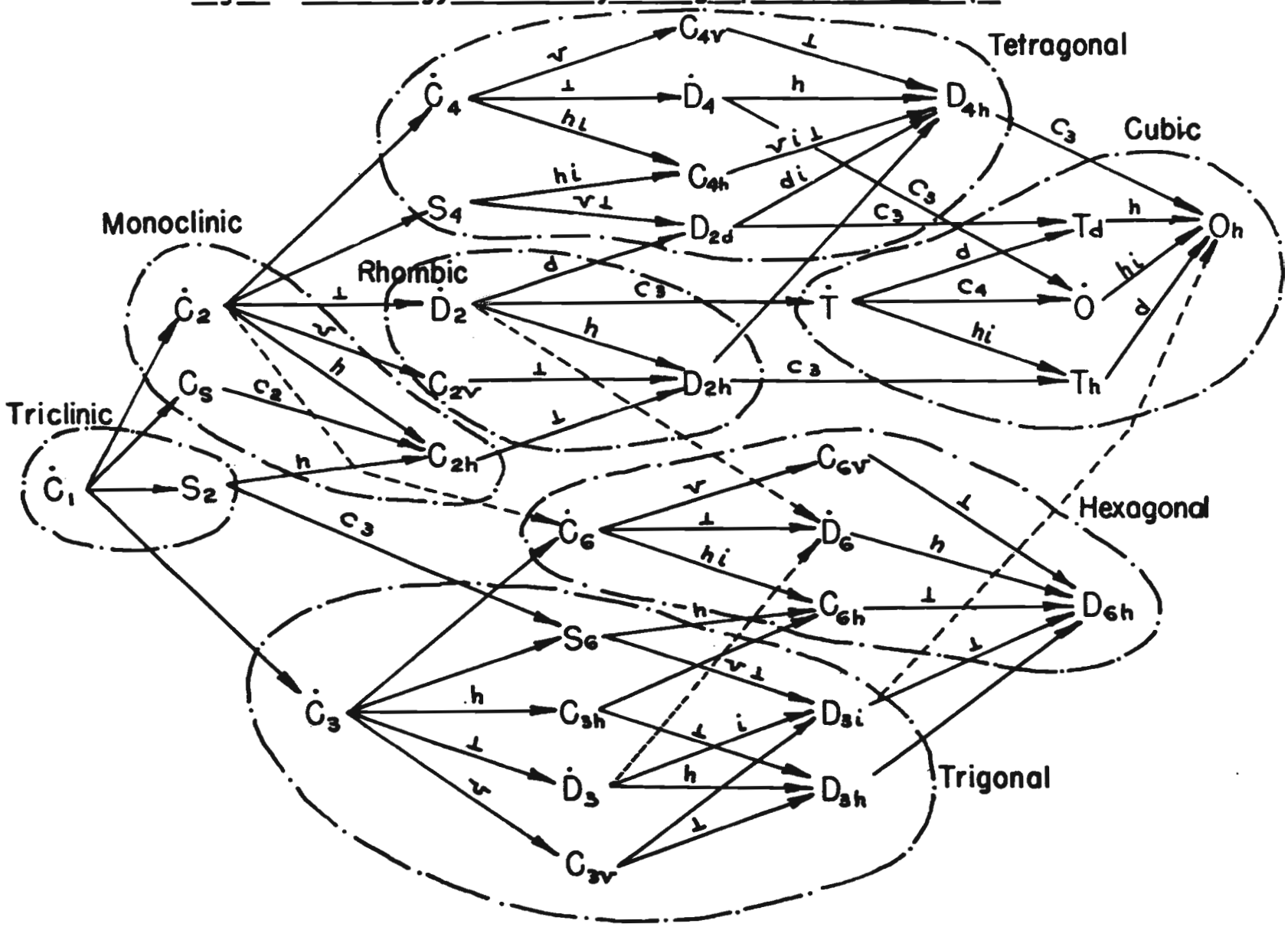
Also $O_h = O \times i$; $T_h = T^h \times i$

The icosahedron group is not one of the 32 crystallographic point groups. Its character table, however, is as follows:

E	$20C_3$	$15C_2$	$12C_5$	$12C_5^2$
1	1	1	1	1
3	0	-1	x	y
3	0	-1	y	x
4	1	0	-1	-1
5	-1	1	0	0

with $2x = 1 + \sqrt{5}$, $2y = 1 - \sqrt{5} = -4 \cos 72^\circ$

Fig.13 - Genealogy of the Crystallographic Point Groups



RULE FOR CONSTRUCTING BASIS VECTORS WHICH TRANSFORM IRREDUCIBLY

If one has a set of basis vectors whose transformation scheme is known for the various group operations, and if the matrices for the group elements appropriate to the various irreducible representations are known, then the procedure described below enables one to construct linear combinations of these basis vectors which transform in fashions appropriate to irreducible representations. In other words, these linear combinations span invariant subspaces. Note that this rule in a certain sense tells one the answer only if one knows the answer, i.e. if the matrices for the irreducible representations are known. Nevertheless it is a useful one when one knows the matrices for irreducible representations and desires to reduce out explicitly some given representation.

