Energy Levels of Atoms in Crystal Fields.

Lecture 1.

The plan of the course is as follows:

I, Atomic Structure

The Schrödinger Equation – Various terms in H
Symmetry, commutation, degeneracy – angular momentum.
Pauli principle.
H_0 – configurations – Slater determinants
H_1 – coupling of angular momenta

Terms – Hund's rules.
Spin orbit coupling – levels.
Magnetic fields – sublevels.

II, Crystal Fields. Transition metal (metal) & rare earth ions in crystals.

Strong, intermediate, and weak fields.

Group theory – Groups, representations, group theory & quantum mechanics
direct products of irred. representations.
perturbations and group theory.

Splitting of terms in crystals: Bethe's method.

– correlation diagrams between the strong, intermediate and weak field cases.

Ligand field theory (molecular orbital theory).

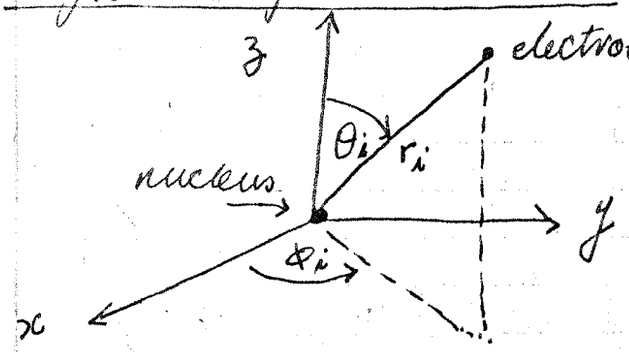
I, ATOMIC STRUCTURE.

Will study by means of quantum mechanics the structure of atoms.

Let the atom contain N electrons,
and the nuclear charge be Ze

Z not necessarily equal to N - also consider ions

Coordinate system: Origin at the nucleus, spherical polar coordinates



3 indep. coordinates

position of electron i is (r_i, θ_i, ϕ_i)
or $\underset{\sim}{r}_i$ i.t.o. vector notation.

known to

angular momentum

Electrons also have a spin α_i or β_i

denote this by $\underset{\sim}{\sigma}_i = \begin{cases} \alpha_i \\ \beta_i \end{cases}$.

- will introduce ang. mom. more formally later.

Then the wave function for the atom, $\underline{\Psi}$, will also be referred to the nucleus as origin, and will also depend on all these coordinates:

$$\underline{\Psi} = \underline{\Psi}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots\ldots, \underset{\sim}{r}_N ; \sigma_1, \sigma_2, \ldots\ldots, \sigma_N)$$

Up till now - you have only dealt with one-electron systems, such as the H atom, $\underline{\Psi} = \underline{\Psi}(\underset{\sim}{r}, \sigma)$.

Now the wave function is determined by the Schrödinger equation:

$$\boxed{\mathcal{H}\underline{\underline{\Psi}} = E\underline{\underline{\Psi}}} \qquad (1)/$$

$\mathcal{H}$ is the Hamiltonian of the system – will come to this in a moment.

Interpretation of $\underline{\underline{\Psi}}$. Having solved the equation (1) for $\underline{\underline{\Psi}}$, recall that the square of $\underline{\underline{\Psi}}$,

$$|\underline{\underline{\Psi}}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots \underset{\sim}{r}_N ; \sigma_1, \sigma_2, \ldots, \sigma_N)|^2$$

– probability that electron 1 is at position $\underset{\sim}{r}_1$ with spin σ_1, ~~with~~ with

electron 2 at position $\underset{\sim}{r}_2$, with spin σ_2,

⋮

electron N at position $\underset{\sim}{r}_N$, with spin σ_N,

– SIMULTANEOUSLY.

In general, recall that eqn (1) will have a number of different solutions,

$$\underline{\underline{\Psi}}_0, \underline{\underline{\Psi}}_1, \ldots\ldots, \underline{\underline{\Psi}}_n, \ldots\ldots$$

each with its energy eigenvalue

$$E_0, E_1, \ldots\ldots, E_n, \ldots\ldots$$

Thus we might write (1) as

$$\mathcal{H}\underline{\underline{\Psi}}_n = E_n\underline{\underline{\Psi}}_n \qquad n = 0, 1, 2, \ldots\ldots$$

$$(1a)/.$$

Recall the properties of these eigenfunctions $^{2}\Psi_n$:

i) Normality:

$$\int\int\cdots\int {}^{2}\Psi_n^{*}(r_1,\ldots,r_N;\sigma_1,\ldots\sigma_N)\,{}^{2}\Psi(r_1,\ldots,r_N;\sigma_1,\ldots\sigma_N)\,d\tau_1\,d\tau_2\ldots d\tau_N = 1 \qquad (2)$$

where each $d\tau_i$, $i = 1,2,\ldots,N$ is the volume element for each electron

$$d\tau_i = r_i^2 \sin\theta_i\, d\theta_i\, d\phi_i\, dr_i$$

$$\int \ldots d\tau_i = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}$$

→ simply means that the total probability of all the electrons over all space must be equal to 1 - reasonable!

ii) Orthogonality

$$\int\int\cdots\int {}^{2}\Psi_n^{*}(r_1\ldots r_N;\sigma_1\ldots\sigma_N)\,{}^{2}\Psi_m(r_1,\ldots r_N;\sigma_1,\ldots\sigma_N)\,d\tau_1\,d\tau_2\ldots d\tau_N = 0 \quad \text{if } n \neq m. \qquad (3)$$

Notation. Write $^{2}\Psi_n(r_1,r_2,\ldots r_N;\sigma_1,\sigma_2,\ldots\sigma_N)$ simply as $|n\rangle$: "ket"

and $^{2}\Psi_n^{*}(r_1,r_2,\ldots r_N;\sigma_1,\sigma_2,\ldots\sigma_N)$ as $\langle n|$: "bra"

Then equation (2) written simply as

$$\langle n|n\rangle = 1 \qquad (2a)$$

└ "bra-ket"

- Rumoured to be Dirac's only joke.

Equation (3) is simply

$$\langle n|m\rangle = 0 \; ; \; n \neq m \qquad (3a).$$

(2a) and (3a) may be written together as

$$\langle n|m\rangle = \delta_{nm} \qquad (4)$$

δ_{nm} = Kronecker delta function

= 1 if $n = m$,
= 0 otherwise.

The Hamiltonian $\mathcal{H}$.

- Contains all the physical information about the problem
  - $\mathcal{H}$ defines the system about which we are talking

In general,

$\mathcal{H}$ = kinetic energy + potential energy
= $T + V$.

Let us then consider N electrons moving around the nucleus. Recall that the origin of all coordinates is at the nucleus, so this is stationary.

Let electron i have momentum $\underset{\sim}{p}_i$.
Then its k.e. is $\frac{p_i^2}{2m}$

Hence the total k.e. will be:

$$T = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

Remember that p_i is a vector - has direction as well as a value.

i. $\underset{\sim}{p_i}$ has 3 components: p_{ix}, p_{iy}, p_{iz}
or $(p_{ir}, p_{i\theta}, p_{i\phi})$ in the spherical polar coord. system

and recall from vector analysis that the square of a vector is given by

$$p_i^2 = (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) \quad \text{or} \quad (p_{ir}^2 + p_{i\theta}^2 + p_{i\phi}^2)$$

Potential energy terms. What is the potential energy of electron i?

It has a charge of $-e$.

The nucleus has a charge of $+Ze$

All other electrons have a charge $-e$ too.

Thus electron i will feel the attraction of the nucleus,

$$\rightarrow \ominus \frac{Ze^2}{r_i}$$

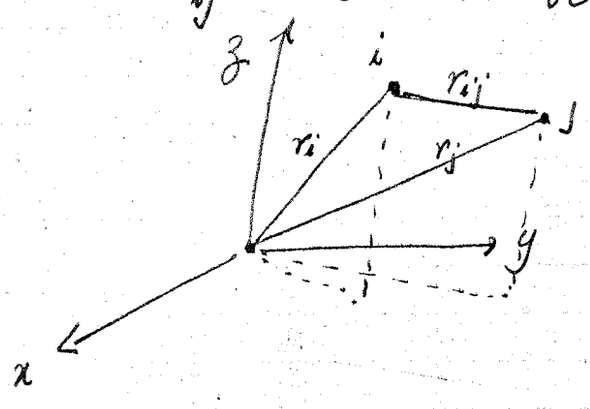
-ve sign indicates attraction

- and the repulsion of all the other electrons

Thus electron 1 will be repelled by electrons 2, 3, 4, ... N.

Hence there is a repulsion $\oplus \frac{e^2}{r_{ij}}$ N.B. $j = 2, 3, 4, \ldots N$

r_{ij} = distance between electrons i & j:



Electron 2 will feel the repulsion of electrons 3, 4, 5, ... N — and <u>electron 1</u>

$\frac{+e^2}{r_{2j}}$

But this taken care of in the first term

$\frac{+e^2}{r_{1j}}$, $j = 2, 3, \ldots$

Hence the <u>total mutual</u> repulsion of all the electrons will be given by

$$\underbrace{\sum_{j=i+1}^{N} \sum_{i=1}^{N}}_{\text{makes sure that } \frac{e^2}{r_{ij}}, \text{ and } \frac{e^2}{r_{ji}} \text{ is counted only once}} \frac{+e^2}{r_{ij}} \quad \text{— written as} \quad \sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$$

Then we have for $\mathcal{H}$ so far:

$$\mathcal{H} = T + V$$

$$= \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$$

Note what we are doing:

Construct $\mathcal{H}$ according to <u>our conception</u> of what the system is like — This is the essence of <u>physics</u>

What else is there in $\mathcal{H}$?

According to classical mechanics - this all. However, there are other smaller relativistic effects, and we will consider the most important of them.

Now introduce a mechanical quantity which we shall consider a great deal:

Electron i is at position $\underset{\sim}{r}_i$, and has momentum $\underset{\sim}{p}_i$ (vectors!). Then the moment of momentum or ANGULAR MOMENTUM is denoted by $\underset{\sim}{l}_i$ and given by

$$\underset{\sim}{l}_i = (\underset{\sim}{r}_i \times \underset{\sim}{p}_i) \qquad (5)/$$

The significance of $\underset{\sim}{l}_i$ will become clearer later when we discuss symmetry properties.

The electron spin is also an angular momentum - although spin does not correspond to any classical quantity - it is a purely relativistic effect. Hence write the spin of electron i, σ_i, in vector notation too: $\underset{\sim}{\sigma}_i$.

(when dealing with relativistic mechanics, $m \to m^*$)

Then since spin is a relativistic phenomenon, we expect some kind of interaction between the spin angular momentum and the orbital angular momentum $\underset{\sim}{l}_i$.

This interaction is known as the SPIN-ORBIT interaction — Gives a potential energy term of the form:

$$\mathcal{H}_{LS} = \frac{e^2\hbar^2}{2m^2c^2} \cdot \sum_{i=1}^{N} \xi'(r_i)\, \underset{\sim}{\sigma}_i \cdot \underset{\sim}{l}_i$$

($\cdot$ ← SCALAR PRODUCT of 2 vectors)

a force tending to align σ_i and l_i

Note dependence on $\frac{1}{c^2}$.
- a) shows relativistic nature
- b) is very small.

or just

$$\mathcal{H}_{LS} = \sum_{i=1}^{N} \xi(r_i)\, \underset{\sim}{\sigma}_i \cdot \underset{\sim}{l}_i \qquad (6)/$$

Thus our total Hamiltonian is now

$$\mathcal{H}_{tot.} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{*j>i=1}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i)\, \underset{\sim}{\sigma}_i \cdot \underset{\sim}{l}_i \qquad (7).$$

[To convert $\frac{p_i^2}{2m}$, $p_{ix} \to -i\hbar \frac{\partial \dots}{\partial x_i}$

$\to -\frac{\hbar^2}{2m} \nabla_i^2$;

$$\nabla_i^2 = \frac{\partial^2 \dots}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial \dots}{\partial r_i} + \frac{1}{r_i^2 \sin\theta_i} \frac{\partial}{\partial \theta_i} \left(\sin\theta_i \frac{\partial \dots}{\partial \theta_i} \right) + \frac{1}{r_i^2 \sin^2\theta_i} \frac{\partial^2 \dots}{\partial \phi_i^2} \;]$$

This shows that ~~state~~ an atom is a most complicated dynamical system — with relativistic effects also coming in.

Hence although we can set up the Schrödinger equation

$$\mathcal{H}_{tot} \Psi = E \Psi$$

with the Hamiltonian (7), it has so far proved completely impossible to solve it

— And even if we could solve it — we wouldn't learn anything from it — would just get streams of numbers on a computer output.

Can (7) be simplified? Or rather, can (7) be simplified in a physically meaningful way?

To start with — forget about the spin-orbit coupling — recall that this is proportional to $\frac{1}{c^2}$ — will consider this term later.

What remains then is a purely classical

— Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} - \frac{Ze}{r_i}\right] + \sum_{j>i=1}^{N}\frac{e^2}{r_{ij}} \qquad (8)/$$

- no spin terms. — the major part of $\mathcal{H}_{tot}$ — explains most of chemistry

This means that the solutions, $\bar{\Psi}_s$, of this equation

Lecture 1.

$$\mathcal{H}\bar{\Psi}_s = E\bar{\Psi}_s,$$

with $\mathcal{H}$ given by (8) can immediately be factorised into space and spin parts! —

— an immediate simplification

$$\bar{\Psi}_s(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots \underset{\sim}{r}_N; \sigma_1, \sigma_2, \ldots \sigma_N) = \bar{\Phi}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots, \underset{\sim}{r}_N)\,\textcircled{H}(\sigma_1, \sigma_2, \ldots, \sigma_N) \qquad (a)/$$

i.e. $\bar{\Psi}_s = \bar{\Phi}\textcircled{H}$ or at least $\sum_k \bar{\Phi}_k \textcircled{H}_k$

— $\mathcal{H}$ acts only on the $\bar{\Phi}$ part:

$$(\mathcal{H}\bar{\Phi})\textcircled{H} = E\bar{\Phi}\textcircled{H} \qquad (10)/$$

Can we then forget all about spin? — Can we simply cancel out $\textcircled{H}$ in equation (9).?

In principle we can — but in fact the spin part $\textcircled{H}$ of $\bar{\Psi}_s$ has a special effect on $\bar{\Phi}$ — This is due to what is known as the Pauli principle. This states, as a Law of Nature, that in every wave function must change when we interchange both space

and spin coordinates of any 2 particles, then either

i) the wave function remains unchanged

or ii) changes sign.

Thus for any wave function

$$\Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots \underset{\sim}{r}_N ; \underset{\sim}{\sigma}_1, \underset{\sim}{\sigma}_2, \ldots \underset{\sim}{\sigma}_N)$$

$$\Psi(\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_i, \ldots, \underset{\sim}{r}_j, \ldots, \underset{\sim}{r}_N ; \sigma_1, \ldots, \sigma_i, \ldots, \sigma_j, \ldots, \sigma_N)$$

i & j have been interchanged

$$= \pm \Psi(\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_j, \ldots, \underset{\sim}{r}_i, \ldots \underset{\sim}{r}_N ; \sigma_1, \ldots, \sigma_j, \ldots, \sigma_i, \ldots \sigma_N)$$

For particles with spin = $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

e.g. electrons, protons, neutrons, — -ve sign

particles with spin $0, 1, 2, \ldots$ +ve sign

e.g. photons, deuterons, He^4, ... etc.

- Pauli Principle arises from the fundamental indistinguishability of identical particles.

- Has tremendous consequences for the whole of chemistry. How this comes about — will be discussed in subsequent lectures.

