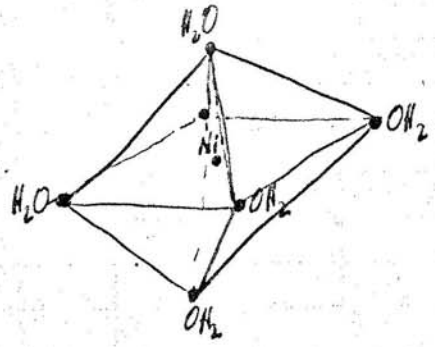
II. Crystal Fields

We now proceed to examine, not the isolated gaseous atom or ion, but the problem of the atom when it is inserted into a crystal.
The theory that we shall develop, has been applied most extensively to the ions of the 1st, 2nd, and 3rd transition series – i.e. involving unfilled shells of 3d, 4d, and 5d electrons, respectively. More recently, the complexes of the rare earth and actinide ions have begun to be studied, and it is here that one finds the theory at its most complicated, but also in its most elegant form.

In order to make progress, we have to choose a physical model. In this case, we regard the atom or ion of interest in the crystal as surrounded by an array of other atoms or ions

e.g. In the crystal of the compound $NiSO_4.7H_2O$, the Ni^{++} ion is surrounded by 6 H_2O molecules lying at the corners of an octahedron:



– this is a typical situation to which the theory is meant to apply.

We ignore covalent bonding between the Ni^{++} ion

and the H_2O molecules completely — Assume there is no interchange of electrons at all. The six H_2O molecules are simply regarded as the sources of an external field, with octahedral symmetry, that perturbs the Ni^{++} ion. We enquire as to what happens to the energy levels and wave functions of the Ni^{++} ion when it is placed in such a field.

Stated in this way, the disadvantages of the theory, the so-called "Crystal Field Theory", are obvious (to a chemist). However, crystal field theory may claim a great deal of success in explaining the spectra, the magnetic properties, the thermodynamic properties, and the stabilities of a very large number of complex ion compounds.

Covalency, or direct bonding between the central ion and the surrounding ~~ions~~ molecules or ions - (~~It~~ referred to as ligands) - is treated by a simplified molecular orbital theory called the Ligand Field Theory. This is a much more empirical theory, and although it does sometimes give a revealing physical picture, it is practically valueless as far as numerical results are concerned. And indeed, in those experiments where numerical data, such as frequencies of absorption bands etc., are obtained — the results can just as satisfactorily be interpreted by the crystal field theory.

Crystal field theory obviously is most suitable where there is little interaction between the outer, unfilled electron shell of the central atom, and the surrounding

ligands. This is probably the case with the rare earth ions, which have unfilled shells of 4f electrons; these are tucked away inside one or two closed shells. In fact in these cases, the interaction between the 4f electrons and the ligands is so small that there are only small crystal field effects: The electronic spectra of such complexes show a wealth of very fine, sharp lines, very similar to what is obtained for free atoms.

But whether we use the crystal field model or the ligand field - molecular orbital theory, please note that we assume that <u>all</u> the electrons in the crystal are <u>tightly bound</u> to their respective molecules or ions. In other words, we <u>ignore any solid state effects</u> such as conduction, which implies free or nearly free electrons and requires consideration of the crystal <u>as a whole</u>, using periodic potentials and the Bloch method for obtaining bands etc.

Thus our physical model is that of an atom or ion inserted into a crystalline field of a particular symmetry (often octahedral). This crystal field is regarded as an <u>external potential energy</u> which we denote by V_{cryst}. We shall not find it necessary to specify V_{cryst} too exactly. There are two important features of V_{cryst}: its magnitude in relation to other

electronic interactions, and its symmetry.

The total Hamiltonian for the $\mathcal{N}$ atoms in the crystal, which we denote by $\mathcal{H}_{cryst}$, is thus given by

$$\mathcal{H}_{cryst} = \mathcal{H}_{tot.} + V_{cryst.} \quad \text{——— (55)/},$$

where $\mathcal{H}_{tot}$

- and we seek the energy levels and wave functions of $\mathcal{H}_{cryst}$, assuming that the problem for $\mathcal{H}_{tot.}$ has been solved.

We recall that $\mathcal{H}_{tot.}$ is the total Hamiltonian for the free atom or ion, and that it is given by

$$\mathcal{H}_{tot} = \mathcal{H}_0 + \mathcal{H}_{ee} + \mathcal{H}_{LS}$$

We assume that the free atom is, to a good approximation, described by LS coupling, so the 3 contributions to $\mathcal{H}_{tot.}$ lie in order of size:

$$\mathcal{H}_0 \gg \mathcal{H}_{ee} \gg \mathcal{H}_{LS}$$

When we now discuss the order of magnitude of $V_{cryst.}$ there are then 3 important cases:

1) <u>Strong crystal field</u>

$$V_{cryst} \gg \mathcal{H}_{ee}$$

- The crystal field is more important than the electron-electron interactions. In this case, it is obvious that we must first find solutions to the problem

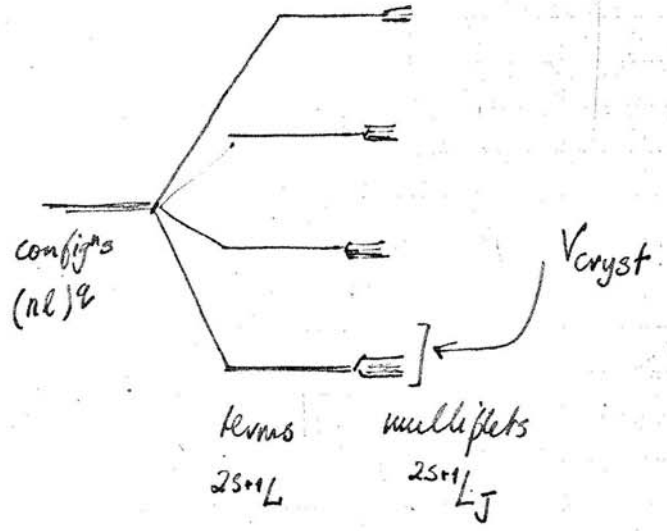
$(\mathcal{H}_0 + V_{cryst})$

and then consider $\mathcal{H}_{ee}$ and $\mathcal{H}_{LS}$ as corrections.

2) Intermediate crystal field

$$\mathcal{H}_{ee} \gg V_{cryst} \gg \mathcal{H}_{LS}$$

i.e. V_{cryst} is small compared to the term splitting, but still large compared to the multiplet splitting:



This case means that we must consider how V_{cryst} affects the various terms, $|\alpha L M_L S M_S\rangle$, of the free atom, and then finally correct for spin-orbit coupling.

This is probably the most common case.

3) Weak crystal field

$$\mathcal{H}_{LS} \gg V_{cryst}$$

i.e. $V_{cryst.}$ is small compared to the multiplet splitting $^{2S+1}L_J$. This case is fairly common too, especially for the rare earth ions, where the 4f electrons are

tucked away inside the central atom or ion. We then start with the complete multiplets for the free atom, $|\alpha SLJM_J\rangle$, and examine the effect of the crystal field on these wave functions and energy levels.

Note that we do not have to assume LS-coupling. If the free atom were described by jj-coupling, so that

$$\mathcal{H}_0 \gg \mathcal{H}_{LS} \gg \mathcal{H}_{ee}$$

there would still be 3 possible cases for the size $V_{cryst.}$ This is, no doubt, a fairly frequent occurrence, but we will assume LS-coupling as this is more familiar from text books.

Note that $V_{cryst.}$ can never be greater than $\mathcal{H}_0$, as this would imply that the electrons on the atom were loosely bound, and could be expected to move freely through the crystal. This possibility was specifically excluded in our model, as this leads to considerations of energy bands, conduction, etc., which is a different class of problem.