Let Ψ be a given basis vector, and let Ψ_R be the basis vector which is generated by applying the operation R, so that $R\Psi = \Psi_R$. Note that $\Psi_E = \Psi$, $R^{-1}\Psi = \Psi_{R^{-1}}$ and $\rho\Psi_{R^{-1}} = \Psi_{\rho R^{-1}}$

The rule is the following: Let the $D^{(\ell_1)}_{\mu\nu}(R)$ be the matrices appropriate to an irreducible representation of dimensionality ℓ_1. Then the basis vectors

$$^{\mu}\Psi_{\nu} = \Sigma_R D^{(\ell_1)}_{\mu\nu}(R)\Psi_{R^{-1}} \quad (\mu \text{ fixed}, \nu \text{ variable}) \qquad (1)$$

are a set of ℓ_1 basis vectors which have the transformation properties appropriate to this given irreducible representation, or in other words

$$R^{\mu}\Psi_{\nu} = \Sigma_{\beta} D^{(\ell_1)}_{\beta\nu}(R)\,^{\mu}\Psi_{\beta} \qquad (2)$$

Proof of (2). One has

$$\rho\,^{\mu}\Psi_{\nu} = \Sigma_R D^{(\ell_1)}_{\mu\nu}(R)\,\Psi_{\rho R^{-1}}$$

or if one sets $R = S\rho$,

$$\begin{aligned}\rho\,^{\mu}\Psi_{\nu} &= \Sigma_S \Sigma_{\beta} D^{(\ell_1)}_{\mu\beta}(S) D^{(\ell_1)}_{\beta\nu}(\rho)\,\Psi_{S^{-1}} \\ &= \Sigma_{\beta} D^{(\ell_1)}_{\beta\nu}(\rho)\,^{\mu}\Psi_{\nu}\end{aligned}$$

There are ℓ_1 choices for μ in (1). This means that our rule is in the most general case capable of giving ℓ_1 sets of basis vectors, each of which transforms in the scheme appropriate to the irreducible representation ℓ_1. This corresponds to the fact that the regular representation contains this representation ℓ_1 times. However, it may happen that the linear combinations given by (1) vanish for certain choices of ℓ_1. In other words, the manifold to be reduced may not span all inavariant subspaces. If, in particular, the given representation is irreducible, it is easily shown that choices of ℓ_1 but one will give one only zero.

Note that the formula (6), p. 114 of Wigner is incomplete and hence misleading, as it gives only one of the ℓ_1 vectors required to span an invariant subspace, viz. the one corresponding to $\mu = \nu$ in (1).

Exercise

Consider the group of elements corresponding to 1, a_1, a_2, a_{2K}, ... , $a_1a_2 \cdots a_{2K}$, -1, $-a_1$, $-a_2$, .., $-a_{2K}$, ..., $-a_1a_2 \cdots a_{2K}$ where the a's are 2K anticommuting quantities such that $a_ia_j + a_ja_i = 2\delta_j^{\ i}$. Show that the total number of elements is 2×2^{2K}.

Case I. 2K even.

Show that the number of classes is $2^{2K} + 1$. Show that there are 2^{2K} one-dimensional representations, and one representation of dimensionality 2^K. Show that this latter representation is faithful. (Hint: a sufficient condition for faithfulness is that no element have the same character as unity.)

Case II. 2K odd.

Show that the number of classes is $2^{2K} + 2$. Show that there are 2^{2K} one dimensional representations, and two representations of dimensionality $2^{K-\frac{1}{2}}$. Show that these two representations are faithful if 2K = 3, 7, 11, and unfaithful if 2K = 5, 9, 13,.... (The latter case shows, incidentally, that it is possible to have a group all of whose representations are unfaithful). Discuss the factor groups in the case of the unfaithful representations of dimensionality greater than one.

The Dirac Theory of Characters (PRS vol. 123).

Dirac's major observation is essentially that the sum of the matrices of all the elements of a given class commutes with all the matrices representing the different elements of the group. He therefore proceeds to diagonalize this sum, which he denotes by the letter omega. The eigenvalues of the omegas may be denoted by affixing primes, and when all the omegas are simultaneously diagonalized we say that the system is Dirac-reduced. Note that the omegas, without primes, have meaning for an arbitrary representation. From the group multiplication table and the rearrangement theorem, it is readily seen that the omegas are the most general polynomial functions of the group elements which commute with all the elements of the group. A given Dirac-irreducible representation is characterized or labelled by the simultaneous eigenvalues of the omegas belonging to the different classes. A matrix representing any element of the group clearly has block structure-relative to these eigenvalues. Note especially that the labelling involves giving the simultaneous, compatible eigenvalues of all the omegas corresponding to the different classes. One wonders at first whether Dirac-irreducibility corresponds to ordinary irreducibility, but it is not difficult to see that the two definitions correspond.* In the first place, his omegas commute with all the matrices representing the different group elements, and hence must be constant within an irreducible representation in the ordinary sense. Furthermore the regular representation shows that a linear dependence between the omegas belonging to different classes is impossible and hence there must be at least as many different sets of eigenvalues of the omegas as there are classes. However, we know that there cannot be more primitive characters than there are classes. Hence no reduction beyond Dirac reduction is possible. As a corollary we have a proof that the number of primitive characters equals the number of classes--- previously we only proved that the number of classes was an upper bound to the number of irreducible representations.

The eigenvalues of the omegas can be calculated from the algebraic equations which they satisfy and which follow from expressing powers of the omegas as linear combinations of omegas by means of the group multiplication table. Dirac defines character as a set of simultaneous eigenvalues of his omegas, divided by the number of elements in each class. Since Dirac deals with eigenvalues rather than diagonal sums the ordinary definition of primitive character differs from the Dirac one by the dimensionality but the latter is readily spotted from the normalization relation satisfied by primitive characters.

*Except, of course for the possibility of a given irreducible representation being repeated. In the latter event diagonalization of the omegas only insures that the blocks be of dimensions In where I is the dimensionality of the irreducible representation and n the number of times it is repeated.

Application of Group Theory to Small Vibrations.