At the moment, the effect of the Pauli Principle on a wavefunction of the form (9) $\Psi = \Phi\Theta$, is such that, although the function is factorised, we cannot simply ignore

the Φ function :- The Pauli principle says that the whole function, $\Phi(H)$, must be antisymmetric towards interchange of any two coordinates

$$(\underset{\sim}{r}_i, \sigma_i) \quad \& \quad (\underset{\sim}{r}_j, \sigma_j)$$

E.g. If Φ were a function of just 2 electrons,

$$\Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$$

- then if this were symmetric

$$\Phi(\underset{\sim}{r}_2, \underset{\sim}{r}_1) = \Phi(\underset{\sim}{r}_1, \underset{\sim}{r}_2),$$

then $\Phi(H)(\sigma_1, \sigma_2)$ must be antisymmetric

- and vice versa.

Summary

$$\mathcal{H}_{tot} = \mathcal{H} + \mathcal{H}_{LS}.$$

$\mathcal{H}_{LS}$ is v. small - and ignored at first - leaves

[for light atoms]

just $\mathcal{H}$. Solutions of $\mathcal{H}$ are of the form

$\Phi(H)$ ← depends only on $\sigma_1, \ldots, \sigma_N$.

depends only on $\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_N$

- but situation is not so simple due to the Pauli principle: $(\Phi(H))$ must be antisymmetric

- Hence $\Phi(H)$ cannot be ignored

Thus is still too complex to solve.

$$\mathcal{H}(\Psi_H) = E(\Psi_H)$$

What now? The trouble with $\mathcal{H}$ is due to the electron-electron interaction term

$$+\sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$$

If this term were absent — i.e. the electrons did not interact with each other at all — the situation would be very much simpler. Would have

$$\sum_{i=1}^{N}\left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i}\right]$$

— which is just the sum of N hydrogen-like atoms — And we know the solutions of this.

However, under no circumstances are the electron-electron repulsions too small to ignore. Instead we replace $\sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$ by an average effective potential $U(r_i)$ — which is the same for all electrons (and is spherically symmetric) — i.e. instead of the e-e interactions — use an effective interaction. We write $\mathcal{H}$ in the form

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N}\left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + U(r_i)\right]}_{\mathcal{H}_0} + \underbrace{\left[\sum_{j>i=1}^{N} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} U(r_i)\right]}_{\mathcal{H}_{ee}}$$

and we hope that $\mathcal{H}_{ee}$ is small — In fact, I have not specified $U(r_i)$; it is chosen so as to make $\mathcal{H}_{ee}$ as small as possible.

$\mathcal{H}_0$ still has the form of a sum of 1-electron atoms and will have solutions similar to those of the H atom — Instead of just $-\frac{Ze^2}{r_i}$, have $-\frac{Ze^2}{r_i} + U(r_i)$ [but not identical]

We have now split up $\mathcal{H}_{tot.}$ as follows:

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

$\mathcal{H}_0$: Can find solutions to this

$\mathcal{H}_{ee}$: Add in as a correction

$\mathcal{H}_{LS}$: disregard

Solutions of $\mathcal{H}_0$. We do not have to specify $U(r_i)$ at all just yet. Just from the form of $\mathcal{H}_0$, we see that the solutions must be of the form

$$\mathcal{H}_0 \Psi_0 = E_0 \Psi_0 \qquad (11)$$

where

$$\Psi_0 = \phi_1(\underset{\sim}{r}_1)\phi_2(\underset{\sim}{r}_2) \ldots\ldots \phi_N(\underset{\sim}{r}_N) \qquad (12)$$

- write as

$$\phi_1(1)\phi_2(2)\ldots\ldots\phi_N(N)$$

- i.e. a [product of 1-electron functions or orbitals]

Equation (11) is the same as saying that each orbital is a solution of a Schrödinger equation:

leave on the board.

$$\left\{ \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + U(r) \right\} \phi_i(\underset{\sim}{r}) = \varepsilon_i \phi_i(\underset{\sim}{r}) \qquad (13)$$

$i = 1, 2, \ldots\ldots, N$

Not necessary to put a subscript here

N.B. is a vector – depends on r, θ, ϕ

and $\sum_{i=1}^{N} \epsilon_i = E_0$ - equation (11)/.

Equation (13) is an equation in 1 electron only, and it also does not contain any spin. Hence each orbital ϕ_i, $i = 1, 2, \ldots, N$ can be multiplied by a single spin function, $\sigma_i = \begin{cases} \alpha_i \\ \text{or} \\ \beta_i \end{cases}$ - and is still a solution of (13)/. Hence the total solution, Ψ_0, of $\mathcal{H}_0$, can be written as

$$\phi_1(1)\phi_2(2)\ldots\ldots\phi_N(N).\ \sigma_1(1)\sigma_2(2)\ldots\ldots\sigma_N(N) \quad \text{— (14)/}$$

However we now recall the Pauli principle, which says that all solutions of $\mathcal{H}_0$ must be antisymmetric towards the interchange of any 2 electrons. This means that from our function (14) we must construct a function that changes sign whenever we interchange any two electron coordinates

e.g. $\{\phi_2(2), \sigma_2(2)\}$ and $\{\phi_i(i), \sigma_i(i)\}$

How do we do this?

Antisymmetrization of orbital wave functions

The easiest way to do this was shown by Slater in 1929.

Example. Consider a function of 3 electrons:

$$\psi_p(1)\,\psi_q(2)\,\psi_r(3)$$

- We want this function to change sign whenever we interchange any two electrons: 1 & 2, 1 & 3, or 2 & 3.

Consider the electrons in their natural order

1 2 3.

There are $N! = 6$ different arrangements of this sequence:

1 3 2
3 2 1
2 1 3
2 3 1
3 1 2

(or permutations)

With each such arrangement, can associate a sign, according to how many single interchanges are necessary to get back to the original sequence.

Thus

1 3 2 $\rightarrow P_{23} \rightarrow$ 1 2 3.

3 2 1 $\rightarrow P_{13} \rightarrow$ 1 2 3

2 1 3 $\rightarrow P_{12} \rightarrow$ 1 2 3

2 3 1 $\rightarrow P_{12} \rightarrow$ 1 3 2 $\rightarrow P_{23} \rightarrow$ 1 2 3

3 1 2 $\rightarrow P_{13} \rightarrow$ 1 3 2 $\rightarrow P_{23} \rightarrow$ 1 2 3.

1 odd interchange
1 — n — odd
1 — n — odd
2 interchanges even
2 — n — even

Now, for a given permutation of the sequence
1 2 3

there are either an even or an odd number of single interchanges necessary to recover the natural sequence — and this number is independent of how one does it.

Now put a -ve sign in front of all odd permutations, and a +ve sign in front of all even permutations — e.g. see above.

Then the function

$$\frac{1}{\sqrt{6!}} \Big[\psi_p^s(1)\psi_q^s(2)\psi_r^s(3) - \psi_p^s(1)\psi_q^s(3)\psi_r^s(2) - \psi_p^s(3)\psi_q^s(2)\psi_r^s(1) - \psi_p^s(2)\psi_q^s(1)\psi_r^s(3) + \psi_p^s(2)\psi_q^s(3)\psi_r^s(1) + \psi_p^s(3)\psi_q^s(1)\psi_r^s(2) \Big]$$

Normalising factor

is completely antisymmetric.

The striking simplifying feature of this is that this can be written as a determinant

$$\frac{1}{\sqrt{6}} \begin{vmatrix} \psi_p^s(1) & \psi_q^s(1) & \psi_r^s(1) \\ \psi_p^s(2) & \psi_q^s(2) & \psi_r^s(2) \\ \psi_p^s(3) & \psi_q^s(3) & \psi_r^s(3) \end{vmatrix}$$

— A SLATER DETERMINANT

Interchanging any 2 electrons, — means interchanging any 2 rows of this determinant, and from the theory of determinants we know that the determinant then changes sign

General case for N electrons.

We have a function of the form of equation (14), (p. 15)

$$\phi_1(1)\phi_2(2)\ldots\ldots\phi_N(N)\,\sigma_1(1)\,\sigma_2(2)\ldots\ldots\ldots\sigma_N(N)$$

or

$$\underbrace{\phi_1(1)\,\sigma_1(1)}_{\psi_1(1)}\;\underbrace{\phi_2(2)\,\sigma_2(2)}_{\psi_2(2)}\ldots\ldots\;\underbrace{\phi_N(N)\,\sigma_N(N)}_{\psi_3(3)}$$

– put each space-spin function with its orbital

Then

$$\sqrt{\frac{1}{N!}}\sum_P \varepsilon_P P\left\{\phi_1(1)\sigma_1(1)\;\phi_2(2)\sigma_2(2)\ldots\ldots\phi_N(N)\sigma_N(N)\right\}$$

Permutes the coords.

– is an antisymmetric towards interchanges of any two space-spin electron coordinates

Parities of P – even (+ve) or odd (–ve)

$$= \sqrt{\frac{1}{N!}}\begin{vmatrix} \phi_1(1)\sigma_1(1) & \phi_2(1)\sigma_2(1) & \ldots\ldots & \phi_N(1)\sigma_N(1) \\ \phi_1(2)\sigma_1(2) & \phi_2(2)\sigma_2(2) & \ldots\ldots & \phi_N(2)\sigma_N(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(N)\sigma_1(N) & \phi_2(N)\sigma_2(N) & \ldots\ldots & \phi_N(N)\sigma_N(N) \end{vmatrix} \quad (15)/$$

– Interchange of any two electrons ≡ interchange of two rows.

Note in addition If I make ϕ_2 the same as ϕ_1 and σ_2 the same as σ_1,

Repeat:

$\hat{H}_0 \Phi_0 = E_0 \Phi_0$

Φ_0 - ~~answer~~ not just a simple product

$\phi_1(1)\phi_2(2) \ldots\ldots \phi_N(N)$

- but have to include spin, and antisymmetrise

Φ_0 = a Slater determinant

$$= \sqrt{\frac{1}{N!}} \begin{vmatrix} \phi_1(1)\sigma_1(1) & \phi_2(1)\sigma_2(1) & \ldots\ldots & \phi_N(1)\sigma_N(1) \\ \phi_1(2)\sigma_1(2) & \phi_2(2)\sigma_2(2) & \ldots\ldots & \phi_N(2)\sigma_N(2) \\ \vdots & & & \vdots \\ \phi_1(N)\sigma_1(N) & \phi_2(N)\sigma_2(N) & \ldots\ldots & \phi_N(N)\sigma_N(N) \end{vmatrix}$$

- Still ~~an eigenfn of~~ $\hat{H}_0$.

- Not more than 2 ϕ_i's the same - and if they are the same, then the σ's must be different

- then if columns 1 and 2 of the determinant are the same, and the theory of determinant tells us that the determinant vanishes.

Thus, since there are only 2 possible spin functions, $\sigma_i = \alpha_i$, or $\sigma_i = \beta_i$, we cannot have more than 2 orbitals ϕ_i the same, and if they are the same, one electron must have α spin, and the other electron β spin

- the PAULI EXCLUSION PRINCIPLE

Lecture 2.

Note how far reaching the effect of this is:

The determinant function (15)/ is an eigenfunction of $\hat{H}_0$, just the same as the simple product function $\bar{\Phi}_0$, (11), or (p. 14) or (14)/

But look at equation (13) again:

$$\left\{ \frac{p^2}{2m} - \frac{Ze^2}{r} + U(r) \right\} \phi_i(\underset{\sim}{r}) = \epsilon_i \phi_i(\underset{\sim}{r})$$

(eqn that determines the ϕ_i)

(depend on each other → SCF method)

- the same equation for all orbitals ϕ_i, $i = 1, 2, \ldots, N$, and

$$\sum_{i=1}^{N} \epsilon_i = E_0$$

Note that E_0, in $\hat{H}_0 \bar{\Phi}_0 = E_0 \bar{\Phi}_0$ is not the SCF energy:-

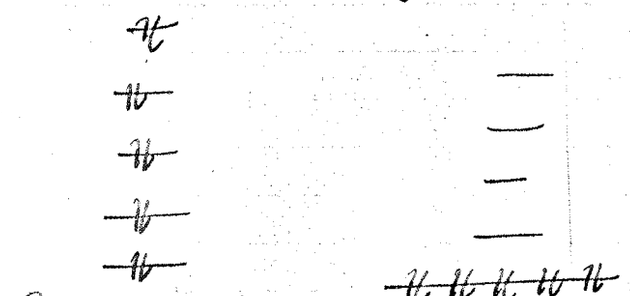
$E_{SCF} = \langle \bar{\Phi}_0 | \hat{H}_0 + \hat{H}_{ee} | \bar{\Phi}_0 \rangle$

There is nothing in this equation that prevents all the orbitals being the same, with the lowest eigenvalue ϵ_i

- Indeed this would give the least total energy E_0.

But this would lead to a wavefunction with more than 2 ϕ_i's the same, and this function will vanish under antisymmetrisation.

Thus, the Pauli exclusion principle keeps all the electrons from crowding into the lowest levels – and forces them to occupy the orbitals in pairs:



Pauli exclusion principle

– not possible.

Now since the orbitals satisfy the same Schrödinger equation (13)/, can require them to be orthonormal [recall lecture 1, p. 4 !]

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad \text{[Notation p. 4 !!]}$$

(16)/

Hence the exclusion principle says that two electrons with different spins, α and β, can occupy the same orbital, but 2 electrons with the same spin must be in orthogonal orbitals ← no overlapping

– i.e. the Pauli principle keeps electrons with the same spin apart

Pauli principle is, in fact, the first law of nature that a newly born baby experiences!

→ Makes matter seem "hard" and impenetrable, even though it consists mainly of empty space.

Summary

Have split up $\mathcal{H} = \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right\} + \sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$

into two parts $\mathcal{H}_0$ and $\mathcal{H}_{ee}$

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

(spherically symmetric)

$\mathcal{H}_0$ contains an averaged 1-electron potential $U(r_i)$ which is the same for all the electrons, and which will be chosen so as to make $\mathcal{H}_{ee}$ as small as possible.

The solutions of $\mathcal{H}_0$:

$$\mathcal{H}_0 \Phi_0 = E_0 \Phi_0$$

are, in the first instance, simple products of orbitals $\phi_1(1)\phi_2(2)\ldots\ldots\phi_N(N)$. However such an orbital product does not obey the Pauli principle, and we must antisymmetrise this function - i.e. form a Slater determinant from it

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\sigma_1(1) & \phi_2(1)\sigma_2(1) & \ldots & \phi_N(1)\sigma_N(1) \\ \phi_1(2)\sigma_1(2) & \phi_2(2)\sigma_2(2) & \ldots & \phi_N(2)\sigma_N(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(N)\sigma_1(N) & \phi_2(N)\sigma_2(N) & \ldots & \phi_N(N)\sigma_N(N) \end{vmatrix}$$

If the individual orbitals ϕ_i are orthonormal,

$$\langle \phi_i | \phi_j \rangle = \delta_{ij},$$

then the Slater determinant is also normalised

The Slater determinant is to be regarded as one single function — please do not try to imagine a sum of $N!$ products. All that is

needed to define a Slater determinant is just the simple product of orbitals:

$$\phi_1(1)\sigma_1(1),\ \phi_2(2)\sigma_2(2),\ \ldots\ldots,\ \phi_N(N)\sigma_N(N).$$

In order to ~~emphasize~~ emphasize that the Slater determinant is just 1 single function, I shall write it in the form:

$$\{\phi_1 \bar{\phi}_2 \phi_3 \bar{\phi}_4 \ldots\ldots \bar{\phi}_N\} \qquad (17)/$$

* $\phi_1, \phi_3, \ldots\ldots$, without a bar on top means that these orbitals are multiplied by $\underline{\alpha}$ spins

$$\sigma_1 = \alpha$$
$$\sigma_3 = \alpha \quad \text{etc}\ldots$$

$\bar{\phi}_2, \bar{\phi}_4, \ldots\ldots$ ~~associated~~ associated with β spins:

$$\sigma_2 = \beta$$
$$\sigma_4 = \beta \quad \text{etc.}$$

The curly brackets mean: "From this function, form the Slater determinant, and multiply it by $\sqrt{\frac{1}{N!}}$."