Group Theory and Quantum Mechanics

I have now defined the physical features of the situation, and the various assumptions underlying the crystal field model. We now proceed to discuss how one actually solves the problem. In the case of free atoms, recall that we used the spherical

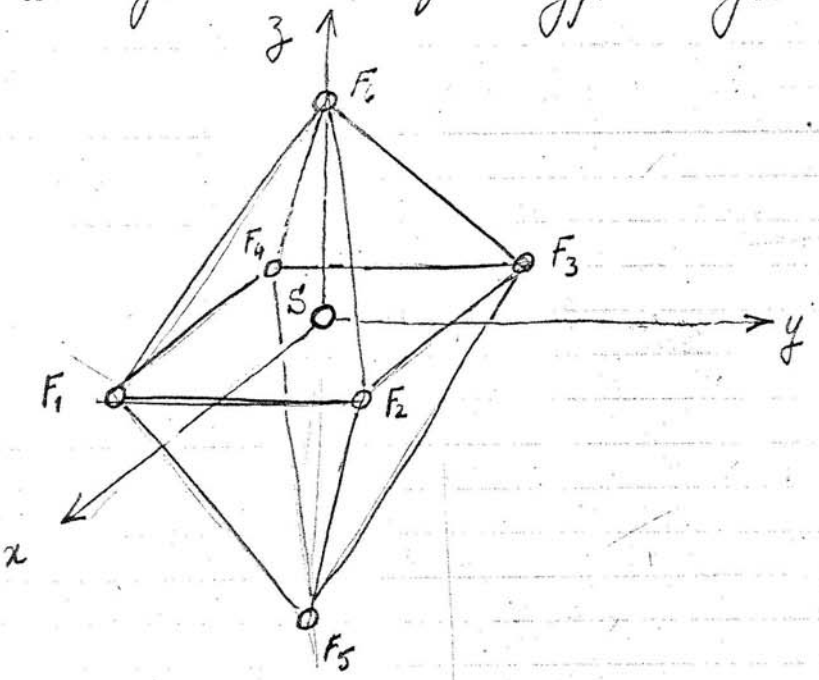
symmetry of the system to avoid solving any secular equations. We exploited this spherical symmetry systematically, by means of the concept of commuting operators, which led naturally to the idea of the coupling of angular momenta.

It seems natural to try to ~~expound~~ exploit the symmetry that an atom or ion has in a crystal field in order to simplify the problem. However symmetries such as the octahedral symmetry of the $Ni(H_2O)_6^{++}$ ion are normally treated, not by the method of finding a set of commuting operators, but by group theory.

It is unfortunate that two different methods are used to ~~expound~~ exploit symmetry, but you will not be surprised to learn that they accomplish exactly the same objective. We now turn to a study of the relevance of group theory and quantum mechanics, and ~~in particular~~ we will discuss the application of group theory to a number of simple molecules i.e. to systems that are not spherically symmetric, and later we will see how the group theory method is carried over to atoms as well, and how this connects with the commuting operator method.

~~Consider a molecule such as Benzene, or~~ the hydrogen atom field at the surface of an

Consider a molecule such as SF_6, which will serve as a good model for a typical crystal field situation.

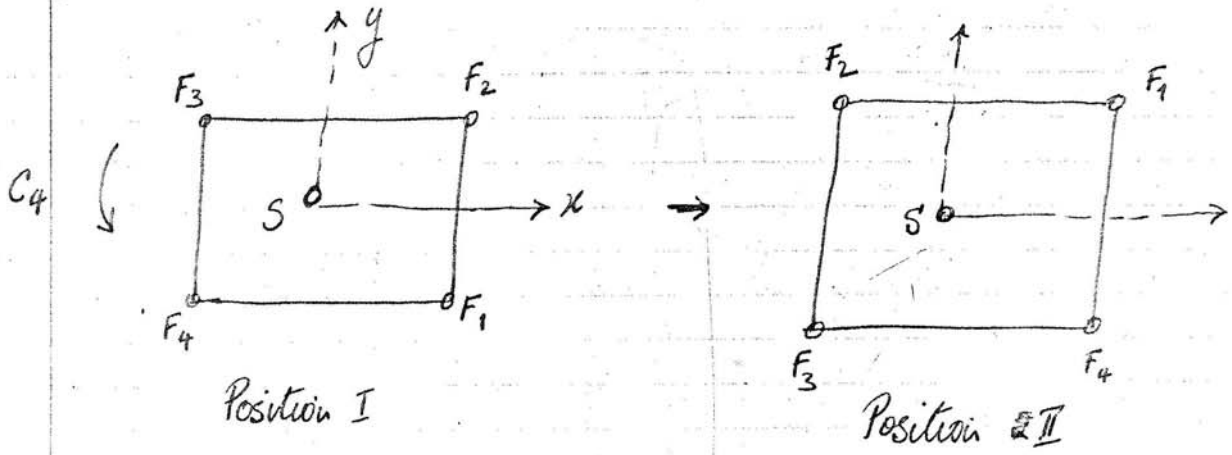


The 6 F atoms lie at the corners of an octahedron. Note that I have drawn in a set of Cartesian axes, with origin at the central S atom.
It is important to note that these axes remain fixed in space – everything else is defined relative to these axes, such as the position of the 6 F atoms, the positions of all the electrons. The total Hamiltonian $\mathcal{H}$, is defined relative to these axes, too

[I could, of course, site these Cartesian axes anywhere, but I simplify the argument, without changing anything, by siting them as in the diagram.

Now, as you all know, I'm sure, there are a number of rotations, and reflections of the molecule that can be carried out, that leave the molecule in a position that is physically equivalent to the original position. The

words, "physically equivalent" are important. An example is rotation of the molecule by $\frac{\pi}{2}$ about the z-axis. Viewed from above this is:



Note the position of the coordinate axes: they have remained unchanged in this operation. The molecule is rotated by $\frac{\pi}{2}$. This operation is denoted by the symbol C_4. We say that, by rotating the molecule from position I to position II, which we are perfectly able to do mathematically, we have physically changed nothing. From a physical point of view, the molecule must look exactly the same in position II as in position I. In this sense is Position II physically equivalent to position I. The operation C_4 which sends the molecule into the physically equivalent position II is known as a symmetry operation.

Upon inspecting the SF_6 molecule, we can discover other symmetry operations, such as rotations by $\frac{\pi}{2}$, or π about the x, or y axes, or reflections in the xy, zy, or xz planes, and so on.

Remember that one possible symmetry operation is that of leaving the molecule alone in its original position! This particular operation is denoted by the symbol E (German: Einheit).

We now collect together all the possible symmetry operations on the SF_6 molecule:

$$E, R_1, R_2, \ldots\ldots, R_g$$

- where we denote the various (possible) symmetry operations by the symbol

$$R_k \; ; \; k = 1, 2, \ldots\ldots, g.$$

Including E, there are thus $g+1$ symmetry operations in all. This set of symmetry operations has the following properties:

1) The combination of any two symmetry operations, R_k and R_ℓ is equivalent to some other single symmetry operation, R_q, which is also a member of the set:

$$R_\ell R_k = R_q$$

This means that we operate on the molecule with R_k first, and then with R_ℓ, and having done that we find that this leaves SF_6 in a physically equivalent position that could have been reach directly by the single symmetry operation R_q.

2) The set of all possible symmetry operations

contains a unit element E, such that the two symmetry operations E and R_k always give just R_k:

$$ER_k = R_k E = R_k.$$

3) Every symmetry operation, R_k, in the set has an inverse R_p, say, that undoes its effect.

i.e. if we operate on the molecule with the symmetry operation R_k, to bring the molecule into some new physically equivalent position, then there must be some other symmetry operation in the set, R_p, that brings the molecule back into its original position. Thus

$$R_p R_k = E$$

so that we can write R_p as R_k^{-1}, giving

$$R_k^{-1} R_k = E$$

4) The triple product of symmetry operations $R_m R_e R_k$ is uniquely defined:

$$R_m(R_e R_k) = (R_m R_e) R_k = R_m R_e R_k$$

remember that each of these combinations is equivalent to some other symmetry operation - by 1)

This means that the set of symmetry operations

$$E, R_1, R_2, \ldots\ldots, R_g$$

above form what is known in mathematics as a group.

We denote this group by the symbol G, and write

$$G = \{E, R_1, R_2, \ldots\ldots, R_g\} \qquad (56)$$

See that a group is really a set of "self consistent" elements, such that combinations of these elements give just another element inside the set — i.e. we can never "jump out" of the set.

All the symmetry operations, or symmetry elements, R_k, consist of either rotations or reflections of the molecule; one point of the molecule is always left unmoved. In the case of SF_6, it is not hard to see that this must be the S atom. For this reason, the group G is called the point symmetry group of the molecule.

What I have said about SF_6 is sufficiently general for you to see that for any molecule, the set of all symmetry operations forms a point symmetry group associated with that molecule.

> The set of all possible symmetry operations on a molecule always forms a group. This group is known as the point symmetry group of the molecule

Molecules may thus be classified according to the point symmetry group to which they belong.—

The point symmetry group of the octahedral molecule

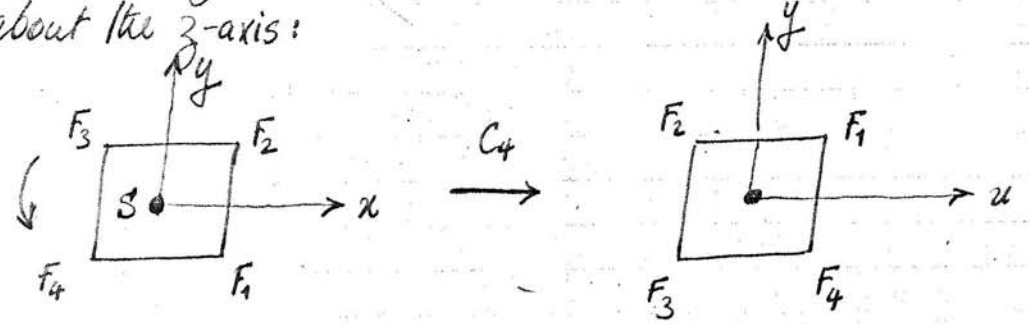
SF_6, G_7 is denoted by the symbol O_h.