References:

Wigner, Gottinger Nachrichten, 1930.
E. B. Wilson, Phys. Rev. 45, 706 (1934).
J. Chem. Phys. 2, 432 (1934).
Rosenthal and Murphy, Rev. Mod. Phys., vol. 8.

The standard theory of small vibrations (any dynamics textbook) is based on potential and kinetic energies that are respectively homogeneous quadratic functions of the displacement coordinates, and corresponding velocities

$$V = \tfrac{1}{2} \Sigma\, a_{rs}\ q_r\ q_s, \qquad T = \tfrac{1}{2} \Sigma\, b_{rs}\ \dot{q}_r\ \dot{q}_s$$

Application of Lagrange's equations leads immediately to the secular equation.

$$\left| - 4\pi^2 \nu^2 b_{jk} + a_{jk} \right| = 0.$$

It can be shown that the kinetic and potential energies are simultaneously transformable to sum of squares, i.e.,

$$T = \tfrac{1}{2} \Sigma_k\, B_k\, \dot{Q}_k^{\,2} \qquad\qquad V = \tfrac{1}{2} \Sigma_k\, A_k\, Q_k^{\,2}$$

The Q_k are simple harmonic functions of the time and called normal coordinates.

At first sight, inspection of the secular equation leads to an algebraic equation of degree $3n$ for determining the vibration frequencies, if the molecule contains n atoms. Allowance, however, for the fact that rigid rotation and translation pretty obviously correspond to zero vibration frequencies, shows us that 6 of the roots must be zero, and that there can be only $3n-6$ independent vibration frequencies. The great service of group theory is to show that actually, when there is symmetry, the secular equation factors, and that roots often coincide, so that actually the algebraic degree is much less.

The starting point is the observation that if we make any of the covering operations corresponding to the covering operations of the group, the new displacements are linear functions of the old, and hence the theory of substitution groups is applicable. The representation is obviously one of dimensionality $3n$. In general it is reducible. This means that by introducing linear transformations from the original q's to appropriately chosen other coordinates, called symmetry coordinates, the $3n$ dimensional carrier space decomposes into invariant subspaces. A simple argument shows that symmetry coordinates corresponding to different irreducible representations are not on "speaking terms" in the secular equation. Furthermore, if an irreducible representation is of dimensionality k, the corresponding vibration frequencies are k-fold degenerate, or in other words the corresponding roots of the secular equation coincide in groups of k. When

account is taken of symmetry, the effective degree of the factored secular equation is the number of times a given irreducible representation is contained in the given original 3n fold (reducible) representation, diminished by the number of times this given irreducible representation is contained in rigid rotation and translation.

To compute the number of times a given irreducible representation occurs in we use the theory of characters. We need to know

(a) the primitive characters of the relevant symmetry group. See the Mulliken tables for this.

(b) the character of the original 3n dimensional representation. The rule for this is

$$\chi_R = (1 + 2\cos\phi_R) \cdot U_R \qquad \text{for a rotation through an angle } \phi_R$$

$$\chi_R = (-1 \mp 2\cos\phi_R) \cdot U_R \qquad \text{for a rotation-reflection.}$$

Here U_R denotes the number of atoms left invariant or unpermuted under the covering operation in question. The upper or lower sign applies according as rotation-reflection is defined as rotation followed by reflection in the center, or as rotation followed by reflection in a plane.

(c) the characters corresponding to rigid translation, viz.

$$\chi_R = (1 + 2\cos\phi_R) \qquad \text{for a rotation}$$

$$\chi_R = (-1 \mp 2\cos\phi_R) \qquad \text{for a rotation-reflection}$$

(d) the character corresponding to rigid rotation, viz.

$$\chi_R = (1 + 2\cos\phi_R) \qquad \text{for a rotation}$$

$$\chi_R = (1 \pm 2\cos\phi_R) \qquad \text{for a rotation-reflection}$$

One subtracts the characters of (c) and (d) from (b). This gives the effective character to be reduced out according to (a).

Note that symmetry coordinates are in general not normal coordinates unless the corresponding irreducible representation occurs only once. The existence of the symmetry coordinates can be inferred from the theory of characters. They can be found by reducing out the group. On the other hand, the determination of the normal coordinates requires in general explicit solution of the factored secular equation to find the appropriate linear transformation to them.

Even though a given type of molecular vibration spectrum exists, it may not show up in absorption spectra, or in other words may be infra-red inactive. Since ordinary absorption can result only if there is an electric dipole moment oscillating with the frequency in question, and since the electric dipole moment transforms like a

vector, i.e. like a translation, only those vibrations are infra-red active whose primitive characters are contained in (c).

In the Raman effect one observes things which transform like a quadratic form. The general quadratic form contains 9 basis vectors, but can be decomposed into (A) an invariant, (B) a 5-dimensional basis corresponding to the remainder of the symmetrical direct product, and (C) the antisymmetrical part. Obviously (A) has the same character as that of the identical representation. The character of (B) is

$$\chi_R = 1 + 2\cos\phi_R + 2\cos 2\phi_R \qquad \text{for a rotation}$$

$$\chi_R = 1 \pm 2\cos\phi_R + 2\cos 2\phi_R \qquad \text{for a rotation-reflection.}$$

The character of (C) is the same as that of (d) above.

In practice (C) seldom occurs in the Raman effect (specifically only if the electronic state of the molecule is degenerate, and one is near resonance), so that one usually forgets all about the possibility (C). The character of (d) is also that of magnetic dipole radiation, but in practice any magnetic moments associated with molecular vibrations are of negligible intensity as regards radiation. A vibration is Raman-active, (barring exceptions of type C) only if its irreducible representation is either the identical one, or has one of the primitive characters contained in (B).