Details of the solutions of $\hat{H}_0$ for atoms.

Let us write out equ^n (13) once more:

$$\left\{\frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} + U(r)\right\}\phi_i(\underset{\sim}{r}) = \epsilon_i \phi_i(\underset{\sim}{r})$$

N.B.

or (13)/

$$\left\{\frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} + U(r)\right\}\phi_i(r,\theta,\phi) = \epsilon_i \phi_i(r,\theta,\phi)$$

This equation has the same form as the Schrödinger equation for an H ~~atom~~-like atom – Instead of

just the $-\frac{Ze^2}{r}$ potential, have the modified potential $-\frac{Ze^2}{r} + U(r)$.

The solutions of (13)/ will ∴ be of the form:

$$\Phi_i(r,\theta,\phi) = \frac{1}{r} R_{nl}(r)\, Y_{lm_l}(\theta,\phi) \qquad (18)/$$

where $Y_{lm_l}(\theta,\phi)$ is the eigenfunction of the square of the angular momentum for the individual electron

$$\hat{l}^2 Y_{lm_l}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm_l}(\theta,\phi)$$

$$\hat{l}_z Y_{lm_l}(\theta,\phi) = m_l \hbar\, Y_{lm_l}(\theta,\phi)$$

The "hat" on $\hat{l}^2, \hat{l}_z$ means that they are operators

$l = 0, 1, 2, \ldots\ldots, n-1.$

$m_l = -l, -l+1, \ldots\ldots, l-1, l.$

$(2l+1)$ values in all.

- So that the function $\Phi_i(r,\theta,\phi)$ is also an eigenfunction of $\hat{l}^2$, and $\hat{l}_z$, and instead of $\Phi_i(r,\theta,\phi)$ we will write the function as with the 3 quantum numbers n, l, m_l:

$$\Phi_{nlm_l}(r,\theta,\phi)$$

or as

$$|nlm_l\rangle \qquad (19)/$$

notation !!

Note that the precise form of $R_{nl}(r)$ depends on

The choice of the potential $U(r)$ in equation (13).

We should also include the spin in the function $\phi_{n\ell m_\ell}(r,\theta,\phi)$:

$\phi_{n\ell m_\ell}\alpha$ or $\phi_{n\ell m_\ell}\beta$

or $|n\ell m_\ell \alpha\rangle$, $|n\ell m_\ell \beta\rangle$,

Recall that orbitals with

$\ell = 0, 1, 2, 3, \ldots\ldots$

are called s, p, d, f, etc orbitals.

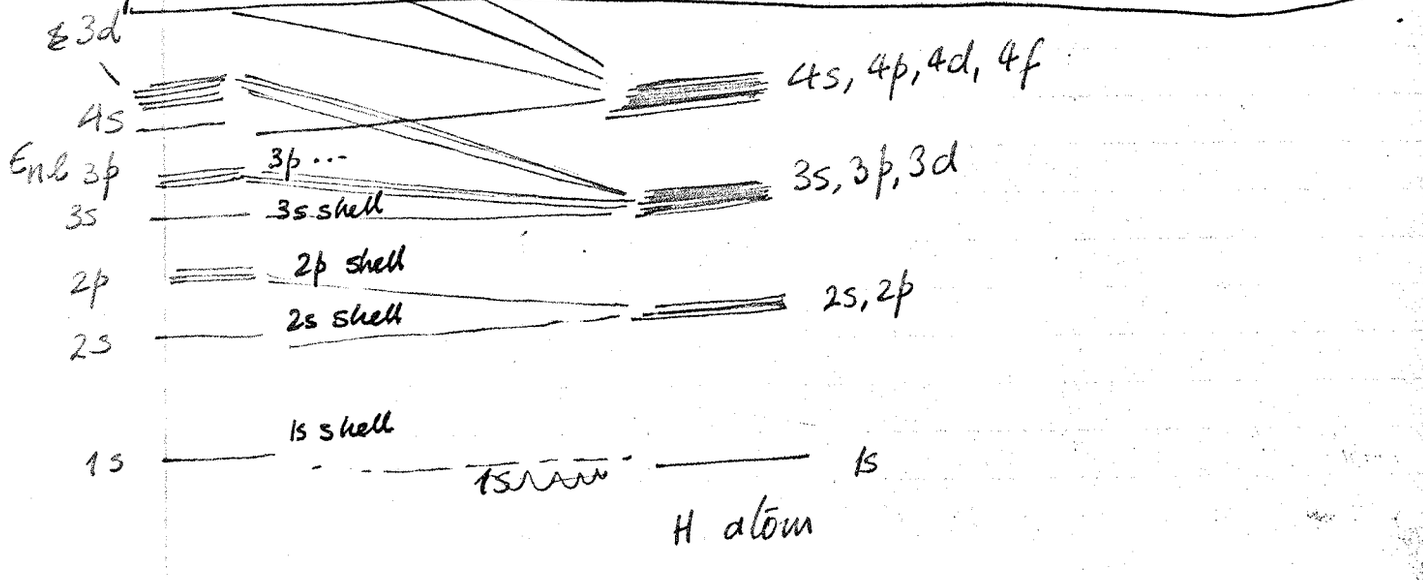
Hence, all the $(2\ell+1)$ orbitals for a given ℓ, $|n\ell m_\ell\rangle$, $(m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell)$, are degenerate - i.e. have the same energy

Thus for p orbitals, $\ell = 1$, $m_\ell = -1, 0, +1$, 3 fold degenerate

d orbitals, $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$

- 5 fold degenerate

Thus the energy in (13), ϵ_i, should be written as $\epsilon_{n\ell}$ - as it only depends on the quantum numbers n and ℓ :- N.B. difference with H atom



We recall that the Pauli exclusion principle states that if two electrons have the same orbitals ϕ_i, then they must have opposite spins – otherwise the Slater determinant vanishes

Translated into the present case, this means that if two electrons have the same quantum numbers n, l, m_l, then they must have opposite spins

Thus there can be no more than 2 functions

$|n l m_l \alpha\rangle$ and $|n l m_l \beta\rangle$

↑

For given l, there are $2l+1$ degenerate orbitals, Including spin, there can be not more than $2\times(2l+1)$ electrons with the energy ϵ_{nl}

$2(2l+1)$ different STATES.

e.g. Maximum of 6 p electrons.
10 d —"—.
14 f —"—.

– Such a set is called a CLOSED SHELL

Thus we may write the Slater determinant

$$\{\phi_1 \bar{\phi}_2 \phi_3 \bar{\phi}_4 \ldots\ldots \bar{\phi}_N\}$$

in the form

[illegible]

or rather

[illegible]

$\{\phi_{1s}\ \bar{\phi}_{1s}\ \phi_{2s}\ \bar{\phi}_{2s}\ \phi_{2p_{-1}}\ \bar{\phi}_{2p_{-1}}\ \phi_{2p_0}\ \bar{\phi}_{2p_0}\ \phi_{2p_{+1}}\ \bar{\phi}_{2p_{+1}}\ \phi_{3s}\}$

or simply

as

$\{1s^2 2s^2 2p^6 3s\}$ - (Na atom)

denotes how many electrons in an $(n\ell)$ shell.

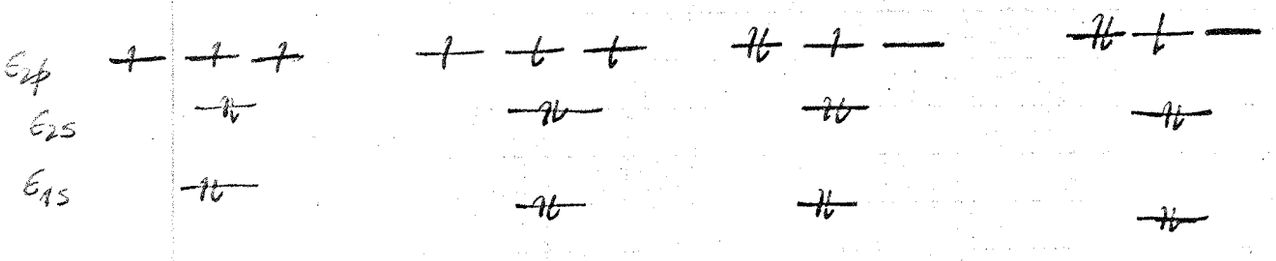
A sequence of such numbers e.g. $1s^2 2s^2 2p^6 3s^2 3p^4$ — is said to specify a CONFIGURATION.

Recall that each orbital $|n\ell m_\ell \alpha\rangle$ or $|n\ell m_\ell \beta\rangle$ is associated with an energy level $\epsilon_{n\ell}$ - i.e. $\epsilon_{n\ell}$ is independent both of m_ℓ and σ ($= \alpha$ or β)

This means that whenever we have a shell of electrons that is not closed — there will be a number of Slater determinants, all with the same total energy E_0. Thus, for example, nitrogen Carbon $\{1s^2 2s^2 2p^3\}$

All the Slater determinants :-

$m_\ell = (-1\ \ 0\ \ +1)\quad (-1\ \ 0\ \ +1)\quad (-1\ \ 0\ \ +1)\quad (-1\ \ 0\ \ +1)$



- will have the same total energy E_0 — because each determinant has 3 electrons in the ϵ_{2p} level.

The number of different Slater determinants corresponding to a given configuration is often enormous. In the case of N $(1s^2 2s^2 2p^3)$ there are 20

In general, consider q_{nl} electrons outside a closed shell: i.e. a configuration

$$(-\text{closed shell})(nl)^q$$

- how many different determinants will there be?

The shell nl can accomodate $2(2l+1)$ electrons altogether, hence there will be

$$\frac{[2(2l+1)]!}{[2(2l+1)-q]!\,q!} \quad \text{determinants} \qquad \text{—— (20)/}$$

For p^3, $(l=1, q=3)$ = 20 - which checks.

For d^3, $(l=2, q=3)$ = 120

For f^3, $(l=3, q=3)$ = 364 —— !!!

In other words, our starting Hamiltonian, H_0, whose solutions are Slater determinants, has a colossal amount of degeneracy associated with its eigenfunction E_0 — As shown above, for 3 f electrons outside closed shells, E_0 has a degeneracy of 364.

Only for <u>closed shells</u>, with $q=0$ in (20) above, is there only 1 determinant so that E_0 is singly degenerate.

Summary

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

Have found solutions to the equation

$$\mathcal{H}_0 \Phi_0 = E_0 \Phi_0 .$$ (Slater determinants) (configurations)

Will now use these ~~zeroth order~~ solutions to construct systematic approximations to Φ_{exact} (exact f^n), by adding onto $\mathcal{H}_0$, the (small) additions $\mathcal{H}_{ee}$ and $\mathcal{H}_{LS}$ and finding the corrections to Φ_0 and E_0.

The order in which we add $\mathcal{H}_{ee}$, $\mathcal{H}_{LS}$ depends on their relative sizes. For light atoms,

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

so we first find the corrections due to $\mathcal{H}_{ee}$, and then, from approximate solutions of $(\mathcal{H}_0 + \mathcal{H}_{ee})$, add in $\mathcal{H}_{LS}$.

For heavy atoms e.g. rare earth atoms and ions,

$$\mathcal{H}_{LS} > \mathcal{H}_{ee} \quad \text{or} \quad \mathcal{H}_{LS} \simeq \mathcal{H}_{ee}$$

In this case, we reverse the procedure.

In addition, please remember that we will also be considering the energy levels of atoms in crystals. We have to consider, in addition to $\mathcal{H}_{ee}$ and $\mathcal{H}_{LS}$, the field due to the ions in the crystal — which we denote by V_{cryst}.

V_{cryst} = potential energy of the atom in the crystal due to the other ions

So that now,

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

and, depending on the magnitude of V_{cryst} relative to $\mathcal{H}_{ee}$ and $\mathcal{H}_{LS}$, we correct for this effect too.

Thus
(case 1) $V_{cryst} \gg \mathcal{H}_{ee}$ – i.e. overcomes electron-electron repulsion
– "strong crystal field"

(case 2) $\mathcal{H}_{ee} \gg V_{cryst} \gg \mathcal{H}_{LS}$ – "intermediate crystal field"

(case 3) $\mathcal{H}_{ee} \gg \mathcal{H}_{LS} \gg V_{cryst}$ – "weak crystal field".

Now, the <u>way</u> in which these corrections are (makes use of) the tremendous degeneracy of E_0.

The <u>reasons</u> for this large degeneracy, and how we make use of it is a subject to which we now turn.

Constants of Motion & Symmetry. Commutation of Operators and Degeneracy

We now try to understand the physical reasons why the energy E_0 of the zeroth order problem

$$\mathcal{H}_0 \Psi_0 = E_0 \Psi_0$$

has so much degeneracy — and how we can use the physical insight thus gained to make corrections to Ψ_0 and to E_0 that result when we add in $\mathcal{H}_{ee}$ and/or $\mathcal{H}_{LS}$.

A great deal of quantum mechanics only becomes clear when we look at the classical problem, and we now turn to this. (The significance of)

Classical Mechanics.

Consider a particle of mass m and velocity $\underset{\sim}{v}$ $\left(= \frac{d\underset{\sim}{r}}{dt}\right)$

Its momentum $\underset{\sim}{p} = m\underset{\sim}{v} = m\frac{d\underset{\sim}{r}}{dt}$.

The essential content of classical mechanics is Newton's second law of motion, which states that

$$\underset{\sim}{F} = \frac{d\underset{\sim}{p}}{dt}$$

where $\underset{\sim}{F}$ is the force on the particle.

If the particle is in free space, with no forces acting on it, then $\underset{\sim}{F} = 0$, and hence

$$\boxed{\underset{\sim}{p} = \text{constant}}$$

The total energy of such a particle is just its

kinetic energy, $\mathcal{T}$

$$E = \frac{p^2}{2m}$$

- and from the conservation of energy principle,

$$\boxed{E = \text{constant}}.$$

also.

Thus in free space, we see that, not only is E constant, but p is constant too:

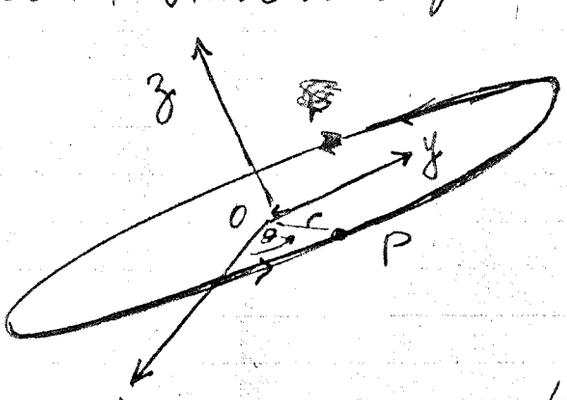
p is a <u>constant of the motion</u>

- and note that ~~xxxxxxx~~ p is constant because of the homogeneity of free space.

From this simple example, we conclude that constants of motion are connected with some kind of <u>symmetry property</u> of the system.

Let us amplify this last statement with another, and possibly more relevant, example.