The molecules CH_4, SiF_4, belong to the point symmetry group T_d, NH_3, CH_3Cl to C_{3v}, H_2O, CH_2Cl_2 to C_{2v}, etc., etc.....

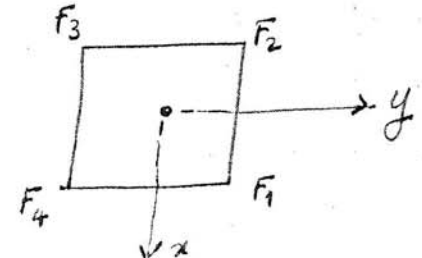
I will not go into the properties of individual point groups — but you should read about them. An excellent reference is Landau & Lifshitz "Quantum Mechanics", Chapter XII. I want to discuss the general properties of point groups and their relevance to quantum mechanics.

Having now introduced the concept of a group, - which I hope was not new to you — and shown that each molecule may be classified by the point symmetry group to which it belongs, — let us now consider the deeper physical meaning behind point symmetry.

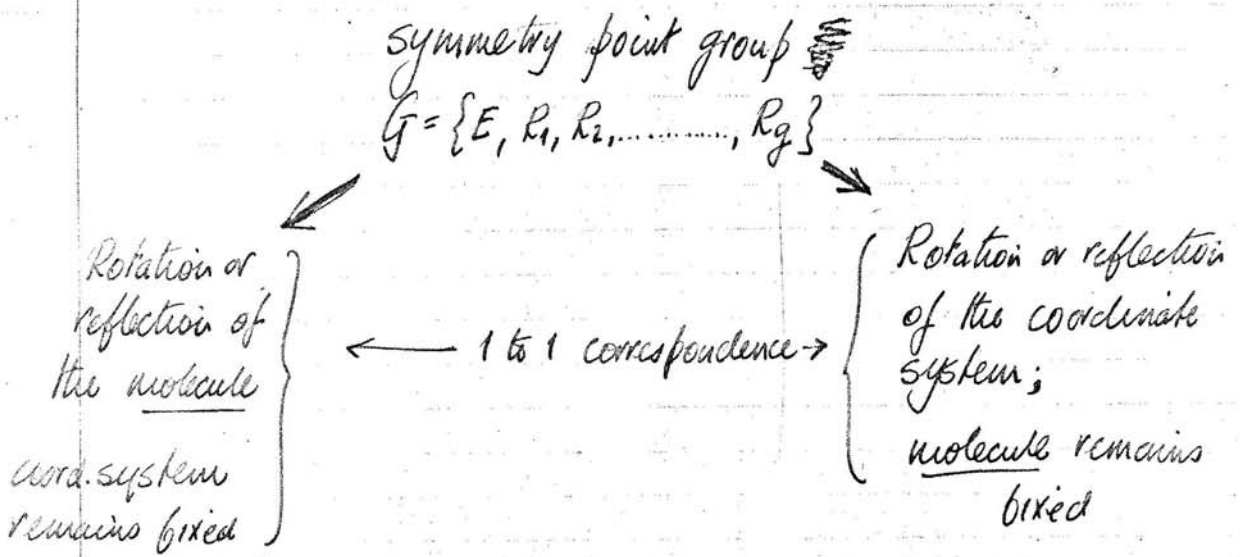
Consider again the rotation of the SF_6 molecule by $\frac{\pi}{2}$ about the z-axis:



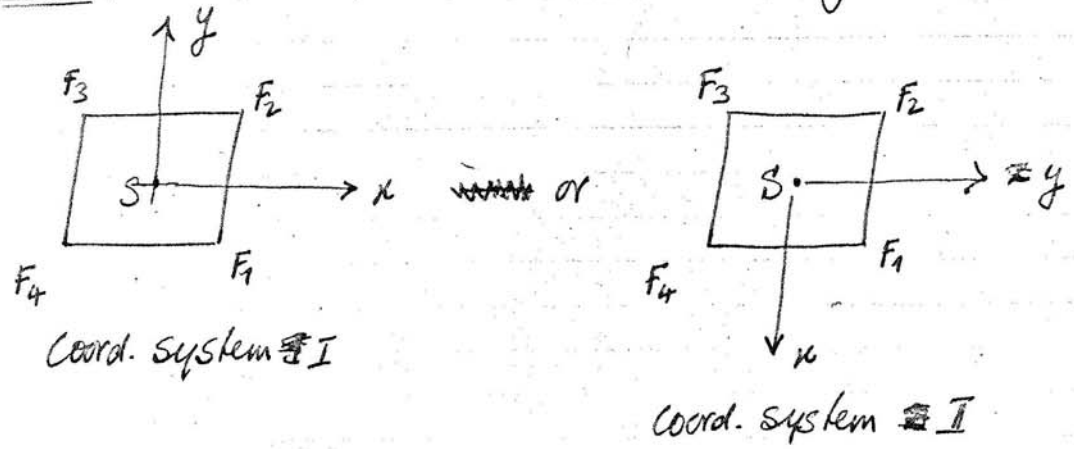
Exactly the same result is achieved by leaving the molecule alone, and rotating the coordinate system by $-\frac{\pi}{2}$:



— i.e. every symmetry operation R_k of the group G can be interpreted either as an operation on the molecule, leaving the coordinates fixed in space, or leaving the molecule alone, and rotating or reflecting the coordinate system:



Now this second interpretation has important physical consequences. Remember that the Hamiltonian of the entire molecular system is written in terms of this coordinate system. The fact that the molecule looks physically the same in either coordinate system



means that the Hamiltonian will look exactly the same, whether it is written in coord. system I, or

word system II. In other words, if R_k is a symmetry operation on the coordinate system, then

$$R_k \mathcal{H} = \mathcal{H} \qquad (57)$$

— the Hamiltonian remains unchanged, or it is said to be INVARIANT under R_k. If you think about this physically, the meaning of equ" (57) will become clear. If a molecule has any symmetry, means that there are a number of points of view from which it looks exactly the same, so that $\mathcal{H}$ must be same when ~~written in~~ looked at from these different points of view. When we transform the coordinate system by a symmetry transformation, $\mathcal{H}$ must remain the same "internally".

This is the true meaning of point symmetry: it is the invariance, or the symmetry of the Hamiltonian towards all the possible symmetry operations [Hard to imagine symmetry operations as coordinate transformations — best thought of as actual rotations etc., of the molecule].

The significance of equ" (57) is brought out by considering what happens when $\mathcal{H}$ acts on a wave function Ψ_n^s, $\mathcal{H}\Psi_n^s$:—

We consider what happens when we transform the function $\mathcal{H}\Psi_n^s$ by the symmetry

operation R_k, interpreted as a coord. transformation

$$R_k(\hat{H}\bar{\Psi}_n)$$

Eqn (57) states that $\hat{H}$ behaves as a constant towards the operation R_k, so we have

$$R_k(\hat{H}\bar{\Psi}_n) = \hat{H}(R_k\bar{\Psi}_n)$$

[compare $\frac{d}{dx}(af(x)) = a\frac{d}{dx}f(x)$]

i.e. $R_k\hat{H} = \hat{H}R_k$

or $[\hat{H}, R_k] = 0$ for all R_k in G ——— (58)/

— in other words, if $\hat{H}$ is invariant under all the operations R_k of the point symmetry group G, then $\hat{H}$ commutes with all the R_k (interpreted as coord. transformations).

lecture 8.

Representations of the Group G.

An immediate consequence of equation (58)/ is as follows:

If $\hat{H}\bar{\Psi}_n = E_n\bar{\Psi}_n$

for any molecular system,

then in general

$$R_k(\hat{H}\bar{\Psi}_n) = R_k(E_n\bar{\Psi}_n)$$

— where we transform both sides by the symmetry operation R_k.

From eqn (58) above, have immediately that

$$\mathcal{H}(R_k \Psi_n) = E_n (R_k \Psi_n) \qquad \text{——— (59)}$$

↑ just a number.

The meaning of this equation is as follows:
If Ψ_n is an eigenfunction of $\mathcal{H}$, then $(R_k \Psi_n)$ is an eigenfunction too, and belonging to the same eigenvalue E_n. Note that $(R_k \Psi_n)$ means the function Ψ_n viewed from the new coordinate system, so it is a new function

i.e. Ψ_n and $(R_k \Psi_n)$ are degenerate eigenfunctions, and in general, a symmetry operator, R_k, can turn one degenerate eigenfunction into another.