Some incidental results regarding the type of polarization in the Raman effect can be obtained by the examination of the characters. The depolarization ratio is defined as the ratio of the intensity of the scattered light whose electric vector is parallel to the incident beam to that perpendicular to this beam, with the understanding that the direction of observation is also perpendicular to this beam. The depolarization ratios are zero if the vibration is totally symmetrical (identical representation) and if the identical representation is not contained in (B). The depolarization ratios for plane and unpolarized light are respectively 3/4 and 6/7 for a non-totally-symmetric vibration contained in (B). A totally symmetric vibration whose character is contained in (B) as well as (A) will in general have a depolarization ratio intermediate between zero and these values. For (C) these ratios are ∞ and 2.

Most General Form of a Spatially Invariant Differential Equation

(Wigner, Chap. XIX.)

$$\Psi^{(J)}_M = \sum_{K=-J} f_K^{(J)} D^{(L)}(\varphi,\theta,\chi)^*_{MK} \qquad \left(D^{(L)}_{MK} = e^{iM\varphi} F^{(L)}_{MK} e^{iK\chi}\right)$$

where φ, θ, χ are Eulerian angles, and the coefficients f are functions only of the "internal coordinates. For the asymmetrical top, these coefficients are constants. For the symmetrical top there is only one term. Thus the representation coefficients $D^{(L)}_{MK}$ are the same as symmetrical top wave functions. Tesseral harmonics correspond to the specialization $K=0$, and Legendre polynomials to the further specialization $M=0$

Reduction of the direct product

$$\Psi^{(L)}_M = \sum_{m_1,m_2} A^{L\,l_1,l_2}_{M\,m_1,m_2} \psi^{(l_1)}_{m_1} \psi^{(l_2)}_{m_2} \qquad (1)$$

If the various functions are consistently normalized, the A's are the celebrated Wigner coefficients. Instead of the method of Chap. XVI of Wigner, a perhaps more elegant method of computing the A's is furnished by the observation that if ξ_1, η_1 and ξ_2, η_2 transform in the same way, then $\xi_1\eta_2 - \eta_1\xi_2$ is an invariant (why?), and hence the coefficient of x^p (x a parameter) in the multinomial of just

$$C(\xi_1\eta_2 - \xi_2\eta_1)^q (\xi_1 + x\xi_2)^{L+M} (\eta_1 + x\eta_2)^{L-M} \Big/ \sqrt{(L+M)!\,(L-M)!} \qquad (2)$$

is a multinomial of just the transformation properties desired for $\Psi^{(L)}_M$ if

$$p+q = 2l_1 \qquad 2L - p + q = 2l_2 \qquad M = m_1 + m_2 \qquad (3)$$

whence $p = L - (l_1 - l_2)$, $q = l_1 + l_2 - L$, $m_1 + m_2 = M$ (why?)

The Wigner coefficients are then given by

$$w^{(L)}_M = \sum_{m_1} A^{L\,l_1,l_2}_{M\,m_1,m_2} \xi_1^{l_1+m_1} \eta_1^{l_1-m_1} \xi_2^{l_2+m_2} \eta_2^{l_2-m_2} \frac{1}{\sqrt{(l_1+m_1)!\,(l_1-m_1)!\,(l_2+m_2)!\,(l_2-m_2)!}}$$

provided the constant C is so determined that the sum of the squares of the coefficients A is unity. Here $w^{(L)}_M$ denotes the coefficient of x^p in (2) chosen in accordance with (3).

For detailed working out of the coefficients in this way see Eckart, Rev. Mod. Phys. vol. 1, p. 351 ff.

Relative Intensities of Zeeman Components by Group Theory.

The key observation is that if the $\Psi^{(L)}_M$ are consistently normalized

$$\int\int \Psi^{(L)*}_M \Psi^{(L)}_{M'} \sin\theta\, d\theta\, d\varphi\, d\chi = \delta^{L'}_{L}\, \delta^{M'}_{M} \cdot \text{const}$$

Hence, since $(x+iy)/\sqrt{2}$, $-iz$, $(x-iy)/\sqrt{2}$ transform like $\frac{1}{\sqrt{2}} \eta_1^2, \xi_1\eta_1, \pm\xi_1^2$

$$\int \cdots \int \psi^{l'}_{m'} \begin{Bmatrix} (x+iy)/\sqrt{2} \\ -iz \\ (x-iy)/\sqrt{2} \end{Bmatrix} \psi^{l}_{m}\, d\tau = C \begin{Bmatrix} A^{l'l1}_{m'm-1} \\ A^{l'l1}_{m'm0} \\ A^{l'l}_{m'm+1} \end{Bmatrix}$$

where C is independent of m or m'.

A very elegant variant of this procedure is the Kramers symbolic method, based on spinor analysis, for which see his collected works, or Proc. Amsterdam Acad. vol. 33, p. 953.