Consider a particle executing some orbit (not necessarily a circular one) around a fixed point. Have the following coordinate system:



Because its orbit is always in a fixed plane - can choose the x, y axes to be in this plane.

The particle P is <u>kept</u> in its orbit because of the existence of some attractive potential between it and some other fixed particle at O.

Its position at any instant will be denoted by the vector $\underset{\sim}{r}$ (which will have 2 components: (x, y) in the Cartesian system), and its momentum at the same instant by $\underset{\sim}{p}$.

Note that $\underset{\sim}{p}$ is now obviously not a constant of the motion, since the direction (if not the magnitude) of $\underset{\sim}{p}$ is changing all the time so that

$$\frac{d\underset{\sim}{p}}{dt} \neq 0.$$

Now consider the angular momentum of P, which we recall was defined by

$$\underset{\sim}{l} = (\underset{\sim}{r} \times \underset{\sim}{p}) \qquad [\text{the "moment of momentum"}]$$

Now

$$\frac{d\underset{\sim}{l}}{dt} = \frac{d}{dt}(\underset{\sim}{r} \times \underset{\sim}{p})$$

$$= \left(\frac{d\underset{\sim}{r}}{dt} \times \underset{\sim}{p}\right) + \left(\underset{\sim}{r} \times \frac{d\underset{\sim}{p}}{dt}\right)$$

$\frac{d\underset{\sim}{r}}{dt} = \frac{1}{m}\underset{\sim}{p}$, $(\underset{\sim}{p} \times \underset{\sim}{p}) = 0$,

$$= \left(\underset{\sim}{r} \times \frac{d\underset{\sim}{p}}{dt}\right)$$

$$= (\underset{\sim}{r} \times \underset{\sim}{F}) \qquad \text{— from Newton's 2nd law} \qquad (21)$$

This last quantity is obviously the moment of a force about the point O.

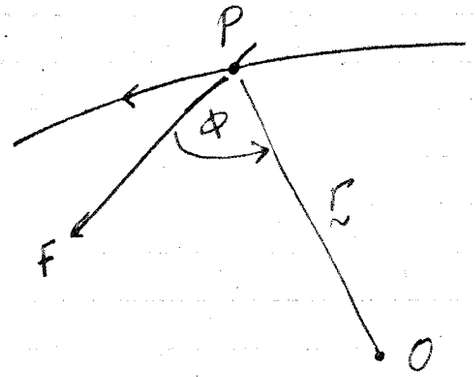
$(\underset{\sim}{r} \times \underset{\sim}{F})$ = moment of force

or TORQUE.

If the torque is zero, then $\frac{d\underset{\sim}{l}}{dt} = 0$, and the

angular momentum $\underset{\sim}{L}$ is constant.

The situation is as follows



If there is some force acting on P — and there must be some force on it — otherwise it wouldn't stay in its orbit, then the moment of force on P is $\underset{\sim}{r} \times \underset{\sim}{F}$, with magnitude

$$rF\sin\Phi$$

The only time that this torque is zero, is if the force acts directly along $\underset{\sim}{r}$:- from P to O, in which case $\Phi = \sin\Phi = 0$.

This happens only if P is in a potential field of the form $V(r)$ — which depends only on the distance from O to P. In this case, the force on the particle $F = -\frac{\partial V}{\partial r}$ and this is directed along $\underset{\sim}{r}$

Thus we see that for a single particle moving in an orbit, the angular momentum

$$\boxed{\underset{\sim}{L} = \text{constant}} \qquad (22)$$

is a CONSTANT of the MOTION

— and that this is so because of a symmetry property of the system i.e. the potential of attraction $V(r)$ is spherically symmetric — has no dependence on angle.

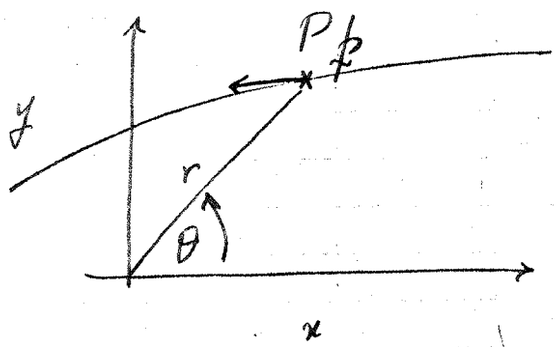
Thus once more we have an example where the symmetry of a dynamical system leads to the existence of constants of motion

The energy has an interesting form.

$$E = \frac{p^2}{2m} + V(r).$$

which is also, of course a constant of motion

Since V is a function of r only, it is convenient to use the following sets of coordinates:



$$x = r\cos\theta$$
$$y = r\sin\theta$$

Now $p^2 = (p_x^2 + p_y^2)$ [the square of a vector: $p^2 \equiv \underset{\sim}{p}\cdot\underset{\sim}{p}$]

$$p_x = \frac{m\,dx}{dt}$$
$$= m\left(\frac{dr}{dt}\cos\theta - r\sin\theta\frac{d\theta}{dt}\right)$$

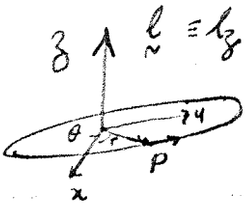
$$p_y = m\frac{dy}{dt} = m\left(\frac{dr}{dt}\sin\theta + r\cos\theta\cdot\frac{d\theta}{dt}\right).$$

So $$\frac{p^2}{2m} = \frac{1}{2}m\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\theta}{dt}\right)^2\right]$$

- $\frac{1}{2}m\left(\frac{dr}{dt}\right)^2$: k.e. associated with the radial motion
- $\frac{1}{2}mr^2\left(\frac{d\theta}{dt}\right)^2$: k.e. associated with the angular motion.

Now, the angular momentum:

$\underset{\sim}{L} = (\underset{\sim}{r} \times \underset{\sim}{p})$



is in this case

$$\underset{\sim}{L}\,(\equiv L_z) = x p_y - y p_x$$

$$= m r^2 \frac{d\theta}{dt}$$

Hence $\dfrac{p^2}{2m}$ can be written in the form

$$\tfrac{1}{2} m \left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2mr^2},$$

So that

$$\boxed{E = \tfrac{1}{2} m \left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2mr^2} + V(r)} \qquad (23)$$

Note the appearance of L^2 in this expression. Have established that for a spherically symmetric $V(r)$, E and $\underset{\sim}{L}$ are constants of the motion, and & we now see that it is L^2 which is significant in the energy expression.

This is why angular momentum is so important in quantum mechanics: Because it is a constant of the motion in classical mechanics, and this is because of the spherical symmetry of the problem.

There is thus an intimate connection between the symmetry of a dynamical systems and the existence of constants of motion.

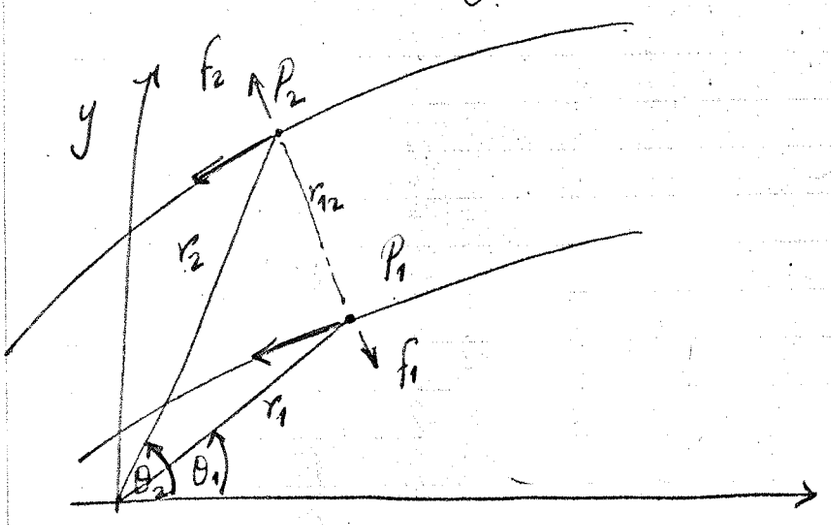
[There are extremely elegant methods in classical mechanics for finding the constants of motion of a dynamical system: the Lagrange and Hamilton formulation of mechanics, and indeed these methods

are the most logical paths to quantum mechanics. It is unfortunate that in order to grasp or at least, to accept, some of the stranger concepts of quantum mechanics, one has to have such an extensive gross knowledge of classical mechanics — which most chemists never have. I've tried to avoid using the Lagrange or Hamilton formulation, but nevertheless to show the essential [results].

Note that the term $\frac{l^2}{2mr^2}$ in (23) above acts as an extra repulsion term added to $V(r)$. It is the centrifugal force arising from the motion.

Thus in a sense, E and l^2 are the constants of the motion.

In the case of more than 1 particle, have the same result, as long as they do not interact



$$E = \tfrac{1}{2}m_1\left(\frac{dr_1}{dt}\right)^2 + \tfrac{1}{2}m_2\left(\frac{dr_2}{dt}\right)^2 + \frac{l_1^2}{2m_1r_1^2} + \frac{l_2^2}{2m_2r_2^2}$$

$$+ V(r_1) + V(r_2)$$

- each individual l_i^2 is a constant of the motion

However if the particles interact e.g. repel one another

- then there is a force acting on each particle that is not in the direction of the r_i — so that the ~~sum~~ individual ℓ_i's are no longer conserved, — but only the total

$$\underset{\sim}{L} = \underset{\sim}{\ell}_1 + \underset{\sim}{\ell}_2 + \ldots\ldots + \underset{\sim}{\ell}_N$$

- and the total energy will then depend only on the total $\underset{\sim}{L}^2$

What happens in quantum mechanics?

Here we have the simple recipe that if a quantity such as E is conserved, then the allowable values of E, E_n, are the solutions of the appropriate eigenfunction equation. In this case, the operator corresponding to E is $\mathcal{H}$, and we have the usual Schrödinger equation:

$$\mathcal{H}|n\rangle = E_n|n\rangle \qquad \text{(notation!)}$$

Now, what do we mean when we say that some quantity, B, is a constant of motion?

We mean that in a quantum mechanical state $|n\rangle$ corresponding to some definite value E_n, the quantity B ~~also~~ also has a definite value, b_μ, say; in other words, $|n\rangle$ must simultaneously be an eigenfunction of the operator $\hat{B}$, corresponding to the property (observable) B.

Thus the same wavefunction $|n\rangle$ must be an eigenfunction, both of $\mathcal{H}$ and of B:

$$\mathcal{H}|n\rangle = E_n|n\rangle$$
$$B|n\rangle = b_\mu|n\rangle$$

- so it would be better to write the eigenfunction

as $|\mu n\rangle$ - to ~~show~~ show that it belongs to the eigenvalue E_n of $\mathcal{H}$, and to the eigenvalue b_μ of $\hat{B}$.

Thus:

$$\left.\begin{aligned} \mathcal{H}|\mu n\rangle &= E_n|\mu n\rangle \\ \hat{B}|\mu n\rangle &= b_\mu|\mu n\rangle \end{aligned}\right\} \quad (24)/$$

- This is a <u>physical</u> argument - based on the principles of qu. mech.

What does this tell us about the operators $\mathcal{H}$, & $\hat{B}$?

It tells us the following:

Since

$$\mathcal{H}\hat{B}|\mu n\rangle = b_\mu \mathcal{H}|\mu n\rangle = b_\mu E_n |\mu n\rangle$$

$$\hat{B}\mathcal{H}|\mu n\rangle = E_n \hat{B}|\mu n\rangle = \underbrace{E_n b_\mu}|\mu n\rangle$$

these are just numbers

Hence

$$(\mathcal{H}\hat{B} - \hat{B}\mathcal{H})|\mu n\rangle = (b_\mu E_n - E_n b_\mu)|\mu n\rangle$$

$$= 0.$$

i.e.

$$\boxed{[\mathcal{H}, \hat{B}] = 0} \quad \text{——— (25)/}$$

where the notation

$$[\mathcal{H}, \hat{B}] \equiv \mathcal{H}\hat{B} - \hat{B}\mathcal{H} \quad \text{——— (26)/.}$$

∴ The operators $\mathcal{H}$, and $\hat{B}$ are said <u>to commute</u>

- This is not an obvious property, as can be seen since $\mathcal{H}$ contains things such as $\frac{\partial^2 \ldots}{\partial r^2}$ etc. — and one might <u>in general</u> expect that the <u>order</u> of $\mathcal{H}$ and $\hat{B}$ to be important.

In textbooks such as Pauling and Wilson, or Eyring, Walter and Kimball, the inverse of this is usually proved i.e. that if $[\hat{H}, \hat{B}] = 0$, then $\hat{H}$ & $\hat{B}$ have a common set of eigenfunctions. But I think that the way I've done it is more acceptable physically.

Also, $[\hat{H}, \hat{B}] = 0$ is sufficient to ensure that $\frac{d}{dt}\langle n|\hat{B}|n\rangle = 0$.

Thus if a dynamical system has symmetry, one can expect that there will be other operators, $\hat{B}$, that will commute with $\hat{H}$. These operators are usually the ones expected from classical theory, and hence by analogy the eigenvalues, b_μ, are called "constants of the motion"

If there is more than one operators e.g. $\hat{B}, \hat{C}, \ldots\ldots$ that commutes with $\hat{H}$, then the eigenf^n $|n\rangle$ is classified according to the different sets of eigenvalues

e.g. $[\hat{H}, \hat{B}] = 0$; $\hat{B}|n\rangle = b_\mu|n\rangle$

$[\hat{H}, \hat{C}] = 0$; $\hat{C}|n\rangle = c_\nu|n\rangle$

$\vdots$ $\qquad\qquad$ $\vdots$

Then we write $|n\rangle$ as $|\mu\nu\ldots\ldots n\rangle$

When all the symmetry of the system has been exhausted, - will find a complete set of operators that all commute with one another: $\hat{H}, \hat{B}, \hat{C}, \ldots\ldots$, - and so all the eigenfunctions of the dynamical system, $|\mu\nu\ldots\ldots n\rangle$ are completely classified

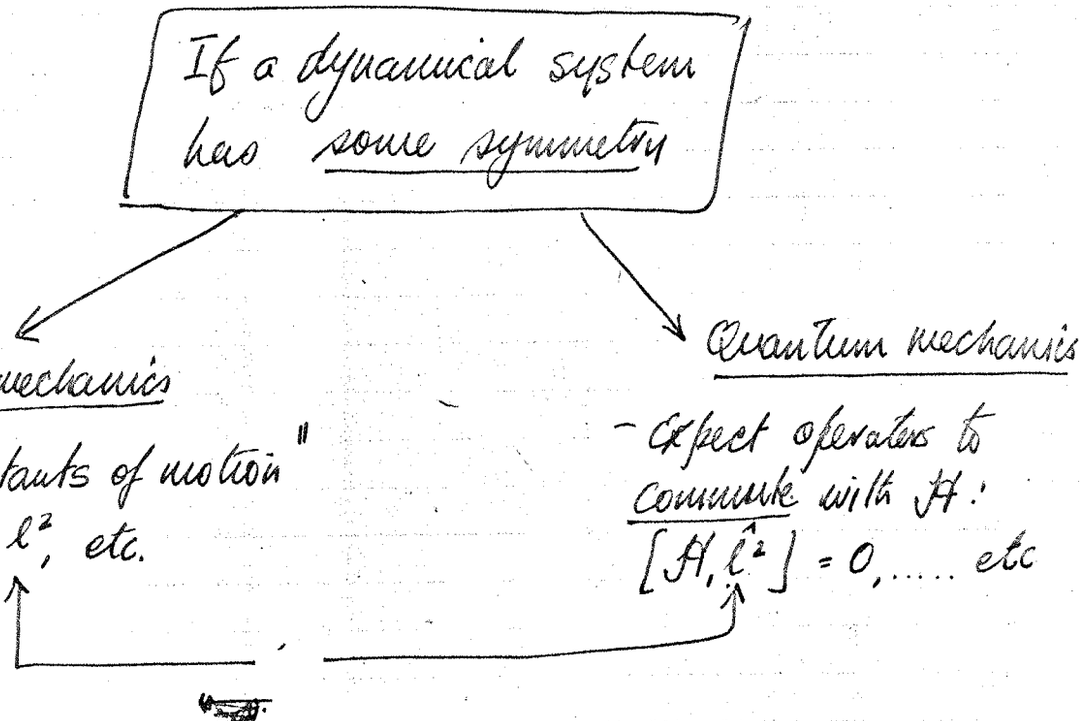
This complete set of commuting operators represents the maximum amount of (precise) information

that quantum mechanics allows us to have about a system – all other quantities run up against the Heisenberg uncertainty principle

– This method of exploiting the symmetry of a dynamical system is due to Dirac – It is the one always used for atoms.