[The best examples of this are in free atoms:
e.g. The 3 2p wave functions, $\Psi_{2p_{+1}}$, Ψ_{2p_0}, $\Psi_{2p_{-1}}$ can all be turned into each other by a suitable rotation of the coordinate system; the 1s fn - spherically symmetric & is singly degenerate]

Now let the energy level E_n be τ-fold degenerate
i.e. let there be τ wave functions

$$\Psi_{n1}, \Psi_{n2}, \ldots\ldots, \Psi_{n\tau}$$

all belonging to the energy level E_n

$$E_n \text{ ——— } \Psi_{n1}, \Psi_{n2}, \ldots\ldots, \Psi_{n\tau}.$$

Let the symmetry operation R_k operate on any one of these wave functions, $\Psi_{n\mu}$, say, where $\mu = 1, 2, \ldots$, or τ

Then by equⁿ (59), the functions

$$\bar{\Psi}^s_{n\mu} \text{ and } (R_k \bar{\Psi}^s_{n\mu})$$

are degenerate eigenfunctions. But since we assumed that there are only $\bar{\imath}$ degenerate eigenf'ns, $(R_k \bar{\Psi}^s_{n\mu})$ must be some linear combination of these, i.e.

$$(R_k \bar{\Psi}^s_{n\mu}) = \sum_{\nu=1}^{\bar{\imath}} a_\nu \bar{\Psi}^s_{n\nu}.$$

This equation is more usually written as

$$\boxed{R_k \bar{\Psi}^s_{n\mu} = \sum_{\nu=1}^{\bar{\imath}} D_{\nu\mu}(R_k)\, \bar{\Psi}^s_{n\nu}} \qquad (60)$$

— i.e. in general a symmetry operation will turn a degenerate eigenfunction into a linear combination of all the other degenerate eigenfunctions.

~~We shall see that the operation symmetry operations of the point symmetry group of~~

If we let the symmetry operation R_k act on all the degenerate eigenfunctions $\bar{\Psi}^s_{n1}, \bar{\Psi}^s_{n2}, \ldots, \bar{\Psi}^s_{n\bar{\imath}}$, ~~we see~~ one by one, we see that we generate a matrix of coefficients $\underset{\sim}{D}(R_k)$

$$\underset{\sim}{D}(R_k) = \begin{bmatrix} D_{11}(R_k) & D_{12}(R_k) & \cdots & D_{1\bar{\imath}}(R_k) \\ D_{21}(R_k) & D_{22}(R_k) & \cdots & D_{2\bar{\imath}}(R_k) \\ \vdots & & & \vdots \\ D_{\bar{\imath}1}(R_k) & D_{\bar{\imath}2}(R_k) & \cdots & D_{\bar{\imath}\bar{\imath}}(R_k) \end{bmatrix}$$

- This matrix is of dimension $\bar{\imath} \times \bar{\imath}$, where $\bar{\imath}$ is the degeneracy of the energy level E_n.

If we do this for <u>all</u> the operations R_k in the point group G, we will generate the following set of $\bar{\imath} \times \bar{\imath}$ matrices:

$$\underset{\sim}{D}(E), \quad \underset{\sim}{D}(R_1), \quad \underset{\sim}{D}(R_2), \ldots\ldots\ldots, \quad \underset{\sim}{D}(R_g)$$

- i.e. 1 matrix for each element R_k in G, $g+1$ in all.

It is easy to see from equation (60) (p. 94, above), that the matrix $\underset{\sim}{D}(E)$ must be the <u>unit matrix</u>:

$$\underset{\sim}{D}(E) = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & & & & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix} \quad \begin{matrix} \uparrow \\ \\ \bar{\imath} \\ \\ \downarrow \end{matrix}$$

$\leftarrow \quad \bar{\imath} \quad \rightarrow$

We now assume that two of the symmetry operators, R_k, and R_ℓ are equal to some other one, R_q, say;

$$R_\ell R_k = R_q$$

Now, from equation (60), we have

$$R_k \overline{\Psi}_{n\mu} = \sum_{\nu=1}^{\bar{\imath}} D_{\nu\mu}(R_k)\, \overline{\Psi}_{n\nu}$$

so that

$$R_\ell R_k \overline{\Psi}_{n\mu} = \sum_{\nu=1}^{\bar{\imath}} D_{\nu\mu}(R_k)\, (R_\ell \overline{\Psi}_{n\nu})$$

$$= \sum_{\nu=1}^{\tau} D_{\nu\mu}(R_k) \left\{ \sum_{\lambda=1}^{\tau} D_{\lambda\nu}(R_\ell)\, \overline{\Psi}_{n\lambda} \right\}$$

$$= \sum_{\lambda=1}^{\tau} \left\{ \sum_{\nu=1}^{\tau} D_{\lambda\nu}(R_\ell)\, D_{\nu\mu}(R_k) \right\} \overline{\Psi}_{n\lambda}.$$

Applying R_q directly to $\overline{\Psi}_{n\mu}$, we have,

$$R_q \overline{\Psi}_{n\mu} = \sum_{\lambda=1}^{\tau} D_{\lambda\mu}(R_q)\, \overline{\Psi}_{n\lambda}$$

These last two equations can only be compatible if

$$D_{\lambda\mu}(R_q) = \sum_{\nu=1}^{\tau} D_{\lambda\nu}(R_\ell)\, D_{\nu\mu}(R_k).$$

But this is just the rule for multiplying the matrices $\underset{\sim}{D}(R_\ell)$ and $\underset{\sim}{D}(R_k)$ together [Indeed this is why matrix multiplication is defined in this way]

Thus the matrices $\underset{\sim}{D}(R_\ell)$, $\underset{\sim}{D}(R_k)$, $\underset{\sim}{D}(R_q)$ satisfy:

$$\underset{\sim}{D}(R_q) = \underset{\sim}{D}(R_\ell)\, \underset{\sim}{D}(R_k). \qquad (61)/$$

– i.e. they faithfully "mirror" the properties of the group G. The set of matrices

$$\underset{\sim}{D}(E),\ \underset{\sim}{D}(R_1),\ \underset{\sim}{D}(R_2),\ \ldots\ldots,\ \underset{\sim}{D}(R_g),$$

generated from the τ-dimensional degenerate level E_n, are said to form a representation of the group G — i.e.

if $R_i R_k = R_q$, then, as before,

$$\underset{\sim}{D}(R_i)\,\underset{\sim}{D}(R_k) = \underset{\sim}{D}(R_q) \quad \text{etc.,} - \text{for } \underline{\text{all}}$$

the operators $R_i, R_k, R_q, \ldots$ etc., in the group. Note that for the matrices to mirror faithfully all the properties of the group G, we must have

$$\underset{\sim}{D}(R_k^{-1}) = \underset{\sim}{D}^{-1}(R_k) \qquad \text{——— (62)}.$$

We thus see that with each energy level of an atomic or molecular system there is associated a representation of the group G. If the energy level is ℓ fold degenerate, then the matrices $\underset{\sim}{D}(R)$ are $\ell \times \ell$-dimensional, and the representation of G is called a ℓ-dimensional representation.

The practical significance of this result depends upon two important properties of the $\underset{\sim}{D}(R_k)$ matrices

1) The matrices $\underset{\sim}{D}(R_k)$ are all unitary matrices

i.e.

$$\underset{\sim}{D}^{-1}(R_k) = \underset{\sim}{D}^{*\,\prime}(R_k) \quad \text{for all } R_k \text{ in } G$$

($*$: complex conj.; $\prime$: transpose)

$$\equiv \underset{\sim}{D}^{\dagger}(R_k)$$

[In individual matrix elements:

$$D^{-1}_{\mu i}(R_k) = D^{*}_{i\mu}(R_k)\ ].$$

Proof: This property follows from the orthonormality of the set of degenerate wave functions:

$$\{\bar{\Psi}_{n1}, \bar{\Psi}_{n2}, \ldots\ldots, \bar{\Psi}_{n\bar{\imath}}\}$$

and $\langle \bar{\Psi}_{n\mu} | \bar{\Psi}_{n\nu} \rangle = \delta_{\mu\nu}$ for $\mu, \nu = 1, 2, \ldots\ldots, \bar{\imath}$.

If this is the case, then the set of transformed wave functions

$$(R_k \bar{\Psi}_{n1}), (R_k \bar{\Psi}_{n2}), \ldots\ldots, (R_k \bar{\Psi}_{n\bar{\imath}}),$$

- where we have used the same R_k throughout - must still be orthonormal!

$$\langle R_k \bar{\Psi}_{n\mu} | R_k \bar{\Psi}_{n\nu} \rangle = \delta_{\mu\nu} \qquad \text{——— (63)}.$$

- This follows because transforming all the $\bar{\Psi}_{n\mu}$ by R_k simply means viewing them from a new coordinate system, so that this cannot change the intrinsic properties of the wave functions.