But the $A^{l\,l\,1}_{m'\,m\,\nu}$ are as follows

(cf. End Chap XVII of Wigner)

l' \ ν	-1	0	1
$l-1$	$\sqrt{\frac{(l+m)(l+m-1)}{2l(2l+1)}}$	$-\sqrt{\frac{(l-m)(l+m)}{l(2l+1)}}$	$\sqrt{\frac{(l-m-1)(l-m)}{2l(2l+1)}}$
l	$\sqrt{\frac{(l-m+1)(l+m)}{2l(l+1)}}$	$\frac{m}{\sqrt{l}\sqrt{l+1}}$	$-\sqrt{\frac{(l+m+1)(l-m)}{2l(l+1)}}$
$l+1$	$\sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+2)}}$	$\frac{\sqrt{(l-m+1)(l+m+1)}}{\sqrt{2l+1}\sqrt{l+1}}$	$\frac{\sqrt{l+m+1}\sqrt{l+m+2}}{\sqrt{2l+1}\sqrt{2l+2}}$

whence

$$(l-1\,m-1|x+iy|l\,m) = C\sqrt{(l+m)(l+m-1)}$$
$$(l-1\,m|-iz|l\,m) = -C\sqrt{l^2-m^2}$$
$$(l-1\,m|x-iy|l\,m) = C\sqrt{(l-m-1)(l-m)}$$

or

$$(l\,m|ix-y|l+1\,m+1) = C'\sqrt{(l+m+1)(l+m+2)}$$

$(C' = \frac{C}{i})$ $$(l\,m|z|l+1\,m) = -C'\sqrt{(l+1)^2-m^2}$$
$$(l\,m|ix+y|l+1\,m-1) = C'\sqrt{(l-m+1)(l-m+2)}$$

London & Shortley have (p. 623)

$$(l\,m|x\mp iy|l+1\,m+1) = -C'\sqrt{(l+m+1)(l+m+2)}$$
$$(l\,m|z|l+1\,m) = C'\sqrt{(l+1)^2-m^2}$$
$$(l\,m|x+iy|l+1\,m-1) = C'\sqrt{(l-m+1)(l-m+2)}$$

This corresponds to replacing y, x by $-x, y$ (rot. thru 90°) and i by $-i$ (taking azimuthal factor in wave function as $e^{im\varphi}$ rather than $e^{-im\varphi}$).

Proof of Identity of Representation Coefficients as given in Wigner with Wave Functions satisfying the Differential Equation of the Symmetrical top, or with ordinary Tesseral Harmonics when one of the Eulerian angles is missing.

(Proof due to John T. Tate, Jr.)

The symmetrical top functions, which are most conveniently expressed in terms of Jacobi polynomials, can be written in the form

$$e^{+i(n'\alpha+n\gamma)}\frac{(-1)^{l-n'}}{(n+n')!}\sqrt{\frac{(l+n)!(l+n')!}{(l-n)!(l-n')!}}\,G_{l-n'}(2n'+1,n'+n+1,x)\,x^{\frac{1}{2}(n+n')}(1-x)^{\frac{1}{2}(n'-n)} \qquad (1)$$

where $x = \frac{1+\cos\beta}{2}$

Here G_N denotes the Jacobi polynomial

$$G_N(\rho,q,x)=\frac{(q-1)!\,x^{1-q}(1-x)^{q-\rho}}{(q+N-1)!}\frac{d^N}{dx^N}\left[x^{N+q-1}(1-x)^{N+\rho-q}\right]$$

so that

$$G_{l-n'}(2n'+1;n+n'+1,x)=\frac{x^{-n-n'}(1-x)^{n-n'}}{(l+n)!}(n+n')!\frac{d^{l-n'}}{dx^{l-n'}}\left[x^{l+n}(1-x)^{l-n}\right] \qquad (2)$$

For proof that the symmetrical top functions are expressible in terms of Jacobi polynomials, see Reiche and Rademacher, Zeits. f. Physik 39, 444 (1926), or Kronig and Rabi, Phys. Rev. 29, 262 (1927). The differential equation of the symmetrical top is

$$\frac{\partial^2\psi}{\partial\beta^2}+\frac{\cos\beta}{\sin\beta}\frac{\partial\psi}{\partial\beta}+\left(\frac{A}{C}+\frac{\cos^2\beta}{\sin^2\beta}\right)\frac{\partial^2\psi}{\partial\alpha^2}+\frac{1}{\sin^2\beta}\frac{\partial^2\psi}{\partial\gamma^2}-\frac{2\cos\beta}{\sin^2\beta}\frac{\partial^2\psi}{\partial\alpha\partial\gamma}+\frac{8\pi^2AE}{h^2}\psi=0$$

where A,B(=A), and C are the principal moments of inertia. To show that (1) actually satisfies the equation of the symmetrical top one first verifies that the equation is satisfied for the special case $n'=l$, and then shows inductively by differentiation that it is satisfied by values of n' progressively one unit smaller. The particular form of the Jacobi polynomials which we use is that given in Courant-Hilbert, Methoden der Mathematischen Physik, p. 75. The wave function (1) is also, except for phase factors, the same as given by the writer in Phys. Rev. 33, p. 476, Eq. (17). (The factorial sign there after 1+d+s+2p is a misprint. In this connection it should be noted that the wave function of (17) is normalized to 2, rather than $4\pi/(2l+1)$.

The ordinary Rodrigue definition of associated Legendre functions is included as a special case, for if we set n=0, the expression (1) becomes

$$e^{+in'\alpha}(-1)^{l-n'}\sqrt{\frac{(l+n')!}{(l-n')!}}\,\frac{x^{-\frac{n'}{2}}(1-x)^{-\frac{n'}{2}}}{l!}\,\frac{d^{l-n'}}{dx^{l-n'}}\left[x(1-x)\right]^l$$

or if we use the notation $\mu=\cos\beta$, $m=-n'$

$$(-1)^m e^{-im\alpha}\frac{1}{2^l}\frac{1}{l!}\sqrt{\frac{(l-m)!}{(l+m)!}}(1-\mu^2)^{m/2}\frac{d^{l+m}}{d\mu^{l+m}}\left[(\mu^2-1)\right]^l$$

Except for a phase factor, this expression is the standard one for defining associated Legendre functions. The factor $\sqrt{(\ell-m)!(\ell+m)!}$ arises because our functions are normalized to $4\pi/(2\ell+1)$ whereas the associated Legendre functions are normalized to $4\pi(\ell+m)!/(\ell-m)!$