Unfortunately, for crystals and molecules, another method for systematically exploiting the symmetry is used: the group theory method – Due to Wigner. In this course we will have to consider both methods – though the Dirac and Wigner methods are in fact equivalent. [We could use either method all the way through – but it's just not convenient – but it might be interesting!!]

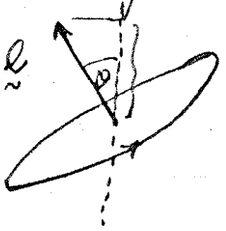
I think it is useful now to summarise what we have done:



Further investigation, expresses the symmetry of a dynamical system means that there are some constants of motion

that do not appear in E.

E.g. For a classical particle in an orbit



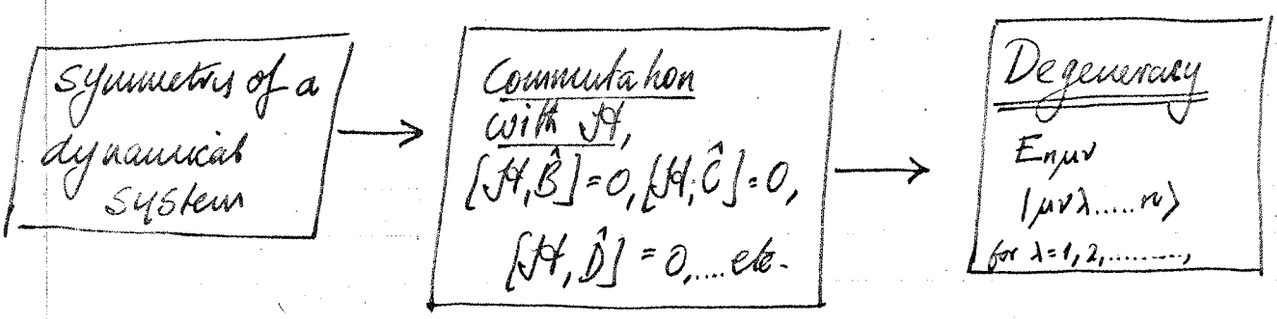
its angular momentum, $\underset{\sim}{L}$, is const. — i.e. has const. magnitude, and const. direction — so that the projection of $\underset{\sim}{L}$ on some axis is also a constant of the motion.

In quantum mechanics this means that we have an operator $\hat{D}$, say, that commutes with $\mathcal{H}$ (const. of motion), $[\mathcal{H}, \hat{D}] = 0$, but whose eigenvalue, d_λ, does not affect the energy

i.e. $|\mu\nu\lambda \ldots n\rangle$,

for a given E_n, b_μ, c_ν, — has the same energy for all values of λ — i.e. the energy level $E_{n\mu\nu}$ is degenerate with respect to λ.

Thus in quantum mechanics, we have the situation:



Application to Atomic Systems

I'm sure you can all see what I'm getting at.

Consider our Hamiltonian $\mathcal{H}_0$:

$$\mathcal{H}_0 = \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} + U(r_i) \right\}$$

What operators commute with $\mathcal{H}_0$? Obviously each individual $\hat{l}_i^2$, and $\hat{l}_{zi}$:

$$\left.\begin{aligned} [\mathcal{H}_0, \hat{l}_i^2] &= 0 \\ [\mathcal{H}_0, \hat{l}_{zi}] &= 0 \end{aligned}\right\} \quad i = 1, 2, \ldots, N \qquad (27)$$

In addition $\mathcal{H}_0$ commutes with the individual spin angular momentum operators, $\hat{S}_i^2$, $\hat{S}_{zi}$:

$$\left.\begin{aligned} [\mathcal{H}_0, \hat{S}_i^2] &= 0 \\ [\mathcal{H}_0, \hat{S}_{zi}] &= 0 \end{aligned}\right\} \qquad (28)$$

- so that according to what we said just before about commuting operators, we can say that each eigenfunction of $\mathcal{H}_0$ can be classified according to the eigenvalues of all the $\hat{l}_i^2$, $\hat{l}_{iz}$, $\hat{S}_i^2$, $\hat{S}_{zi}$:

$$\Phi_0 \equiv |(n_1 l_1 m_{l_1} \sigma_1)(n_2 l_2 m_{l_2} \sigma_2) \ldots\ldots (n_N l_N m_{l_N} \sigma_N)\rangle$$

- which is exactly the result we obtained before - Slater determinants - Each different Slater determinant is specified by exactly the set of quantum numbers $(n_i l_i m_{l_i} \sigma_i)$ for each electron.

The degeneracy in E_0 arises because the energy does not depend on the quantum numbers m_{l_i} or σ_i - and this is so due to:

a) the spherical symmetry of the dynamical system

b) the fact that the electrons are assumed to be non-interacting —

- so that each individual $\underset{\sim}{l}_i^2$, is a constant of the motion, so that there are individual degeneracies from each electron. (and $\underset{\sim}{s}_i$)

Lecture 4.

Now, what happens when we add to $\mathcal{H}_0$ the first correction $\mathcal{H}_{ee}$?

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

$$= \mathcal{H}_0 + \left[\sum_{\substack{i,j \\ j>i=1}}^{N} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} U(r_i) \right]$$

$$= \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{j>i=1}^{N} \frac{e^2}{r_{ij}}$$

Let us write the eigenfunctions of $\mathcal{H}$ as $\bar{\Phi}$

$$\mathcal{H}\bar{\Phi} = E\bar{\Phi}$$

What can be said about the symmetry of $\mathcal{H}$? i.e. with what does $\mathcal{H}$ commute?

Well from our classical arguments we can say at once that $\mathcal{H}$ will no longer commute with the individual l_i^2's, but only with the total: L^2 i.e. the individual constants of motion of the electrons are destroyed by the interaction, and only their sum total remains:

$$\left.\begin{aligned} [\mathcal{H}, L^2] &= 0 \\ [\mathcal{H}, L_z] &= 0 \end{aligned}\right\} \quad (29)$$

Where

$$\hat{\underset{\sim}{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= (\hat{l}_{1x} + \hat{l}_{2x} + \ldots\ldots + \hat{l}_{Nx})^2 + (\hat{l}_{1y}^2 + \hat{l}_{2y}^2 + \ldots\ldots + \hat{l}_{Ny}^2)$$
$$+ (\hat{l}_{1z}^2 + \hat{l}_{2z}^2 + \ldots\ldots + \hat{l}_{Nz}^2) \quad \text{——— (30)/}$$

$$\hat{L}_z = \hat{l}_{1z} + \hat{l}_{2z} + \ldots\ldots + \hat{l}_{Nz} \quad \text{——— (31)/}$$

Now we do the same with the spin angular momentum. $\hat{H}$ commutes with the total $\hat{S}^2$, and with the total $\hat{S}_z$:

$$\left.\begin{aligned} [\hat{H}, \hat{S}^2] &= 0 \\ [\hat{H}, \hat{S}_z] &= 0 \end{aligned}\right\} \quad \text{——— (32)/}$$

Hence we have the following set of commuting operators:

$$\hat{H}, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$$

If we number the eigenfunctions of $\hat{H}$ by the letter γ: $\hat{H}\bar{\Phi}_\gamma = E_\gamma \bar{\Phi}_\gamma$

etc
$\gamma = 3$ ——
$\gamma = 2$ ——
$\gamma = 1$ ——

- then each of these energy states will also be characterised by the quantum numbers L, M_L, S, M_S.

So instead of writing $\bar{\Phi}$, or $\bar{\Phi}_\gamma$ for the eigenfunction of $\hat{H}$: $\hat{H}\bar{\Phi}_\gamma = E_\gamma \bar{\Phi}_\gamma$,

we may write:

$$\boxed{\bar{\Phi}_\gamma \equiv |\gamma L M_L S M_S\rangle} \quad \text{——— (33)/}$$

~~We now use this result to make the corrections~~

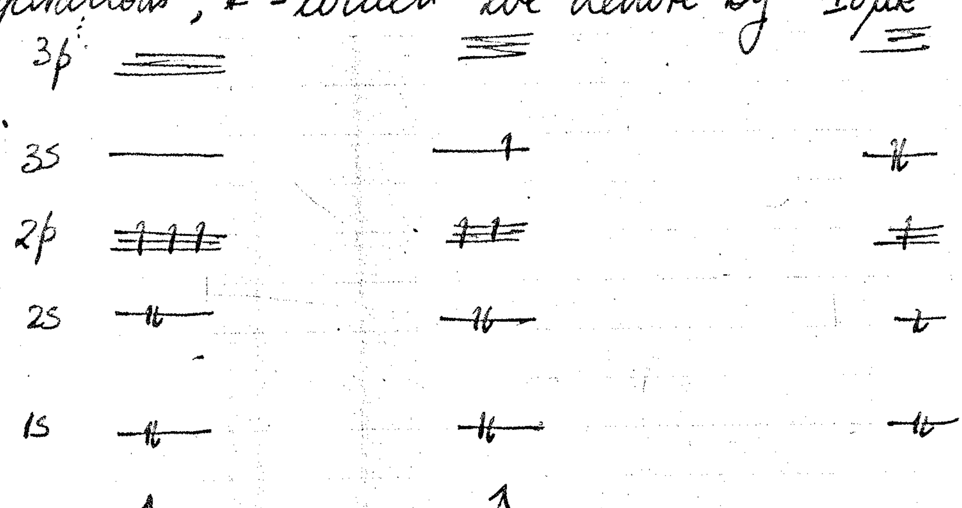
– This is true of the *exact* eigenfunctions of $\mathcal{H}$. Before we show how we use this in order to make corrections to Φ_0, we may summarise the situation thus:–

$\mathcal{H}_0$	$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ee}$
Exact eigenf^n Φ_0	Exact eigenfunction Φ_γ
$\equiv \lvert (n_1 l_1 m_{l_1} \sigma_1) \ldots\ldots\ldots (n_N l_N m_{l_N} \sigma_N) \rangle$	$\equiv \lvert \gamma L M_L S M_S \rangle$

Now how do we pass from the $(\mathcal{H}_0, \Phi_0)$ problem to the $(\mathcal{H}, \Phi_\gamma)$ problem?

If we knew *all* the eigenfunctions of $\mathcal{H}_0$; – i.e. not just the ground state configuration, but *all* excited configurations, – which we denote by $\Phi_{0\mu k}$

e.g. N atom



Φ_{01} – ground state config^n $(1s^2 2s^2 2p^3)$	Φ_{02} – 1st excited config^n $(1s^2 2s^2 2p^2 3s)$	Φ_{03} – $(1s^2 2s^2 2p\, 3s^2)$
E_{01} 20 fold degenerate	$E_{02} = 15 \times 6 =$ 30. fold degenerate	E_{03} 6-fold degenerate
$k = 1, 2, \ldots\ldots, 20$	$k = 1, 2, \ldots\ldots 90$	$k = 1, 2, \ldots, 6$

– etc., etc. . .

– then we could always write the $\lvert \gamma L M_L S M_S \rangle$

as a sum over all the $\Phi_{0\mu}$'s exactly

$$|\gamma L M_L S M_S\rangle = \sum_{\mu=1}^{\infty} \left[\sum_{k=1}^{\tau_\mu} C_{\mu k}^{\gamma L M_L S M_S} \Phi_{0\mu k} \right] \qquad (34)/$$

- the sum over k ≡ sum over all the different Slater determinants belonging to a given configuration μ - with energy $E_{0\mu}$; τ_μ = degeneracy of $E_{0\mu}$

- the sum over μ ≡ sum over all the excited configurations

Now, we know from perturbation theory that the coefficients $C_{\mu k}^{\gamma L M_L S M_S}$ for the excited configurations are proportional to

$$\frac{1}{(E_{0\mu} - E_{01})}$$

If the eigenvalues $E_{0\mu}$ of $\mathcal{H}_0$ are widely spread, $(E_{0\mu} - E_{01})$ will be v. large, so the contributions to $|\gamma L M_L S M_S\rangle$ from the excited configurations $\Phi_{0\mu k}$, $\mu \neq 1$, will be small.

As a first approximation, we neglect all these excited state configurations, and write

$$|\gamma L M_L S M_S\rangle = \sum_{k=1}^{\tau_1} C_{1k}^{\gamma L M_L S M_S} \Phi_{01k} \qquad (35)/$$

$$= \sum_{k=1}^{\tau} C_{k}^{\gamma L M_L S M_S} \Phi_{0k}$$

- have dropped all unnecessary suffices
- know we are dealing with $\mu = 1$.