The unitary property of the $\underset{\sim}{D}$'s now follows from (63). Applying the important eqn (60) twice, we have

$$\langle R_k \bar{\Psi}_{n\mu} | R_k \bar{\Psi}_{n\nu} \rangle$$

$$= \sum_{\lambda=1}^{\bar{\imath}} D^*_{\lambda\mu}(R_k) \langle \bar{\Psi}_{n\lambda} | R_k \bar{\Psi}_{n\nu} \rangle$$

$$= \sum_{\lambda,\sigma=1}^{\bar{\imath}} D^*_{\lambda\mu}(R_k) D_{\sigma\nu}(R_k) \underbrace{\langle \bar{\Psi}_{n\lambda} | \bar{\Psi}_{n\sigma} \rangle}_{\delta_{\lambda\sigma}}$$

$$= \sum_{\lambda=1}^{\bar{\imath}} D^*_{\lambda\mu}(R_k) D_{\lambda\nu}(R_k)$$

$$= \delta_{\mu\nu}.$$

This is only possible if

$$D^{*}_{\lambda\mu}(R_k) = D^{-1}_{\mu\lambda}(R_k) \qquad \text{Q.E.D.}$$

2) The second important property of the $\underset{\sim}{D}$ matrices is also connected with their unitary property.

Now since all the set of wave fn's

$$\{ \underline{\Psi}_{n1}, \underline{\Psi}_{n2}, \ldots\ldots, \underline{\Psi}_{n\bar{\imath}} \}$$

belong to ~~same energy~~ the same energy level, E_n, - there is nothing unique about this set: Any linear combination of them would be equally satisfactory:

$$\underline{\Phi}_{nr} = \sum_{\mu=1}^{\bar{\imath}} a_{\mu r}\, \underline{\Psi}_{n\mu} \qquad \text{---------- (64)}$$

$r = 1, 2, \ldots\ldots, \text{or } \bar{\imath}$

The only restriction on the $a_{\mu r}$ coefficients comes from the condition that the new set of wave functions, $\underline{\Phi}_{nr}$, should also be orthonormal:

$$\langle \underline{\Phi}_{nr} | \underline{\Phi}_{ns} \rangle = \delta_{rs} \; ; \quad r, s = 1, 2, \ldots\ldots, \bar{\imath}$$

By the same ~~proof~~ proof as above, means that the $a_{\mu r}$ coefficients must form a unitary matrix

i.e. if $\underset{\sim}{A} = \begin{bmatrix} a_{11} & a_{12} & \ldots\ldots & a_{1\bar{\imath}} \\ a_{21} & a_{22} & \ldots\ldots & a_{2\bar{\imath}} \\ \vdots & & & \\ a_{\bar{\imath}1} & a_{\bar{\imath}2} & \ldots\ldots & a_{\bar{\imath}\bar{\imath}} \end{bmatrix}$,

then $\underset{\sim}{A}^{-1} = \underset{\sim}{A}^{\dagger} \quad \left[= (\underset{\sim}{A}^{*})' \;\; !! \right]$.

Hence (64) can easily be inverted:

$$\underline{\Psi}_{n\mu} = \sum_{r=1}^{\bar{\imath}} (a)^{-1}_{r\mu}\, \underline{\Phi}_{nr} \qquad \text{- always true,}$$

$$= \sum_{r=1}^{\bar{\imath}} a^{*}_{\mu r}\, \underline{\Phi}_{nr} \qquad \text{, since } \underset{\sim}{A} \text{ is unitary}$$

---------- (64a).

Example:

The p levels in free atoms. This is triply degenerate ($\bar{\imath} = 3$), and there are two, equally satisfactory, sets of wave functions:

a) The set
$$[np_x, np_y, np_z]$$

b) The set
$$[np_{+1}, np_{-1}, np_0]$$

The transformation between them is given by:

$$[np_{+1}, np_{-1}, np_0] = [np_x, np_y, np_z] \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 & 0 \\ i & -i & 0 \\ 0 & 0 & \sqrt{2} \end{bmatrix}$$

The $\hat{A}$ matrix is $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 & 0 \\ i & -i & 0 \\ 0 & 0 & \sqrt{2} \end{bmatrix}$ and is easily shown to be unitary.

How do the set of wave fns $\{\bar{\Phi}_{n1}, \bar{\Phi}_{n2}, \ldots\ldots, \bar{\Phi}_{n\bar{\imath}}\}$ now transform under a symmetry operation R_k?

From equ's (64) [p. 99] and (60)/ [p. 94],

$$R_k \bar{\Phi}_{n\nu} = \sum_{\mu=1}^{\bar{\imath}} a_{\mu\nu} R_k \bar{\Psi}^s_{n\mu}$$

$$= \sum_{\mu,\nu=1}^{\bar{\imath}} a_{\mu\nu} D_{\nu\mu}(R_k) \bar{\Psi}^s_{n\nu}$$

$$= \sum_{\mu,\nu=1}^{\bar{\imath}} \sum_{s=1}^{\bar{\imath}} a_{\mu\nu} D_{\nu\mu}(R_k) a^*_{\nu s} \bar{\Psi}^s_{ns}$$

$$= \sum_{s=1}^{\bar{\imath}} \left[\sum_{\mu,\nu=1}^{\bar{\imath}} a_{\mu\nu} D_{\nu\mu}(R_k) a^*_{\nu s} \right] \bar{\Phi}_{ns}$$

i.e.

$$R_k \Phi_{nr} = \sum_{s=1}^{\bar{\imath}} \Delta_{sr}(R_k)\, \Phi_{ns} \qquad (65)$$

where the matrices $\underset{\sim}{\Delta}(R_k)$ and $\underset{\sim}{D}(R_k)$ are related by

$$\underset{\sim}{\Delta}(R_k) = \underset{\sim}{A}^{\dagger}\, \underset{\sim}{D}(R_k)\, \underset{\sim}{A} \qquad (66)$$

Since there are an infinite no. of unitary transformations, $\underset{\sim}{A}$, would appear that instead of a given, definite representation of G:

$$\underset{\sim}{D}(E),\ \underset{\sim}{D}(R_1),\ \underset{\sim}{D}(R_2) \ldots\ldots,\ \underset{\sim}{D}(R_g)$$

there are an infinite no. of $\bar{\imath}$-dimensional representations

$$\underset{\sim}{\Delta}(E),\ \underset{\sim}{\Delta}(R_1),\ \underset{\sim}{\Delta}(R_2) \ldots\ldots,\ \underset{\sim}{\Delta}(R_g).$$

However But note that there is one property of these matrices that remains constant whatever the transformation $\underset{\sim}{A}$:

We define the sum of the diagonal elements of a representation matrix $\underset{\sim}{D}(R_k)$ as the TRACE or CHARACTER of the matrix. Denoted by the symbol $\chi(R_k)$.

$$\chi(R_k) = \sum_{\mu=1}^{\bar{\imath}} D_{\mu\mu}(R_k) \qquad (67)$$

Now note that

$$\sum_{r=1}^{\bar{\imath}} \Delta_{rr}(R_k) = \chi'(R_k), \text{ say,}$$

$$= \sum_{r=1}^{\bar{\imath}} \left[\sum_{\mu,\nu=1}^{\bar{\imath}} a_{\mu r}\, D_{\nu\mu}(R_k)\, a^{*}_{\nu r} \right]$$

$$= \sum_{\mu,\nu=1}^{\bar{\imath}} D_{\nu\mu}(R_k) \Big[\underbrace{\sum_{r=1}^{\bar{\imath}} a^*_{\nu r}\, a_{\mu r}}_{= \delta_{\mu\nu} \text{ because } \underline{\underline{A}} \text{ is unitary}} \Big]$$

$$= \sum_{\mu=1}^{\bar{\imath}} D_{\mu\mu}(R_k) = \chi(R_k).$$

- i.e. the character $\chi(R_k)$ is unchanged by the unitary transformation $\underline{\underline{A}}$.

Hence the set of characters

$$\{ \chi(E), \chi(R_1), \chi(R_2), \ldots\ldots, \chi(R_g) \}$$

"characterises" a particular representation of G.

Because of this, the representation

$$\underline{\underline{\Delta}}(E), \underline{\underline{\Delta}}(R_1), \ldots\ldots, \Delta(R_g)$$

is said to be EQUIVALENT to the representation

$$\underline{\underline{D}}(E), \underline{\underline{D}}(R_1), \ldots\ldots, \underline{\underline{D}}(R_g).$$

- Have the same set of characters.