If we use the Leibnitz rule for differentiation, viz.,

$$\frac{d^N}{dx^N}(ab) = \frac{d^N a}{dx^N} b + N \frac{d^{N-1} a}{dx^{N-1}} \frac{db}{dx} + \cdots$$

we see that the expression (2) is the same as

$$x^{-n'-n}(1-x)^{n-n'}(n+n')! \sum_{K=0}^{\ell-n'} \frac{(-1)^{\ell-n'-K}(\ell-n')!(\ell-n)!}{K!(\ell-n'-K)!(\ell+n-K)!(n'-n+K)!} x^{\ell+n-K}(1-x)^{n'-n+K}$$

Hence (1) is the same as

$$e^{+i(n'\alpha+n\gamma)} \sum_K (-1)^K \frac{\sqrt{(\ell-n')(\ell+n')(\ell-n)!(\ell+n)!}}{K!(\ell-n'-K)!(\ell+n-K)!(n'-n+K)!} x^{\ell-K+\frac{1}{2}(n-n')}(1-x)^{K-\frac{1}{2}(n-n')}$$

This is the same as Wigner's formula (27), p. 167, if we identify K, n, n' with ν, μ, μ'.

As a corollary of our proof, note that we have verified the normalization factor in (1), which requires a little calculation by the direct approach.

Review Topics

Physics 264

1. Definitions. Group, order, sub-group, coset, period, etc. Criterion for identity of two cosets.
2. The rearrangement theorem.
3. Prove that the order of a subgroup is a divisor of the order of the entire group.
4. The concept of class. Self-conjugate subgroups. Factor groups.
5. Isomorphy and homomorphy.
6. Representation of a group by linear substitutions or matrices. The concept of carrier space spanned by basis vectors. Unitary and orthogonal transformations.
7. Prove that the transformation matrix of the coordinates is the transpose of the reciprocals of the transformation matrix of the basis vectors.
8. Suppose we have two manifolds M and $\overline{M}$ connected by a transformation S. Then a transformation D applied to M generates in $\overline{M}$ the transformation $S^{-1}DS$. This theorem is very important. Be able to prove.
9. The concept of reducibility and interpretation in terms of invariant subspaces.
10. Faithful (isomorphic) and unfaithful (homomorphic) representations.
11. Elementary algebraic definitions and theorems. The concept of an equivalence or canonical transformation. Unitary and Hermitean matrices. Invariance of diagonal sum. Equivalence of reduction of matrix to diagonal form by means of a unitary transformation to transformation of a Hermitean matrix to sum of squares of moduli. Note that the equivalence is lost when the transformation is not unitary.
12. Characteristic values of matrices. Does a matrix have characteristic values even if not diagonalizable?
13. Know the theorem that any Hermitean or any unitary matrix can be diagonalized by means of a unitary transformation, but omit proof.
14. Omit proof that any two matrices differing from each other only in corresponding permutations of rows and columns can be transformed into each other by means of an equivalence transformation.
15. Necessary and sufficient condition for a matrix to have a reciprocal is that its determinant not vanish.
16. Prove that the necessary and sufficient condition that two diagonalizable matrices be simultaneously diagonalizable is that they commute.
17. Prove that any matrix which commutes with all the elements (matrices) of an irreducible representation is a constant.
18. Prove that every representation of a group with non-vanishing

18. determinant can be brought into unitary form by means of an equivalence transformation.

19. State Schur's lemma. Be able to prove, assuming the results of 18.

20. Derive the "wonderful orthogonality theorem" from Schur's lemma.

21. Character. Why is it so important and useful? What are primitive characters?

22. The two kinds of orthogality relations for primitive characters. Be able to deduce the first kind from the "wonderful orthogonality theorem". Derivation of the relation of the second kind from that of the first kind merely utilizes the equivalence of left and right sided reciprocals.

23. Dirac's approach to character.

24. The regular representation. Prove that the number of different sets of primitive characters cannot be greater or less than the number of classes.

25. Prove that the regular representation contains each irreducible representation a number of times equal to its dimensionality.

26. The "machine" for constructing basis vectors which transform in a fashion appropriate to an irreducible representation. Prove. Note that the machine may not furnish basis vectors for all the different irreducible representations, as the carrier space to which it is applied may not contain all possible types of invariant subspaces.

27. The direct product of two representations. The symmetrical and antisymmetrical product of a representation with itself. Distinguish between the direct product of two representations and the closely allied concept of the direct product of two groups.

28. Omit proof of the Lorentz invariance of the Dirac equation by means of the properties of a certain group with 17 classes.

29. Don't attempt to memorize the 32 different point groups, or their representations. Know, however, what the notation means.

30. The transformation properties of vectors, second rank symmetrical (Raman) and anti-symmetrical (magnetic dipole) tensors under rotation and reflection. (Elementary, but basic and important).

31. Molecular vibrations. Idea that the transformation of the small displacements under the symmetry operations furnishes a representation of the group, in general reducible. Subtracting out of irrelevant rigid translations and rotations. Be able to indicate schematically how the secular equation factorizes in terms of different irreducible representations and their components. Omit proof.

32. Given the model of the molecule, the molecular symmetry type and its character table, be able to determine how the secular equation factorizes, and whether a vibration is infra-red active, and whether it is Raman active. Omit polarization properties of the Raman effect.

33. The generalization of the "wonderful orthogality theorem" and the orthogonality relations for character to continuous groups.