- The degeneracy of E_{01}, τ, we recall is given, for 1 open shell: (closed shell) $(n\ell)^q$ by

$$\tau = \frac{(2(2\ell+1))!}{q!\,[(2(2\ell+1))-q]!}$$

The coefficients $C_k^{\gamma L M_L S M_S}$ are given by the secular equation

$$\sum_{k=1}^{\tau} \left[\langle \Phi_{0k} | \mathcal{H} | \Phi_{0\ell} \rangle - E_\gamma^{(1)} \delta_{k\ell} \right] C_k^{\gamma L M_L S M_S} = 0 \qquad (36)$$

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

From the general theory of linear equations — which I won't go into — this equations only has solutions for the $C_k^{\gamma L M_L S M_S}$ if

$$\det \left[\langle \Phi_{0k} | \mathcal{H} | \Phi_{0\ell} \rangle - E_\gamma^{(1)} \delta_{k\ell} \right] = 0 \qquad (37)$$

Let me write $\langle \Phi_{0k} | \mathcal{H} | \Phi_{0\ell} \rangle$ in the form $\mathcal{H}_{k\ell}$ — then this equation has the form:

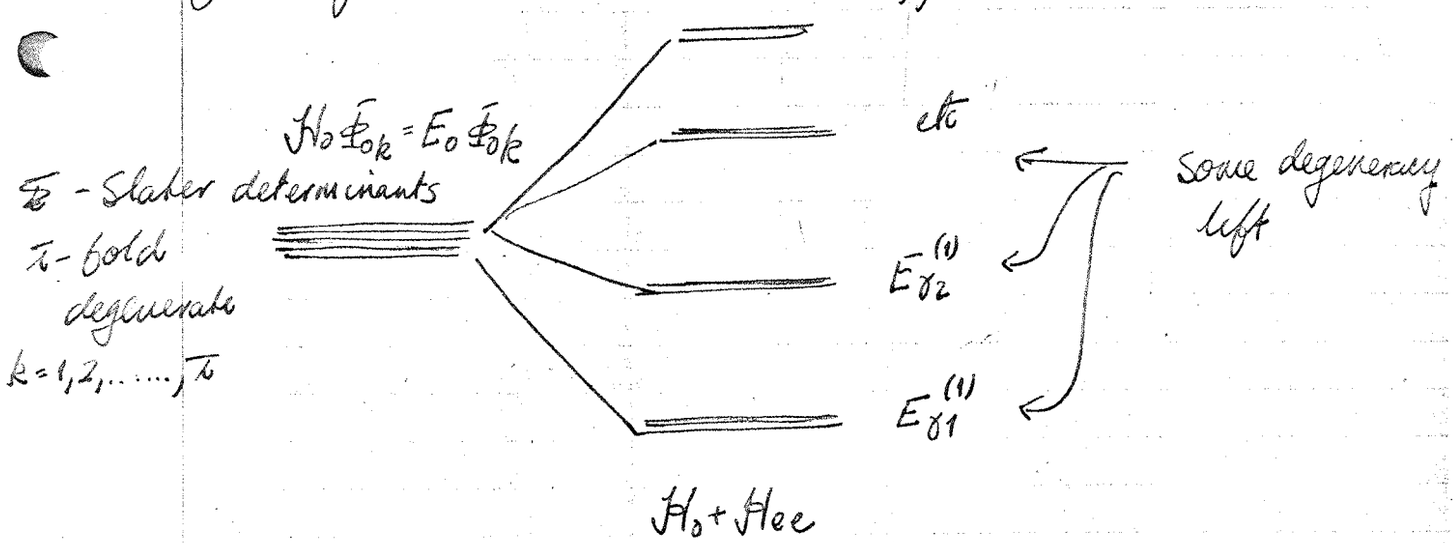
$$\begin{vmatrix} (\mathcal{H}_{11} - E_\gamma^{(1)}) & \mathcal{H}_{12} & \mathcal{H}_{13} & \cdots & \mathcal{H}_{1n} \\ \mathcal{H}_{21} & (\mathcal{H}_{22} - E_\gamma^{(2)}) & \mathcal{H}_{23} & \cdots & \mathcal{H}_{2n} \\ \vdots & \vdots & \vdots & & \\ \mathcal{H}_{n1} & \mathcal{H}_{n2} & \mathcal{H}_{n3} & \cdots & (\mathcal{H}_{nn} - E_\gamma^{(1)}) \end{vmatrix} = 0$$

This is a polynomial of order $\bar{\tau}$ in the unknown, $E_0^{(1)}$, so there will be a maximum of $\bar{\tau}$ solutions

$$E_{\gamma 1}^{(1)},\ E_{\gamma 2}^{(1)},\ \ldots\ldots,\ E_{\gamma\bar{\tau}}^{(1)}$$

each one of these will have an appropriate set of coefficients $\{C_k^{\gamma L M_L S M_S}\}$ to go with it

In fact - not all the $E_0^{(1)}$'s will be different - i.e. there will still be a considerable amount of degeneracy left. What has happened is as follows:



- This is an extremely common situation in quantum mechanics: Have a system with some degeneracy, and set up a system of secular equations to split the degeneracy.

However, actually carrying out this task is extremely laborious. Just remember that the dimensions of the secular equation are not small: Recall that for

p^2, $\bar{\tau} = 15$ — means evaluating $(15)^2$ matrix elements $\langle \bar{\Phi}_{0k} | \mathcal{H} | \bar{\Phi}_{00} \rangle$

d^3, $\bar{\tau} = 120$ — " " " $(120)^2$

f^3, $\bar{\tau} = 364$ — " " " $(364)^2$ " " "

I will not discuss the evaluation of these matrix elements, for 2 reasons.

1) This is a standard, specialist problem - which you can look up in the texts by ~~Racah~~ Condon & Shortley (an excellent book), and the 2 volumes of Slater "Atoms".

2) We shall use our ~~easy~~ physical insight into the system that we have gained from discussing ~~Eso~~ symmetry properties in quantum mechanics, and we shall see that, because of the high symmetry that atoms have, we can completely avoid solving the secular equation!!

But before we do so, it is worth while discussing for a few moments as to how good is our 1st approx^n for $|\gamma L M_L S M_S\rangle$

$$= \sum_{k=1}^{\bar{\imath}} c_k^{\gamma L M_L S M_S} \Phi_{ok}$$

- sum over degenerate Slater dets. only.

It is a good approx^n as long as the splitting caused by H_{ee} is small compared to the separation of the lowest excited ~~state~~ configuration from the ground config^n:

E_{o2} ———

E_{o1} ——— H_0

$H_0 + H_{ee}$

a) Approx^n is good

E_{o2} ———

E_{o1} ———

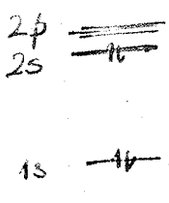
b) Approx^n is not good.

In case b), one would have to take into account the first excited configuration <u>at least</u> – i.e. this is an example where <u>configuration interaction</u> is important

e.g. Be atom. The ground state config^n – although it is just a single Slater determinant – is not good enough:

$\{1s^2 2s^2\}$

– the 2p level is very close to the 2s



A better approx^n would be

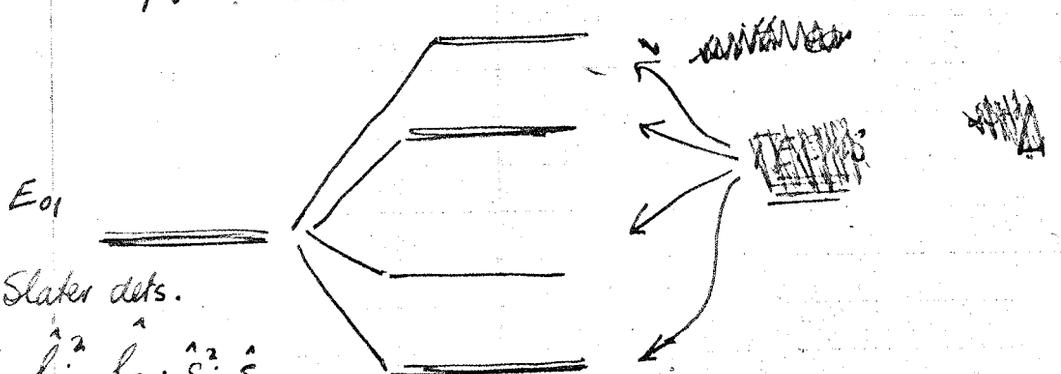
$\{1s^2 2s^2\} + C_2^{J0000}\{1s^2 2p^2\}$

Remember notation !!

– and here one <u>always</u> has to solve a secular equation for the coefficients $C_{jk}^{JLM_LSM_S}$ – however much symmetry there is.

Now we see how we can evaluate the coefficients $C_k^{JLM_LSM_S}$ <u>without</u> calculating all the integrals, and without solving the secular equation

The situation is



– Slater dets.

$\mathcal{H}_0, \hat{l}_i^2, \hat{l}_{zi}, \hat{s}_i^2, \hat{s}_{zi}$

– all commute

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ee}$;

$\mathcal{H}, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$, – all commute

$|JLM_LSM_S\rangle$

- Because $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ all commute with $\mathcal{H}$, - there is with each of the split levels associated a particular value of L, M_L, S, M_S

- so that the coefficients $c_k^{\sigma L M_L S M_S}$ in

$$|\sigma L M_L S M_S\rangle = \sum_{k=1}^{I} c_k^{\sigma L M_L S M_S} \Phi_{0k}$$

are just those that arise when all the individual angular momenta $\underset{\sim}{l}_i, \underset{\sim}{\sigma}_i$, are coupled together to form the resultants $\underset{\sim}{L}, \underset{\sim}{S}$:

$$\underset{\sim}{L} = \underset{\sim}{l}_1 + \underset{\sim}{l}_2 + \ldots\ldots + \underset{\sim}{l}_N$$

$$\underset{\sim}{S} = \underset{\sim}{\sigma}_1 + \underset{\sim}{\sigma}_2 + \ldots\ldots + \underset{\sim}{\sigma}_N$$

Note that closed shells make no contribution to $\underset{\sim}{L}$ and $\underset{\sim}{S}$:

$$\left.\begin{aligned} \underset{\sim}{l}_1 + \underset{\sim}{l}_2 + \ldots\ldots + \underset{\sim}{l}_{N-q} &= 0 \\ \underset{\sim}{\sigma}_1 + \underset{\sim}{\sigma}_2 + \ldots\ldots + \underset{\sim}{\sigma}_{N-q} &= 0. \end{aligned}\right\} \quad (38)$$

- The result is obvious for spins $\uparrow\downarrow$ } all spins are paired

- but it is also true for orbital angular momenta - when all states $m_l = l, l-1, \ldots\ldots -l$ are filled.

So that for a configuration

$$(-\text{closed shell}-)\,(n.l)^q,$$

all the total spin and total orbital angular momentum comes from the q outer electrons only.

What we have just said is that the physical effect of the electron-electron interaction is to couple together all the individual $\underset{\sim}{l}_i$'s to form a resultant $\underset{\sim}{L}$, and all the individual $\underset{\sim}{s}_i$'s to form a resultant $\underset{\sim}{S}$ — and the coefficients $C_k^{\alpha LM_L SM_S}$ are just the vector coupling coefficients necessary to do this.

The $C_k^{\alpha LM_L SM_S}$ can therefore be evaluated by algebraic methods - from a study of vector coupling in quantum mechanics. This is a problem that appears throughout quantum mechanics — not only in atoms, but in molecular spectra - rotation spectra, NMR, ESR, electronic spectra, etc., etc., etc., — and hence is worthwhile looking at in some detail. nuclear shell theory

Coupling of Angular Momenta

Consider two particles — it doesn't matter what they are, electrons, molecules etc.— that don't interact.

Let particle 1 have angular momentum $\underset{\sim}{j}_1$,
and particle 2 — " — " — $\underset{\sim}{j}_2$.

Again, $\underset{\sim}{j}_i$ can be equal to $\frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ etc - so we cover both the cases of orbital and spin angular momentum.

Denote the wavefunctions of the 2 particles by

$$\boxed{|j_1 m_1\rangle \text{ and } |j_2 m_2\rangle}$$

- There might be some additional radial wave functions -

but again this is not important for the present discussion. Each wavefunction is an eigenfunction of its individual angular momentum operator:

$$\left.\begin{aligned} \hat{j}_i^2 |j_i m_i\rangle &= j_i(j_i+1)\hbar^2 |j_i m_i\rangle \\ \hat{j}_{zi} |j_i m_i\rangle &= m_i \hbar |j_i m_i\rangle \qquad i = 1, 2 \end{aligned}\right\} \quad (39)$$

- and the $(2j_i+1)$ functions $|j_i m_i\rangle$

$$m_i = j_i, j_i - 1, \ldots\ldots, -j_i$$

are all degenerate.

What is the "law of addition" of angular momenta in quantum mechanics?

i.e. What are the possible angular momentum states of the total system of the two particles?

This is of course what we are seeking.

Now, the complete set of products

$$|j_1 m_1\rangle |j_2 m_2\rangle$$

- for all m_1 & m_2 (there will be $(2j_1+1)(2j_2+1)$ such products)

covers all the possible states for the 2 particles. Hence if we denote the total eigenfunction for the total angular momentum for the 2 particles by

$$|JM\rangle,$$

then $|JM\rangle$ can always be written as a linear combination of the products above:

$$|JM\rangle = \sum_{m_1} \sum_{m_2} \underbrace{a^{JM}_{j_1 m_1 j_2 m_2}} \, |j_1 m_1\rangle |j_2 m_2\rangle$$

↑ instead of this, we write the coefficient as

$$\langle j_1 j_2 m_1 m_2 | JM \rangle ,$$

so we have

$$\boxed{|JM\rangle = \sum_{m_1} \sum_{m_2} \langle j_1 j_2 m_1 m_2 | JM \rangle \, |j_1 m_1\rangle |j_2 m_2\rangle} \qquad (40)$$

This is one of the most important formulae in quantum mechanics.

The coefficients $\langle j_1 j_2 m_1 m_2 | JM \rangle$ are called vector-addition or Clebsch-Gordan or Wigner coefficients. The formula (40) is easy to remember – if you know what you are doing:

on the LHS have $|JM\rangle$, & on the RHS have $|j_1 m_1\rangle |j_2 m_2\rangle$ – so the coefficients simply have the form $\langle j_1 j_2 m_1 m_2 | JM \rangle$; they connect the LHS and RHS together

There is an analytical formula for $\langle j_1 j_2 m_1 m_2 | JM \rangle$ – given in Wigner's book "Group Theory" or in any of the books on angular momenta such as Rose, Edmonds, Brink & Satchler. They also give tables of formulae for the Clebsch-Gordan coeffs. for various simple cases.

- All this is not important - you can just look them up if you want them.

What is important - the general properties of these coefficients which we now study.

Now the wave function $|JM\rangle$ is an eigenfunction of $\hat{J}^2 = (\hat{j}_1 + \hat{j}_2)^2$, and of

$\hat{J}_z = \hat{j}_{z1} + \hat{j}_{z2}$. Thus:

$$\left.\begin{aligned} \hat{J}^2 |JM\rangle &= J(J+1)\hbar^2 |JM\rangle \\ \hat{J}_z |JM\rangle &= M\hbar |JM\rangle \end{aligned}\right\} \quad (41)$$

Now the individual terms in (40)/ are also eigenfunctions of $\hat{J}_z$:

$$\hat{J}_z |j_1 m_1\rangle |j_2 m_2\rangle = (\hat{j}_{z1} + \hat{j}_{z2}) |j_1 m_1\rangle |j_2 m_2\rangle$$

$$= (m_1 + m_2) |j_1 m_1\rangle |j_2 m_2\rangle.$$

- Hence $\boxed{M = m_1 + m_2}$ (42)/

- and the sum in (40) includes only those values of m_1 and m_2 such that $m_1 + m_2 = M$.

E.g. If I were coupling the angular momenta together of 2 p electrons - to form a resultant $|J\,M=0\rangle$, then I could only include the wave functions $|l_1 m_{l_1}\rangle |l_2 m_{l_2}\rangle$ as follows:

$$|p+1\rangle|p-1\rangle \quad , \quad |p\,0\rangle|p\,0\rangle \quad , \quad |p-1\rangle|p+1\rangle$$

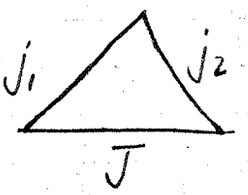
- each of these has $m_{s_1} + m_{s_2} = 0$.

However the most important property of the $\langle j_1 j_2 m_1 m_2 | JM \rangle$ coefficients is that they are non-zero only if J has the following values:

$$\boxed{j_1 + j_2 \geq J \geq |j_1 - j_2|} \qquad (43)$$

[i.e. $J = j_1+j_2, j_1+j_2-1, \ldots\ldots, |j_1-j_2|$]

- the "triangular condition" - must be able to form a triangle with sides j_1, j_2, J:



If we have 2 equivalent particles i.e. $j_1 = j_2$, then the Clebsch-Gordan coefficient has the following symmetry property when the 2 particles are exchanged

lecture 5.

$$\langle j j\, m m' | JM \rangle = (-1)^{J-2j} \langle j j\, m' m | JM \rangle \qquad (44)$$

(particles interchanged)

- the C-G coefficient changes sign when the 2 particles are exchanged if $(J-2j)$ is odd, and remains unchanged if $(J-2j)$ is even

For this case, if we denote the state of each particle i by $|\rangle_i$, then

$$|JM\rangle = \sum_{mm'} \langle j j\, mm' | JM \rangle |jm\rangle_1 |jm'\rangle_2$$

$$= \frac{1}{2} \sum_{mm'} \langle j j\, mm' | JM \rangle \left\{ |jm\rangle_1 |jm'\rangle_2 + (-1)^{J-2j} |jm'\rangle_1 |jm\rangle_2 \right\} \qquad (45)$$

- The state for the two particles, $|JM\rangle$, is symmetric or antisymmetric towards interchange of the 2 particles according to whether $2J-2j$ is even or odd. If j is an orbital angular momentum, then $2j$ is even - so $|JM\rangle$ is symmetric or antisymmetric according to whether J is even or odd

In the case that we have 2 electron spins,

$$j = \tfrac{1}{2}$$

so $J-2j = J-1$.