In fact $\{\underline{\underline{D}}(R_k)\}$ and $\{\underline{\underline{\Delta}}(R_k)\}$ regarded as the same representation

A particular set of representation matrices

is signified by the symbol $\underline{\underline{\Gamma}}$. Will refer to "the representation Γ of G" meaning the set of representation matrices $\{\underline{\underline{D}}(R_k)\}$ or $\{\underline{\underline{\Delta}}(R_k)\}$.

It is thus not usually necessary to specify a representⁿ Γ more completely than to give the set of characters:

$$\{\chi(E), \chi(R_1), \ldots\ldots\ldots, \chi(R_g)\}.$$

One final, and supremely important, property about the representation Γ:- It can be shown that, whatever the unitary transformation $\underset{\sim}{A}$, we can never obtain a set of matrices $\underset{\sim}{\Delta}(R_k)$ of the form, say,

$$\underset{\sim}{\Delta}(R_k) = \begin{array}{c} \overset{\leftarrow \bar{\imath}_1 \rightarrow}{\leftarrow} \overset{\bar{\imath}_2}{\rightarrow} \overset{\bar{\imath}_3}{\rightarrow} \\ \begin{array}{|ccc|} \hline \Delta_1(R_k) & 0 & 0 \\ 0 & \Delta_2(R_k) & 0 \\ 0 & 0 & \Delta_3(R_k) \\ \hline \end{array} \end{array}$$

for all R_k in G simultaneously.

$$\bar{\imath}_1 + \bar{\imath}_2 + \bar{\imath}_3 = \bar{\imath}$$

This is because if this were possible, it would mean that the original set of wave functions

$$\{\bar{\psi}_{n1}, \bar{\psi}_{n2}, \ldots\ldots\ldots, \bar{\psi}_{n\bar{\imath}}\}$$

had been broken up into 3 independent sets:

$$\{\bar{\psi}_{n1}, \bar{\psi}_{n2}, \ldots\ldots, \bar{\psi}_{n\bar{\imath}_1}\}, \{\bar{\psi}_{n\bar{\imath}_1+1}, \ldots\ldots \bar{\psi}_{n\bar{\imath}_1+\bar{\imath}_2}\},$$

$$\{\bar{\psi}_{n\bar{\imath}_1+\bar{\imath}_2+1}, \ldots\ldots\ldots, \bar{\psi}_{n\bar{\imath}}\}$$

each of which would each set by itself generating a representation of G:

i.e. the first set generates a $\bar{\imath}_1$-dimensional representation $\{\Delta_1(R_k)\}$,

the second set a $\bar{\imath}_2$-dim. representation $\{\Delta_2(R_k)\}$, etc.

– i.e. the τ-dimensional representation Γ would have been reduced to 3 reps. of smaller dimensions.

This never happens. We can never find a transf^{m}n $\hat{A}$ that accomplishes this. All the $\Psi_{n\mu}$ transform into all of the others under one or other of the R_k.

The representation Γ is termed an IRREDUCIBLE REPRESENTATION.

Summary

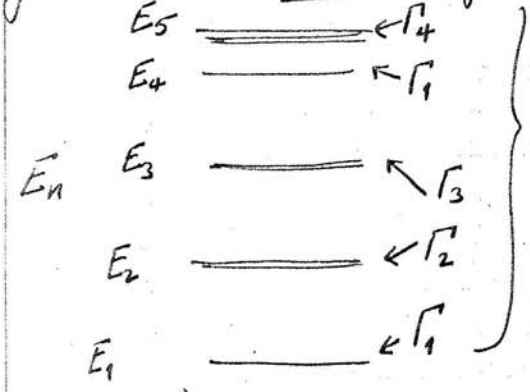
Thus, if the Hamiltonian of an atomic or molecular system is invariant under all operations of a group G:

$$G = \{E, R_1, R_2, \ldots\ldots, R_g\}$$

$$[\mathcal{H}, R_k] = 0 \quad \text{for all } R_k \text{ in } G,$$

then every energy level, E_n, of $\mathcal{H}$ can be labelled by one of the irreducible representations, Γ_i, of G.

The set of wave fn's $\{\Psi_{n1}, \ldots\ldots, \Psi_{n\tau}\}$ belonging to E_n generate the matrices of Γ. Thus



The problem thus shifts to that of finding all the irreducible reps., Γ_1, Γ_2, ..., etc., of a given group G. This is a purely algebraic problem — and there are

several general methods for doing this – developed at the beginning of this century and associated with the names of the German mathematicians Frobenius and Schur.

Frequently it is only necessary to find the sets of characters associated with the different $\Gamma_1, \Gamma_2, \ldots$, etc. This is sufficient if we wish to know only about the energy levels, selection rules, perturbation splittings etc., For information on the wave functions — need to know the complete set of matrices.

Thus, you see that to find the irred. reps., Γ, of a given G, — are led into abstract group theory – Will not go into this – a separate problem.

Group Theory and Perturbation Splitting

The typical case (with $\hat{H}$) which we have been dealing is a system whose total Hamiltonian is given by a sum of two contributions:

$$\hat{H} = \hat{H}^0 + V \qquad (68)$$

Usually assume $\hat{H}^0 \gg V$, but this is not necessary in what follows now. We do assume that V can be varied continuously, from 0 to its final value, i.e. we can write

$$\hat{H}_\epsilon = \hat{H}^0 + \epsilon V$$

and assume ϵ varies from 0 to 1. Sometimes this can be achieved physically e.g. an electric or magnetic field, but can always imagine this to be the case. e.g. In the crystal field case, imagine the

surrounding molecules or ions gradually brought up from, or removed to, infinity.

Now, in general $\mathcal{H}^\circ$ will be invariant under some group G°:

$$[\mathcal{H}^\circ, R_k] = 0 \quad \text{for all } R_k \text{ in } G^\circ.$$

The addition of V to $\mathcal{H}^\circ$ usually "lowers" the symmetry of the system — i.e. $\mathcal{H}$ will be invariant under some group G,

$$[\mathcal{H}, R_k] = 0 \quad \text{for all } R_k \text{ in } G,$$

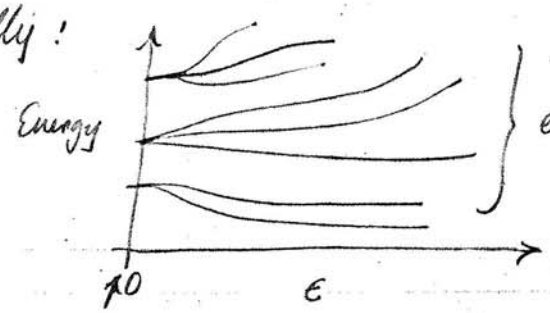
which is smaller than the group G° — G is usually a subgroup of G°; thus:

$$G^\circ : \{\underbrace{E, R_1, R_2, \ldots\ldots, R_g}_{G}, R_{g+1}, \ldots\ldots, R_{g_\circ}\}$$

The energy levels of $\mathcal{H}$ will all be labelled by one of the irred. reps. of G: $\Gamma_1, \Gamma_2, \ldots\ldots, \Gamma_N$; the wave fn's of each level will generate the matrices of the corresponding Γ: $\{\underset{\sim}{D}(R_k)\}$.

Now consider what happens as ϵ is varied continuously; the energy levels and wave functions vary continuously too — but the various representations $\{\underset{\sim}{D}(R_k)\}$ assoc. with each level cannot make some discontinuous change into some other representation — So as ϵ is varied continuously to zero, the only thing that can happen is that several energies coalesce into one.

Diagramatically:



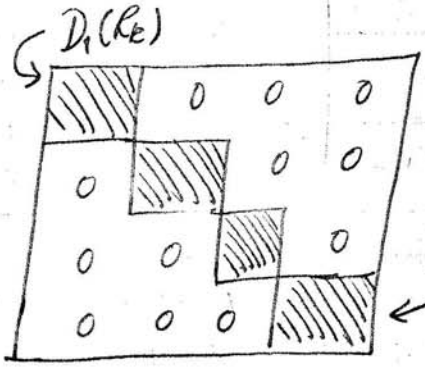
energy levels of $\mathcal{H}^\circ$

This means now that several representations of $\mathcal{H}_\epsilon$

$$D_1(R_k),\ D_2(R_k),\ \ldots\ldots\ D_N(R_k)$$

go to make up one matrix of a representation of G°

i.e. $\underset{\sim}{D}^\circ(R_k) =$



It is usual to write a matrix of this form out as

$$\underset{\sim}{D}^\circ(R_k) = D_1(R_k) + D_2(R_k) + \ldots\ldots\ldots + D_N(R_k) \qquad (69)_1$$

This shows that an irreducible representation Γ° of G° forms a REDUCIBLE representation Γ of G.

Thus an energy level of $\mathcal{H}^\circ$ assoc. with a represent^n Γ°, which can be reduced to the form $(69)_1$, will SPLIT into N components, when the perturbation V is introduced.