34. Identification of class for the rotation group with the amount of "total rotation". Deduction of characters for the irreducible representations from the elementary properties of spherical harmonics. How is the irreducibility proved? Show that the orthogonality property, furnishes uniquely, except for a constant factor, the volume element appropriate to the integration. This element is hard to obtain in a direct, rigorous fashion.

35. The homomorphy of the unitary group in two variables and the rotation group. Resulting machine for generating the transformation coefficients or matrices for the irreducible representations of the rotation group.

36. Correlation of the degree of degeneracy of quantum-mechanical energy levels with the dimensionality of the irreducible representation. Prove that the solutions of the Schrodinger equation transform in a fashion appropriate to irreducible representations of whatever groups leave this equation invariant. Any perturbation calculation can blend together in the expansion only solutions belonging to the same irreducible representation as long as the symmetry is preserved.

37. Determination of the most general angular dependence of the solution of a differential equation which is invariant of the choice of axes. This is accomplished by expressing the solution in a fixed coordinate system in terms of one travelling with the particles or with the point of observation. In the case of only one particle, or an ordinary x,y,z problem, one of the Eulerian angles drops out, and so we see that except for a normalization factor, the D_{-mo}^{*} must be the same as the conventional Tesseral harmohics (provided of course we use exponential rather than cosine or sine azimuth factors). Similarly, the general $D_{mm'}$ must be essentially the wave functions of the symmetrical top, since the latter involve both azimuth angles through exponential factors.

38. Use of group theory to determine splitting pattern of energy levels as molecule is submitted to fields of progressively lower symmetry.

39. Interpretation of the reduction of the direct product of two representations of the rotation group in terms of the vector model--private versus community spacial quantization. Show that the character scheme gives the same enumeration of states as does the vector model.

40. Explicit reduction of the direct product. Wigner coefficiehts. Determination of these by the psi-eta calculus.

41. Derivation of selection rules, and relative intensities of Zeeman components by means of group theory. Advantage as compared to explicit integrations, that the number of particles is arbitrary.

42. Double-valued representations of the rotation group. They actually have a physical meaning for systems with odd numbers of electrons when spin is considered. Two-fold degeneracy persists in any electric field, regardless of how unsymmetrical. (This is the Kramers theorem--It cannot be established in an elementary way if the symmetry is too low.)

43. Interpretation of angular momentum operators in terms of infinitesimal rotations.

44. Permutation group. The allowable characters for orbital permutations are severaly restricted by the requirement of the Pauli exclusion principle that only antisymmetric solutions are allowed when both spin and orbit are permuted. Occurrence of different spin states determined by branching rule. Devices for avoiding group theory--Slater determinants and the Dirac vector model.

The character table for the double-valued cubic group 48 elements (Bethe, Ann. der Physik 3,133 (1929).

E	R	$6C_2$	$6C_4$	$6C_4^3$	$12C_{2'}$	$8C_3$	$8C_3^2$
1	1	1	1	1	1	1	1
1	1	1	-1	-1	-1	1	1
2	2	2	0	0	0	-1	-1
3	3	-1	1	1	-1	0	0
3	3	-1	-1	-1	1	0	0
2	-2	0	$\sqrt{2}$	$-\sqrt{2}$	0	1	-1
2	-2	0	$-\sqrt{2}$	$\sqrt{2}$	0	1	-1
4	-4	0	0	0	0	-1	1

(R, C_4^3, C_3^2 denote rotation through 360, 270, 240 degrees. Rotations through θ and $2\pi-\theta$ belong to different classes, whereas θ, $-\theta$ remain in same class).

Problems

1. Derive by group theory the addition theorem for surface harmonics, i.e. show that the relation

$$P_\ell^0(\cos\theta) = P_\ell^0(\cos\theta')P_\ell^0(\cos\beta) + 2\sum_{m=1}^{\ell}\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(\cos\theta')P_\ell^m(\cos\beta)\cos m(\varphi'-\alpha)$$

is essentially the same as Eq. (15.30) of Wigner. Also derive a transformation relation more general than that given in books on surface harmonics, in which left hand side is a general Tesseral harmonic than a Legendre polynomial; coefficients on right will involve the general D's or symmetrical top functions.

2. Derive (except for possible ambiguities of sign) from Eq. (17.15) p. 138 of Wigner the following recursion formulas for associated Legendre functions:

$$\cos\theta P_\ell^m = \frac{(\ell-m+1)P_{\ell+1}^m + (\ell+m)P_{\ell-1}^m}{2\ell+1}, \quad \sin\theta P_\ell^m = \frac{P_{\ell+1}^{m+1} - P_{\ell-1}^{m+1}}{2\ell+1}$$

3. By elementary application of the psi-eta calculus for reducing the direct product, derive the top line of the table of Wigner coefficients given at bottom of p. 193 of Wigner.

4. Give the decomposition pattern for L=4 in a field of cubic symmetry, and then the further decomposition when the symmetry is lowered to trigonal by stretching the cube along a body diagonal.

5. Derive the above character table of the double-valued cubic group.

6. Discuss the decomposition of J=9/2 in field of cubic symmetry.

7. Derive the formulas for angular momentum matrices (including selection rules) by treating them as infinitesimal rotations.

8. Derive the characters of the icosehedron group.

9. Write out the formulas for some of the D's explicitly for $\ell=2$ by (a) Wigner's formulas, and (b) direct application of the psi-eta calculus and show that they reduce, except for normalization factors, to Tesseral harmonics when m=0.

10. Derive the formulas for the energy levels of a three electron system with permutation degeneracy (a) by reducing the regular representation (b) by using Slater determinants (Phys. Rev. 34, 1293 (1929), and (c) the Dirac vector model (PRS. 123, 714 (1929) or Physical Rev. 45, 405 (1934). Results should agree with treatment of problem in Wigner, Zs. f. Physik 40, 492.