From the triangle condition, $J = 1$ or 0.

For $J=1$, (triplet state, usually written $S=1$)

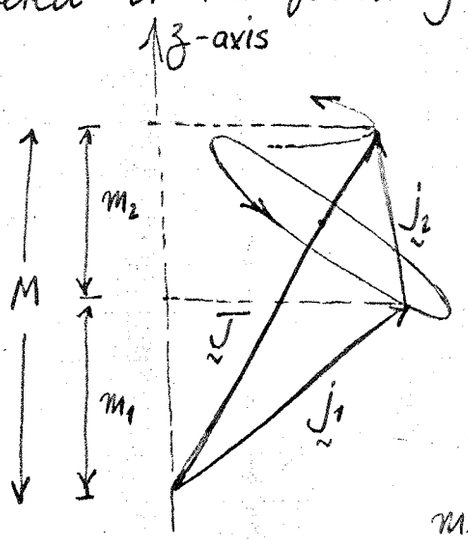
:- $|JM\rangle$ is symmetric

$J=0$ (singlet), $|JM\rangle$ is antisymmetric

} which is well-known.

- These considerations will be important in a moment.

The vector coupling formula (40) is usually interpreted in terms of a vector model. We imagine $\underset{\sim}{j}_1$, $\underset{\sim}{j}_2$, & $\underset{\sim}{J}$ to be represented by 3 vectors, and then the formula (40) is interpreted in the following diagram:



The precession of $\underset{\sim}{j}_1$ & $\underset{\sim}{j}_2$ about $\underset{\sim}{J}$, and its projection on the z-axis represents the indeterminacy in their individual z components, m_1 & m_2, although their sum M remains constant.

The square of the C.-G. coefficient

$$|\langle j_1 j_2 m_1 m_2 | JM\rangle|^2$$

is the probability that a measurement in the state $|JM\rangle$ gives the particular values m_1 & m_2 for $\hat{J}_{z1}$ & $\hat{J}_{z2}$.

Final remark on the formula (40)/:

$$|JM\rangle = \sum_{m_1}\sum_{m_2} \langle j_1 j_2 m_1 m_2 | JM\rangle \, |j_1 m_1\rangle |j_2 m_2\rangle$$

↑ eigenfunction of $\hat{J}^2, \hat{J}_z, \hat{j}_1^2, \hat{j}_2^2$ — together with some Hamiltonian $\mathcal{H}$, form a complete set of commuting operators

eigenfunction of $\hat{j}_1^2, \hat{j}_2^2, \hat{J}_{z1}, \hat{J}_{z2}$ — also, together with $\mathcal{H}$, form a complete set of commuting operators.

Can regard this equation as a linear transformation from (j_1, j_2, m_1, m_2) quantization on the RHS to (J, M, j_1, j_2) quantization on the LHS. The C.G. coefficients form a unitary matrix ($U_{kl} = (U^{-1})^*_{lk}$ ~), so that this transformation can easily be inverted:

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_J \sum_M \langle JM | j_1 j_2 m_1 m_2\rangle \, |JM\rangle \qquad (40a)/$$

Examples of Coupling of Angular Momenta in Quantum Mechanics.

i) Coupling of electron spins.

The spin angular momentum $\sigma = \pm\frac{1}{2}$, ~~associated with the~~ for an individual electron

with $\hat{S}^2\sigma = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\sigma$

and $\hat{S}_z\sigma = \begin{cases} \frac{1}{2}\hbar\sigma & \text{if } \sigma \equiv \alpha \\ -\frac{1}{2}\hbar\sigma & \text{if } \sigma \equiv \beta \end{cases}$

So if we couple to spins together, σ_1 & σ_2, from our ~~known~~ formulae, the total spin S

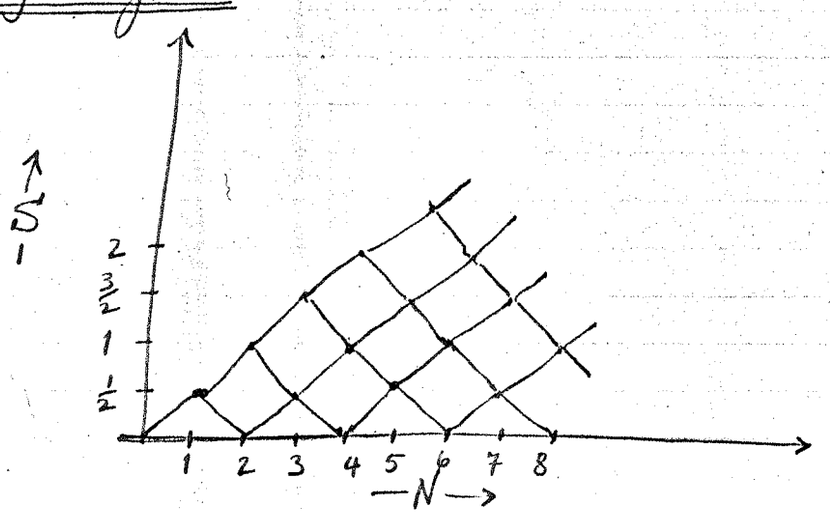
$$S = \sigma_1+\sigma_2,\ \sigma_1+\sigma_2-1, \ldots \text{ etc}$$
$$= 1, \text{ or } 0. \quad - \text{as before}$$

Continuing, if we have a system of N electrons with ~~spin~~ total spin S, and we couple another electron spin to it, then the $(N+1)$-electron system may have a spin

$$S+\sigma,\ S+\sigma-1, \ldots \text{ etc}$$

i.e. $S+\frac{1}{2}$, or $S-\frac{1}{2}$.

This process can be represented very effectively on the branching diagram.



Note that for $N=3$, have 1 quartet ($S=\frac{3}{2}$)
2 doublets ($S=\frac{1}{2}$)

i) electrons 1 & 2 form a singlet ($S=0$)
ii) electrons 1 & 2 form a triplet ($S=1$).

etc.... [f^N_S = total no. of ways of reaching a point (S,N)]

From this diagram, can see that for any system consisting of N electrons, the allowable total spins S are given by

$$S = \tfrac{1}{2}N,\ \tfrac{1}{2}N-1,\ \tfrac{1}{2}N-2,\ \ldots\ldots,\ \tfrac{1}{2} \text{ or } 0$$

depending on whether N is even or odd.

Usually only observe the last few possibilities

e.g. O_2 molecule (16 electrons) - can have total spins $S=0,\ 1,\ 2,\ \ldots$

↑ this is the ground state.

N atom (7 electrons)

$S = \frac{1}{2},\ \frac{3}{2},\ \frac{5}{2},\ \ldots\ldots$

↑ ground state.

ii) Coupling of Orbital Angular Momentum.

If we have 2 electrons outside a closed shell, with orbital angular momenta l_1 and l_2, then the possible values of the total L are:

$$L = l_1+l_2,\ l_1+l_2-1,\ \ldots\ldots,\ |l_1-l_2|$$

Spectroscopic notation. Coupled states with

$$L = 0,\ 1,\ 2,\ 3,\ 4,\ \ldots\ldots$$

are called S, P, D, F, G, ... states.

e.g. consider an atom

(– closed shell –) $3p\,3d$ [excited state of Si]

Then $l_1 = 1$, $l_2 = 2$

So $L = 3$, 2 or 1,

F, D, or P states produced.

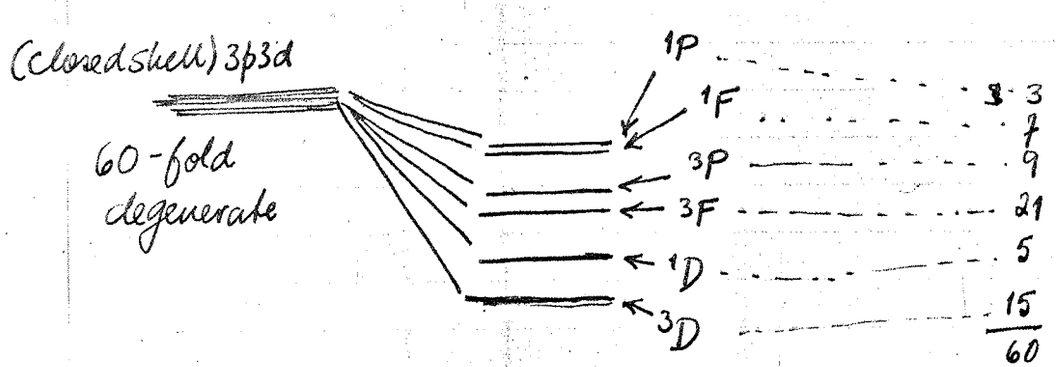
[In addition, there are the 2 uncoupled spins — so that we can have total spins $S = 1$ or 0
triplet singlet]

Thus from the configuration $(3p3d)$, we expect that the electron-electron interaction will cause the electrons to couple together to form the following states: $(2S+1)$

^3F, ^1F, ^3D, ^1D, ^3P, ^1P,

– and we have thus solved the secular equation

Degeneracy $(2S+1)(2L+1)$



– actually observed in Si ($3s^2 3p3d$)

These energy levels are called TERMS and are always designated by ^{2S+1}L

Each term is degenerate w.r.t. M_L and M_S:–

i.e. $(2S+1)(2L+1)$-fold degenerate

The actual wavefunctions

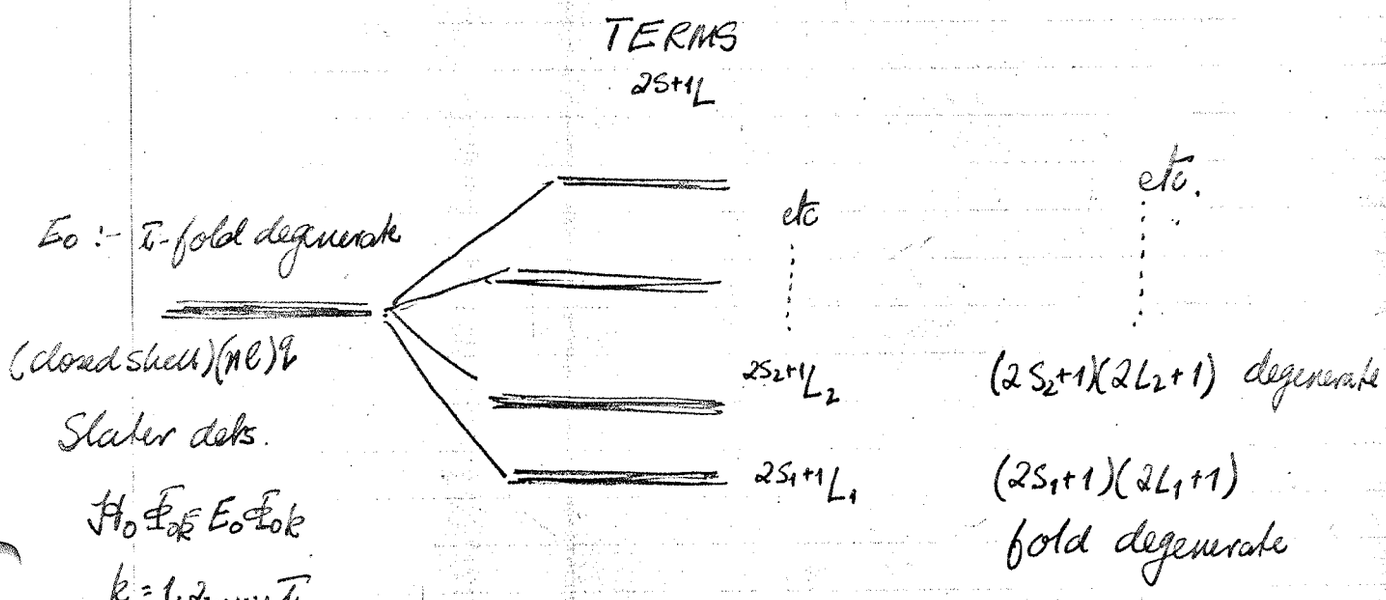
$$|\gamma L M_L S M_S\rangle = \sum_{k=1}^{\bar{\imath}} c_k^{\gamma L M_L S M_S} \Phi_{0k}$$

- are given very easily: The $c_k^{\gamma L M_L S M_S}$ coefficients are simply the product of 2 C.-G. coefficients needed to couple the spins together and the orbital angular momentum.

E.g.

$$c_k^{\gamma L M_L S M_S} = \text{[illegible]} \langle l_1 l_2 m_{l_1} m_{l_2} | L M_L \rangle \langle \tfrac{1}{2} \tfrac{1}{2} \sigma_1 \sigma_2 | S M_S \rangle$$

In the general case, have the following:



and the coefficients $c_k^{\gamma L M_L S M_S}$ are just products of a number of C.-G. coefficients:

$$\langle l_1 l_2 m_{l_1} m_{l_2} | L' M_L' \rangle \langle L' l_3 M_L' m_{l_3} | L'' M_L'' \rangle \ldots\ldots \langle \tfrac{1}{2} \tfrac{1}{2} \sigma_1 \sigma_2 | S' M_S' \rangle \times$$
$$\langle \tfrac{1}{2} S' \sigma_3 M_S' | S'' M_S'' \rangle \ldots\ldots$$

However, this is not the whole story. We have not mentioned the fact that all the wavefunctions, both the Slater dets. Φ_{0k} and the $|\gamma L M_L S M_S\rangle$ are of

course antisymmetric.

The antisymmetry principle works in a very interesting and subtle way to forbid some terms which one might expect to appear on the basis of simple coupling of angular momenta.

The best way of seeing this is to take as an example two electrons outside a closed shell. We considered before an excited state of Si ($3s^2 3p3d$). Here - the 3p and 3d electrons are in different shells — and no difficulty with the ~~exc~~ Pauli principle arises.

Now consider 2 electrons in the same shell

e.g. (— closed shell) $(3d)^2$ [E.g. V^{++} ion (V^{III})]

$l_1 = l_2 = 2$, so from the coupling of ang. mom. expect states with $L = 4, 3, 2, 1, 0$

G, F, D, P, S

But, we recall that if we couple 2 similar angular momenta together [pps. 56 & 57], ~~the~~ ~~get~~ the coupled states, in this case $|L M_L\rangle$ are symmetric or antisymmetric according to whether L = even or odd.

w.r.t. interchange of the 2 electrons

Thus G, D, S, symmetric

F, P antisymmetric.