Thus the group-theoretic procedure for examining the effect of a perturbation on a system is as follows:

Start with $\mathcal{H}^\circ$, and the complete group G°.

For a particular energy level E° of $\mathcal{H}^\circ$, have an irreducible rep:

$$\{\underbrace{\underset{\sim}{D}^\circ(E), \underset{\sim}{D}^\circ(R_1), \underset{\sim}{D}^\circ(R_2), \ldots \underset{\sim}{D}^\circ(R_g)}_{\text{This set of matrices forms a reducible rep. of } G.}, \underset{\sim}{D}^\circ(R_{g+1}), \ldots\ldots, D^\circ(R_{g_0})\}$$

Now seek a unitary transformation $\underset{\sim}{A}$, so that for every R_k in G,

$$\underset{\sim}{A}^\dagger \underset{\sim}{D}^\circ(R_k) \underset{\sim}{A} = \underbrace{\underset{\sim}{D}_1(R_k) + \underset{\sim}{D}_2(R_k) + \ldots\ldots + D_N(R_k)}_{\text{irred. reps. of } G}$$

The matrix $\hat{A}$ then gives the (1st order) corrections to the eigenfunctions of $\mathcal{H}^\circ$:

$$\bar{\Phi}_{nr} = \sum_{\mu=1}^{\bar{\imath}} a_{\mu r} \bar{\Psi}_{n\mu}$$

$\bar{\Phi}_{nr}$: correct linear combinations of $\bar{\Psi}_{n\mu}$'s to form irred. reps. of G

$\bar{\Psi}_{n\mu}$: eigenf^{n}s of $\mathcal{H}^\circ$, forming irred. reps. of G°

[Compare the method of coupling ang. momenta to obtain the coeffs. $a_{\mu r}$ in the secular equation].

A great aid in this is the use of the characters of the two groups G°, and G. Thus can immediately see in eqn^{n} (69) [p. 107], that the characters are related by:

$$\chi^\circ(R_k) = \chi_1(R_k) + \chi_2(R_k) + \ldots\ldots + \chi_N(R_k) \qquad (70)$$

Thus if a complete table of the characters for each of the irred. reps. of the two groups G^0 and G were available, would be able to see from inspection how a matrix $D^0(R_k)$ of G^0 is reduced on going to G.

This is the core of the method for crystal field theory. The group G^0 is the group of the free atom - consists of all rotations about any axis through the nucleus through any angle, and all reflections in any plane through the nucleus.

The group G is a subgroup of this: The rotations and reflections are restricted to those angles and axes appropriate to, say, the octahedral group.

Method was worked out as long ago as 1929 by H. Bethe. His original paper is still the best reference; have given enough material in these lectures for you to read this paper fairly easily:

H. Bethe, Annalen der Physik, Vol. 3, pps 133-206, (1929).

English translation: Consultants' Bureau Inc.

[S.F. Mason has a copy].

6th January 1968.

Double Groups.

First of all – important to distinguish between isomorphism and homomorphism.

Hence, Appendix B.

Definition: Two groups G_1 and G_2 are homomorphic if some element of G_2 can be associated with every element of G_1, such that if

$$P_1 Q_1 = R_1; \quad P_1, Q_1, R_1 \in G_1,$$

then

$$P_2 Q_2 = R_2; \quad P_2, Q_2, R_2 \in G_2,$$

where P_1 corresponds to P_2, Q_1 to Q_2, & R_1 to R_2

homomorphism.

Isomorphism: Two groups said to be isomorphic if there exists a one-to-one correspondence between the elements $A_1, B_1, C_1, \ldots$ of G_1 and $A_2, B_2, C_2, \ldots$ of G_2, such that if $P_1 Q_1 = R_1$, then $P_2 Q_2 = R_2$ and vice versa.

January 6th 1968.

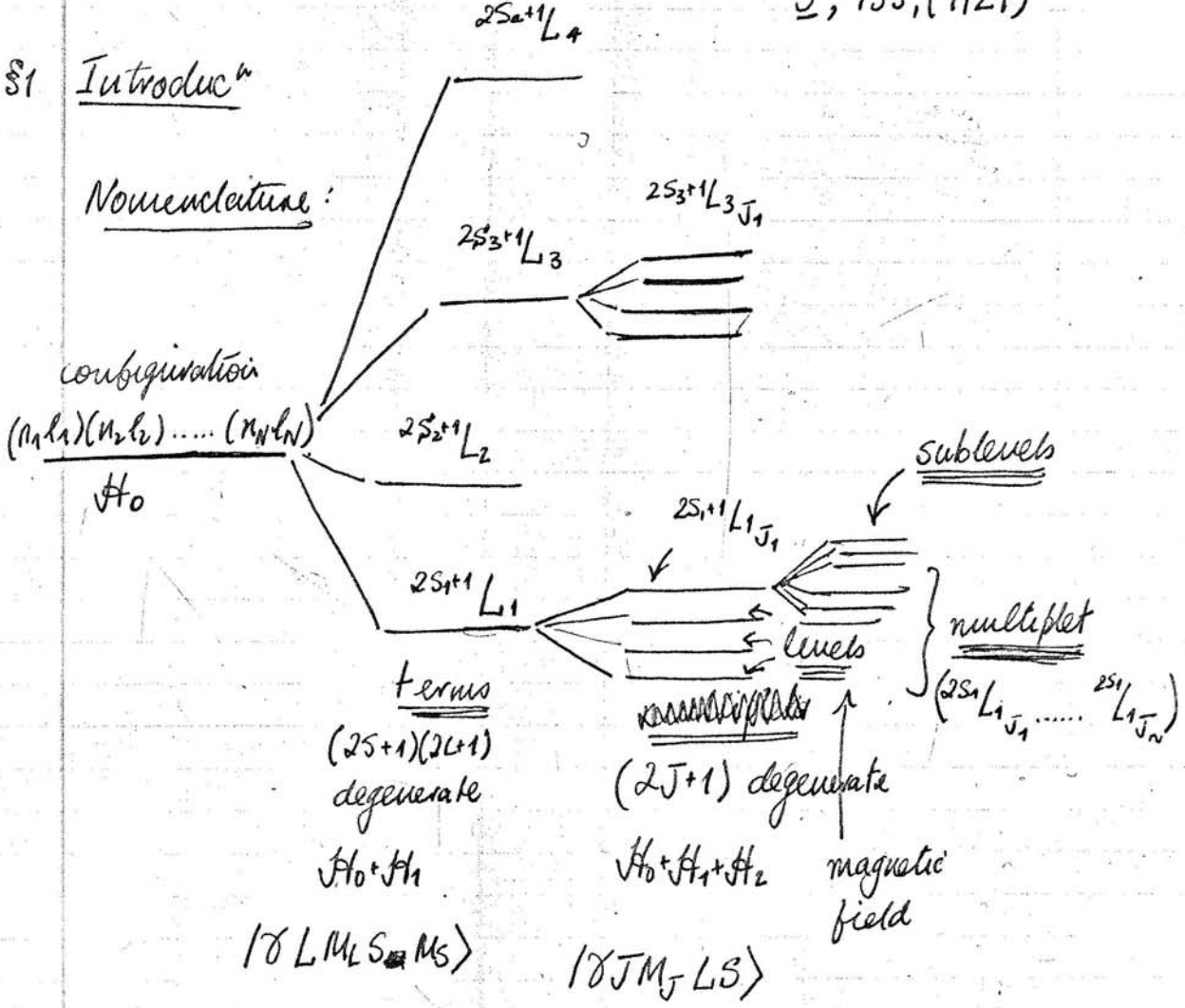
Miss Morgan. - Maths. & Phys.
- Translation of Bethe's article.

Splitting of Terms in Crystals

Hans Bethe Ann. der Physik 3, 133, (1929)

§1 Introduc^{n}

Nomenclature:



Bethe distinguishes 3 cases:

1) Xtal field is large compared to separation of different multiplets - i.e. Xtal field is larger than $\mathcal{H}_1$ and $\mathcal{H}_2$. Start with a wave f^{n}

$V_{cryst} \gg \mathcal{H}_1$

$$\Psi = (n_1l_1)\ldots(n_il_i)\ldots(n_Nl_N)$$

1st approx^{n}: - then consider the effect of V_{cryst} on this

2nd approx^{n} - bring in $\mathcal{H}_1$, and finally bring in $\mathcal{H}_2$

2) Xtal field of intermediate size i.e. small compared to separation of different multiplets, but large compared to separation of levels within a single multiplet

i.e. $\mathcal{H}_1 \gg V_{cryst} \gg \mathcal{H}_2$

- probably the most frequent case

Start with $|\gamma L M_L S M_S\rangle$, then examine effect of V_{cryst}, and finally study the spin-orbit interaction

3) Xtal field is small in comparison with the separations of levels within a multiplet

i.e. $\mathcal{H}_1 \gg \mathcal{H}_2 \gg V_{cryst}$

Hence start with $|\gamma J M_J L S\rangle$ and examine the effect of V_{cryst} on this.