Further exercises.

11. The three electron permutation degeneracy problem has a Hamiltonian

$$\mathcal{H} = V_0 + J_{12} P_{12} + J_{13} P_{13} + J_{23} P_{23}$$

Whe the "machine for constructing irreducably transforming basis vectors" to construct orbital wave functions which transform irreducably, out of product wave functions. Note that this problem is equivalent to reducing out explicitly the regular representation of our dagger group. Use the "machine" also to construct the correponding ~~adjoint~~ associated spin functions, and by taking the scalar product of the orbital and ~~adjoint~~ associated spin functions, get a total wave function that satisfies the Pauli principle. Show, in a typical case, that the wave function thus obtained can be written as a sum of Slater determinants.

The projection operator which is unity within a given irreducible representation ~~is~~ (and zero otherwise) is

$$\frac{l_r}{h} \sum_C \chi_C^{(r)*} \Omega_C \qquad (C = \text{class})$$

(The $\chi_C^{(r)}$, coventional characters, and the Ω's, the Dirac Ω operators. By using this projection operator, evaluate the energy for the orbital represetnations which occur only once. In this case only the trace of the energy is needed. Also evaluate the energy for the energy levels involved in the representation which occurs twice. In this case you will need to evaluate the trace of $\mathcal{H}$ and also the trace of $\mathcal{H}^2$.

Results for this problem can be checked against Wigner, Zeits. f. Physik 40, 492.

12. Derive the relative intensities of Zeeman components for the transition $l \to l+1$ by the Krumers symbolic method.

13. Give the qualtative splitting pattern for the various components of a ^4F level in a cubic field when spin-orbit interaction is included (including (a) the case that the crystalline field is weak (b) that it is strong, compared to the spin-orbit intaeraction.

Some useful formulas for decomposition in a cubic crystalline field (Bethe's notation).

J	
0	$\to \Gamma_1$
1	$\to \Gamma_4$
2	$\to \Gamma_3 + \Gamma_5$
3	$\to \Gamma_2 + \Gamma_4 + \Gamma_5$
4	$\to \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
5	$\to \Gamma_3 + 2\Gamma_4 + \Gamma_5$

J	
1/2	$\to \Gamma_6$ (Γ_6)
3/2	$\to \Gamma_8$
5/2	$\to \Gamma_7 + \Gamma_8$
~~7/2~~	~~$\to \Gamma_7 + \Gamma_8 + \Gamma_9$~~
7/2	$\to \Gamma_6 + \Gamma_7 + \Gamma_8$

Clearly if a_1, a_2, a_3 are the components of a vector, an integral such as

$$\int\int (a_1 x + a_2 y + a_3 z)^4 d\omega$$

is invariant of the choice of axes, and so must be proportional to $(a_1^2 + a_2^2 + a_3^2)^2$. By spotting coefficients, one can thus see, without integrating, that

$$\int\int x^2 y^2 d\omega = \frac{1}{3}\int\int x^4 d\omega$$

This is essentially the type of argument used by Kramers (p.405 of collected works) only he uses spinor rather than vector analysis. If a,b and A,B be two constant spinors (i.e. two sets of quantities, each of which transform like ξ, η from one set of axes to another), then

$$\int\cdots\int \left[\sum_{m=-l}^{l} \sqrt{\frac{(2l)!}{(l-m)!(l+m)!}}\, \psi_m^{l*}\, a^{l-m}\, b^{l+m}\right]^{2l'} \left[-(x-iy)A^2 + 2ABz + B^2(x+iy)\right]^{n} \left[\sum_{m'=-l'}^{l'} \sqrt{\frac{(2l')!}{(l'+m')!(l'-m')!}}\, \psi_{m'}^{l'*}\, a^{l'-m'}\, b^{l'+m'}\right]^{2n'} d\tau_1 \cdots d\tau_n$$

is invariant, or symbolically

$$\int (a\xi^* + b\eta^*)^{2l} \left[A^* X + B^* Y\right]^{2} \left[a^*\xi + b^*\eta\right]^{2l'} \cdots$$

$X^2 \sim -(x+iy)$, etc.
X, Y a spinor over which one integrates like ξ, η

The integral must, because of the invariance, be a polynomial in $(aa^* + bb^*)(A^*a + B^*b)(A^*b - a^*B^*)$. The relative intensities of Zeeman components can thus be obtained by spotting coefficients. This procedure is in many ways more elegant than reducing a triple to a double product by means of Wigner coefficients,--the procedure given on another sheet. Note that the selection rules on l can also be obtained from the products it is possible to construct. Note also that the selection rules apply equally well to anything that "transforms like" $-(x-iy)$, z, $x+iy$. Instead of x,y,z we could have L_x, L_y, L_z (not considering parity).

Another elegant way of obtaining the angular momentum matrices is to note that they can be generated by an infinitesimal rotation; for instance, $\xi = \xi + \frac{1}{2}i\varepsilon\xi$, $\eta = \eta \pm i\varepsilon\eta$ generates $\varepsilon L_z/\hbar$ (cf. Eckart, Rev. Mod. Phys. 2, p. 349.)

Note that the invariance considerations we have presented above do not determine the relative intensities of lines in a multiplet--only the relative intensities of the Zeeman components for a given line of a multiplet. The determination of the relative intensities of the multiplet comonents is a more difficult problem, but can be done by extension of the spinor analysis (somewhat similar to that we used to get the Wigner coefficients, but Kramers does not introduce the Wigner coefficients as such). In an immediately following paper in his collected works, he shows how to use the ξ, η method to get the matrix elements of the electrostatic interaction between electrons.