Bethe's nomenclature:

λ "azimuthal xtal quantum no.[3] to specify the orientation of $\underset{\sim}{L}$ in the xtal"
i.e. irred. rep. of total $\underset{\sim}{L}$.

λ_i - irred. rep. of the individual (i^{th}) electron

l_i - ordinary ang. mom. in free atom

μ - irred. rep. of $\underset{\sim}{J}$ in the xtal.

Hence an atom is characterised by the following quantum nos: —

1) Large xtal splitting : $n_i, l_i, \lambda_i, \lambda, \mu$.

2) intermediate —"— —"— : $n_i, l_i, L, \lambda, \mu$.

3) small —"— —"— n_i, l_i, L, J, μ.

For the moment, treat the 3 possible cases: orientation of l_i, orientation of L, orientation of J in the xtal, together, & make group theoretical calc^{ns} of the number of components into which a term splits for given angular momentum (represent^{n} of the rotation group) & given symmetry of the site of the atom in the xtal. The case of $\frac{1}{2}$-integral J (double-valued represent^{n} of the rot^{n} group) will have to be treated separately.

I Group Theoretical Solution

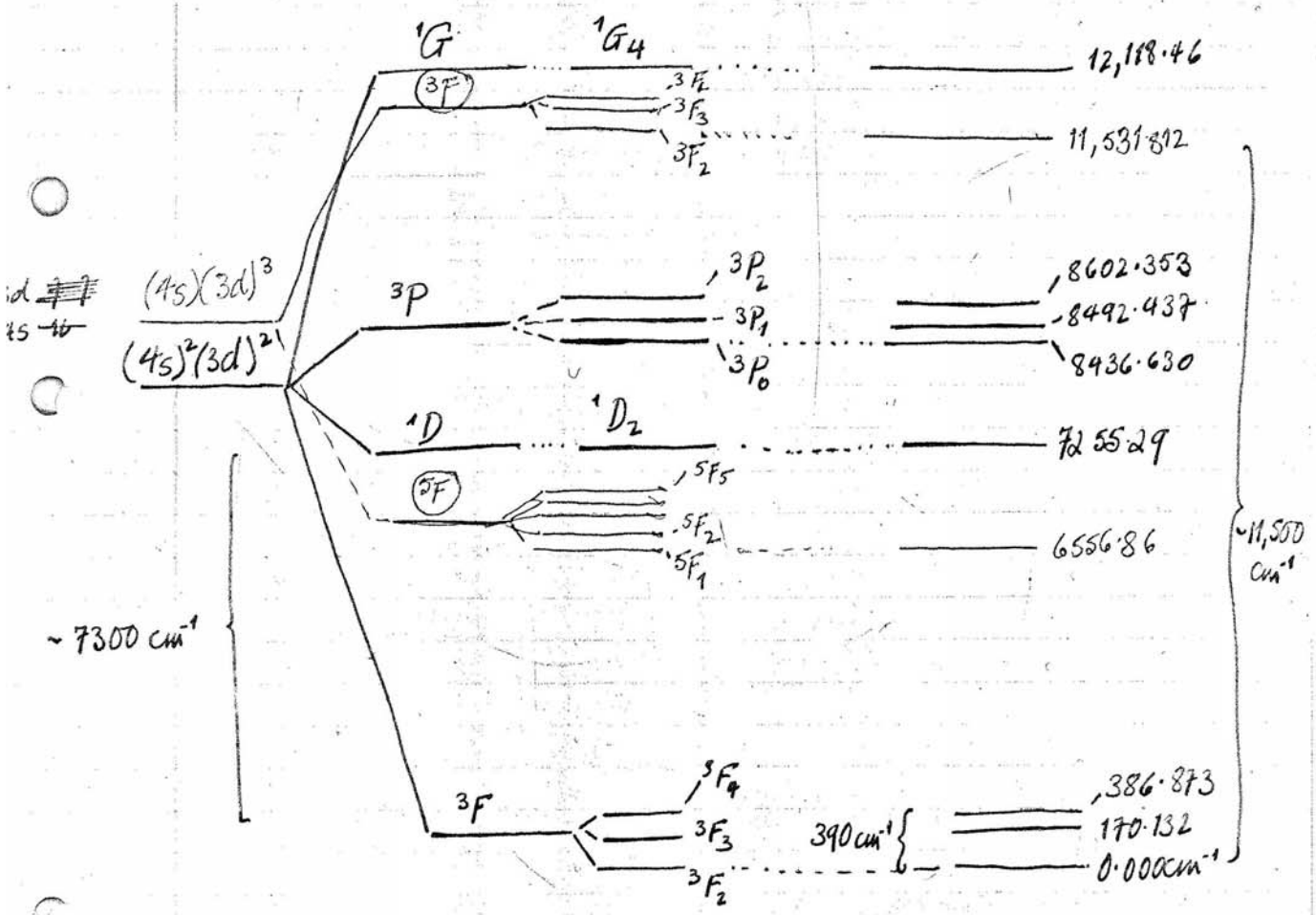
§2

8th Jan. 1968.

Free ion atom

Energy levels of Ti $(4s)^2(3d)^2$ (Moore, Atomic Energy Levels).

Terms expected from d^2: ^3F, ^3P, ^1G, ^1D, ^1S.

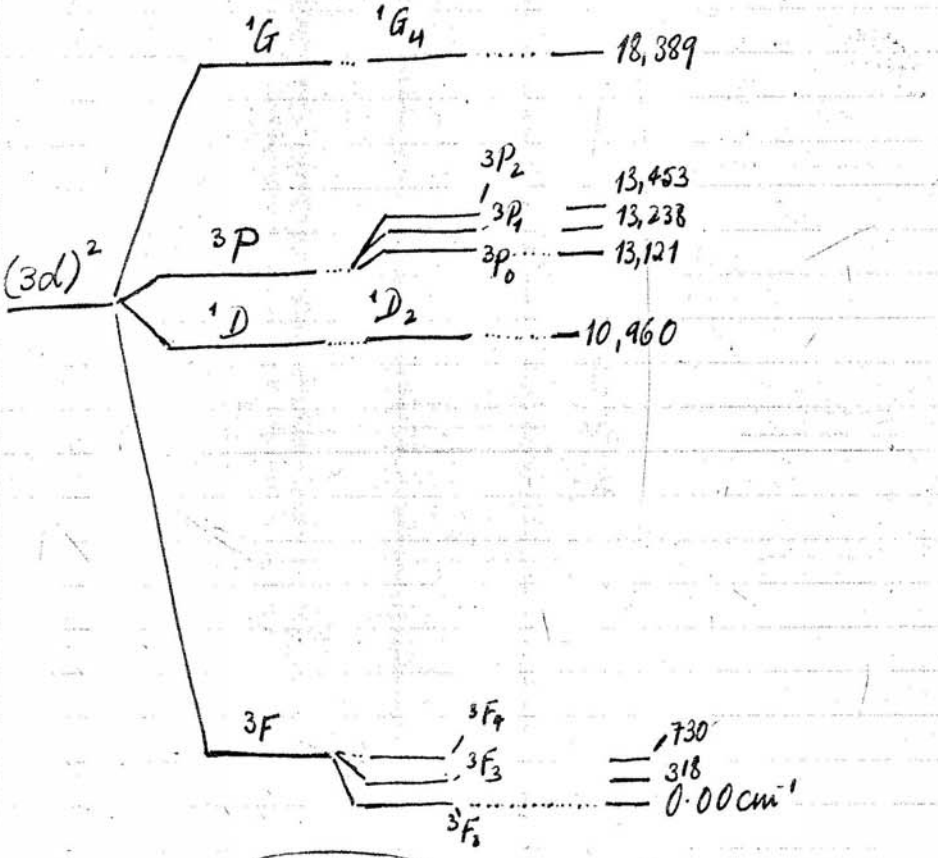


The nearest configuration that can interact with $(4s)^2(3d)^2$ is $(4s)(3d)^3$ - as this gives $^3F_2$, $^3F_3$, $^3F_4$ levels which can interact with the ground state multiplet

Free ion

V ground state : $(4s)^2(3d)^3$

V^{III} : $(3d)^2$. Also in $V(H_2O)_6^{3+}$



4s
3d

observed

The nearest configuration to this is (3d)(4s)

– the lowest level being $^3D_1$ at 96,195 cm^{-1}, and the lowest level that could interact with any of the $(3d)^2$ levels is the (3d)(4s) $^1D_2$ at 100,204 cm^{-1}

observed

The lowest configuration that could interact with V^{III} ground state is $3d(^2D)4p$, $^3F_2^o$ at 147,133 cm^{-1}