Similarly with spins: $S = 0$ (singlet) - antisymmetric

$S = 1$ (triplet) - symmetric

So that ~~for~~ since the total wavefunction must be

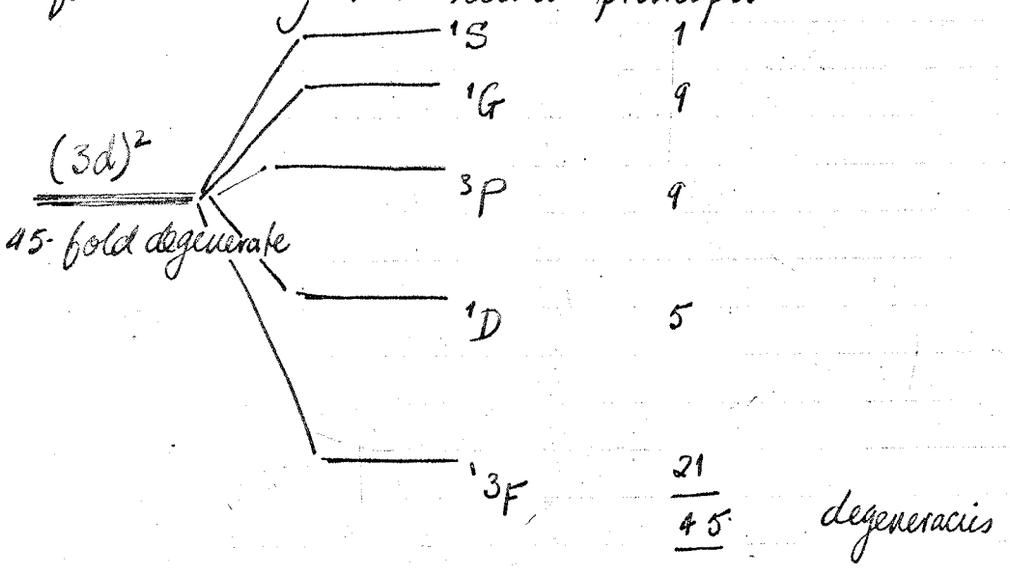
antisymmetric, in terms ^{2S+1}L arising from 2 similar electrons $(n\ell)^2$, we can only allow those where L = even is combined with $S=0$

L = odd " —— " —— " $S=1$

So for $(3d^2)$, we obtain the terms:

^1G, ^1D, ^1S, ^3F, ^3P

– terms such as ^3G or ^1F do not arise as they are forbidden by the Pauli principle



When there are 3, 4, ... or more electrons in the same shell — the situation is the same, but it is a little more complicated to derive which are the allowed terms. There are a number of general methods for doing this — which you can look up in the standard texts (Condon & Shortley or Slater volumes).

The results are as follows:

Terms allowed

p^2, p^4 : ^1D, ^3P, ^1S

p^3 ^4S, ^2D, ^2P.

d^2, d^8: $^3F, ^3P, ^1G, ^1D, ^1S$

d^3, d^7: $^4F, ^4P, ^2H, ^2G, ^2F$, two ^2D's, ^2P

d^4, d^6: $^5D, ^3H, ^3G$, two ^3F's, ^3D, two ^3P's, ^1I, two ^1G's, ^1F, two ^1D's, two ^1S's

d^5: $^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H$, two ^2G's, two ^2F's, three ^2D's, $^2P, ^2S$.

In deriving these allowed terms, we make use of a simplifying feature: This is that the 2 configurations

(closed shell) $(n\ell)^q$ (closed shell) $(n\ell)^{2(2\ell+1)-q}$

(q "holes" in the shell)

give the same allowed terms:

Thus p^2, p^4 have the same terms — So this, & p^3 are all that were needed for p shells.

(d^3, d^7), (d^4, d^6), etc....

Hund's rule: terms with the highest $(2S+1)$ will lie lowest — Lowest level will be with the highest allowable L for this $(2S+1)$.

Final remark. As you can see from the table, the number and complexity of the terms increases very rapidly: (d^4, d^6) are not easy, nor is d^5. By the time $f^2, f^3, \ldots$ etc are reached the problem has long got out of hand. # Some extremely elegant and sophisticated methods have been developed to deal with this problem. I will not go into this, but just mention it since these methods are finding more and more use in Chemistry. Essentially what one does, is to say that given a configuration (closed shell)$(n\ell)^q$, for which you know

all the energies terms ^{2S+1}L, their energies E_{SL}, and their wavefunctions $|\alpha L M_L S M_S\rangle$, we derive from this, all the relevant quantities for the configuration

(closed shell) $(nl)^{q+1}$

- by coupling an extra electron to the system and antisymmetrising. In this way, we can build up systematically to any configuration, starting from the very simple ones. These methods are due to G. Racah, and are described in the book by B.R. Judd, "Operator Techniques in Atomic Spectroscopy" - Applications to ions in crystal fields are also given.

Summary

$\mathcal{H}_0$; eigenf's are Slater dets. Φ_{0k}
- energies E_0 are $\bar{\imath}$ fold degenerate
$k = 1, 2, \ldots, \bar{\imath}$

$\mathcal{H}_0 + \mathcal{H}_{ee}$; in the 1st approx^n, the eigenf's $|\alpha L M_L S M_S\rangle$ given by a linear combination of Slater dets. $\sum_{k=1}^{\bar{\imath}} C_k^{\alpha L M_L S M_S} \Phi_{0k}$

- by coupling the spins $\underset{\sim}{s}_1 + \underset{\sim}{s}_2 + \ldots + \underset{\sim}{s}_q = \underset{\sim}{S}$
& the orbital ang. mom. $\underset{\sim}{l}_1 + \underset{\sim}{l}_2 + \ldots \underset{\sim}{l}_q = \underset{\sim}{L}$
Energy levels, ^{2S+1}L, known as terms

Lecture 6

(Room 25, Seminar Block I)

Spin-Orbit Coupling.

We now consider what the corrections are to the terms

^{2S+1}L when we add on the spin-orbit coupling $\mathcal{H}_{LS}$, which we recall was given by:

$$\mathcal{H}_{LS} = \sum_{i=1}^{N} \xi(r_i)\, \hat{\sigma}_i \cdot \hat{l}_i$$

Thus we now have:

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

$$|\gamma L M_L S M_S\rangle$$

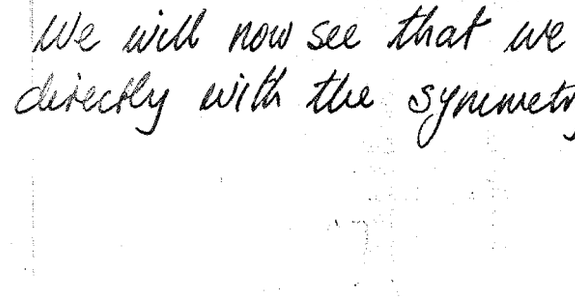
& we assumed that

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

Always true that $\mathcal{H}_0 \gg \mathcal{H}_{ee}$ or $\mathcal{H}_{LS}$,

but the order of $\mathcal{H}_{ee}$, $\mathcal{H}_{LS}$ changes as we go to heavier atoms — will consider this case in a moment.

→ This means that we are assuming that corrections due to $\mathcal{H}_{LS}$ are small compared to the spacing between terms:



We will now see that we can attack this problem more directly with the symmetry methods now at our disposal.

We note first of all that because of the presence of $\mathcal{H}_{LS}$, $\mathcal{H}_{tot.}$ commutes neither with $\hat{\underset{\sim}{L}}^2$ nor with $\hat{\underset{\sim}{S}}^2$, but only with

$$\hat{\underset{\sim}{J}}^2 = (\hat{\underset{\sim}{L}} + \hat{\underset{\sim}{S}})^2.$$

Thus

$$\left.\begin{aligned} [\mathcal{H}_{tot.}, \hat{\underset{\sim}{L}}^2] &\neq 0 \\ [\mathcal{H}_{tot.}, \hat{\underset{\sim}{S}}^2] &\neq 0 \end{aligned}\right\} \quad -(46)$$

But,

$$\left.\begin{aligned} [\mathcal{H}_{tot}, \hat{\underset{\sim}{J}}^2] &= 0 \\ [\mathcal{H}_{tot}, \hat{J}_z] &= 0 \end{aligned}\right\} \quad -(47)$$

where

$$\left.\begin{aligned} \underset{\sim}{J} &= \underset{\sim}{L} + \underset{\sim}{S} \\ J_z &= L_z + S_z \end{aligned}\right\} \quad -(48)$$

Hence if we label the eigenvalues of $\mathcal{H}_{tot}$ by α: as

$\alpha = 3$ ——

$\alpha = 2$ —— etc., then with each such eigenvalue is

$\alpha = 1$ —— associated a state of definite J & M_J:—

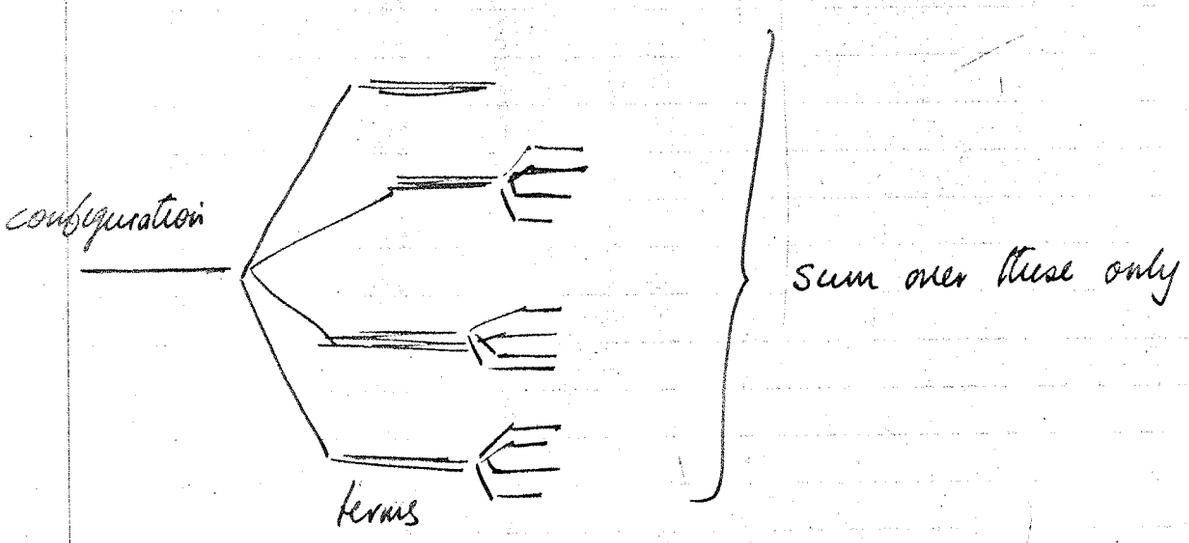
$$|\alpha J M_J\rangle$$

$$\left.\begin{aligned} \mathcal{H}_{tot}\,|\alpha J M_J\rangle &= E_\alpha\,|\alpha J M_J\rangle \\ \hat{\underset{\sim}{J}}^2\,|\alpha J M_J\rangle &= J(J+1)\hbar^2\,|\alpha J M_J\rangle \\ \hat{J}_z\,|\alpha J M_J\rangle &= M_J \hbar\,|\alpha J M_J\rangle \end{aligned}\right\} \quad -(49)$$

Proceeding as before, we expand the states $|\alpha J M_J\rangle$ in all the terms $|\gamma L M_L S M_S\rangle$:

$$|\alpha J M_J\rangle = \sum_{L,M_L} \sum_{S,M_S} d^{\alpha J M_J}_{\gamma L M_L S M_S} \, |\gamma L M_L S M_S\rangle$$

- where the sum is over all the terms $|\gamma L M_L S M_S\rangle$ that arise from a single configuration. This is consistent with our previous approximation of neglecting configuration interaction:



Further approximation:- Since we assumed that the splittings due to $\mathcal{H}_{LS}$ are small compared with the term separations — regard $|\alpha J M_J\rangle$ as being derived from just one term ^{2S+1}L only

$$|\alpha J M_J\rangle = \sum_{M_L} \sum_{M_S} d^{\alpha J M_J}_{\gamma L M_L S M_S} \, |\gamma L M_L S M_S\rangle \qquad (60)$$

[- Again this is consistent with regarding $\mathcal{H}_0 \gg \mathcal{H}_{ee} \gg \mathcal{H}_{LS}$.]

~~This was a way to say that the effect of $\mathcal{H}_{LS}$ is~~ We may hence label the eigenfunctions as

$$|\alpha S L J M_J\rangle$$

important

- to indicate from which term it is derived. $|\alpha SLJM_J\rangle$ is an eigenf^n of $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, and $\hat{S}^2$ but not of L_z, S_z · see diagram p. 57

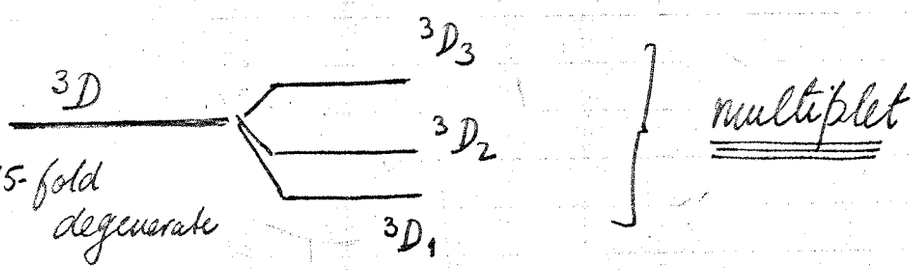
We can now say that the effect of $\mathcal{H}_{LS}$ is to couple together the $\underset{\sim}{L}$ and $\underset{\sim}{S}$ vectors in a term to give a resultant $\underset{\sim}{J}$. The possible values of J are:

$$L+S,\ L+S-1,\ \ldots\ldots,\ |L-S|$$

e.g. ~~from a term configuration~~ from a term ^3D $(L=2, S=1)$

would get $J = 3, 2, 1$.

- The term then splits into 3 levels, denoted by $^{2S+1}L_J$



Each multiplet is still $(2J+1)$-fold degenerate - all the different M_J's.

The coefficients $d^{\alpha JM_J}_{\gamma LM_L SM_S}$ are then nothing else but the C-G. coefficients $\langle LSM_L M_S | JM_J\rangle$, and we have

$$|\alpha SLJM_J\rangle = \sum_{M_L, M_S} \langle LSM_L M_S | JM_J\rangle\, |\gamma LM_L SM_S\rangle \qquad (50a)$$

Note that in some books $\mathcal{H}_{LS}$ is ~~given~~ sometimes given as $A\,\underset{\sim}{L}\cdot\underset{\sim}{S}$

This is because it can be shown that

$$\langle \alpha SLJM_J | \mathcal{H}_{LS} | \alpha SLJM_J \rangle$$

$$= A \langle \alpha SLJM_J | \hat{\underset{\sim}{S}} \cdot \hat{\underset{\sim}{L}} | \alpha SLJM_J \rangle \qquad (51)$$

This, in fact gives a method for calculating these matrix elements very simply:

$$\underset{\sim}{J}^2 = (\underset{\sim}{L} + \underset{\sim}{S})^2 = \underset{\sim}{L}^2 + \underset{\sim}{S}^2 + 2\underset{\sim}{S} \cdot \underset{\sim}{L}$$

Hence

$$A \hat{\underset{\sim}{S}} \cdot \hat{\underset{\sim}{L}} = \tfrac{1}{2} A \left(\hat{\underset{\sim}{J}}^2 - \hat{\underset{\sim}{L}}^2 - \hat{\underset{\sim}{S}}^2 \right)$$

Then

$$\langle \alpha SLJM_J | \mathcal{H}_{LS} | \alpha SLJM_J \rangle$$

$$= \tfrac{1}{2} A \hbar \left\{ J(J+1) - L(L+1) - S(S+1) \right\} \qquad (52)$$

~~So [illegible] diagonal [illegible] gives (52).~~ Equation (52) thus gives the energy levels directly.

The constant A depends only on the particular term, ^{2S+1}L, we have chosen, and can be found from the separation of the multiplet levels.

Thus the difference between the levels J, and J-1 is given from (52) by

$$A\hbar J$$

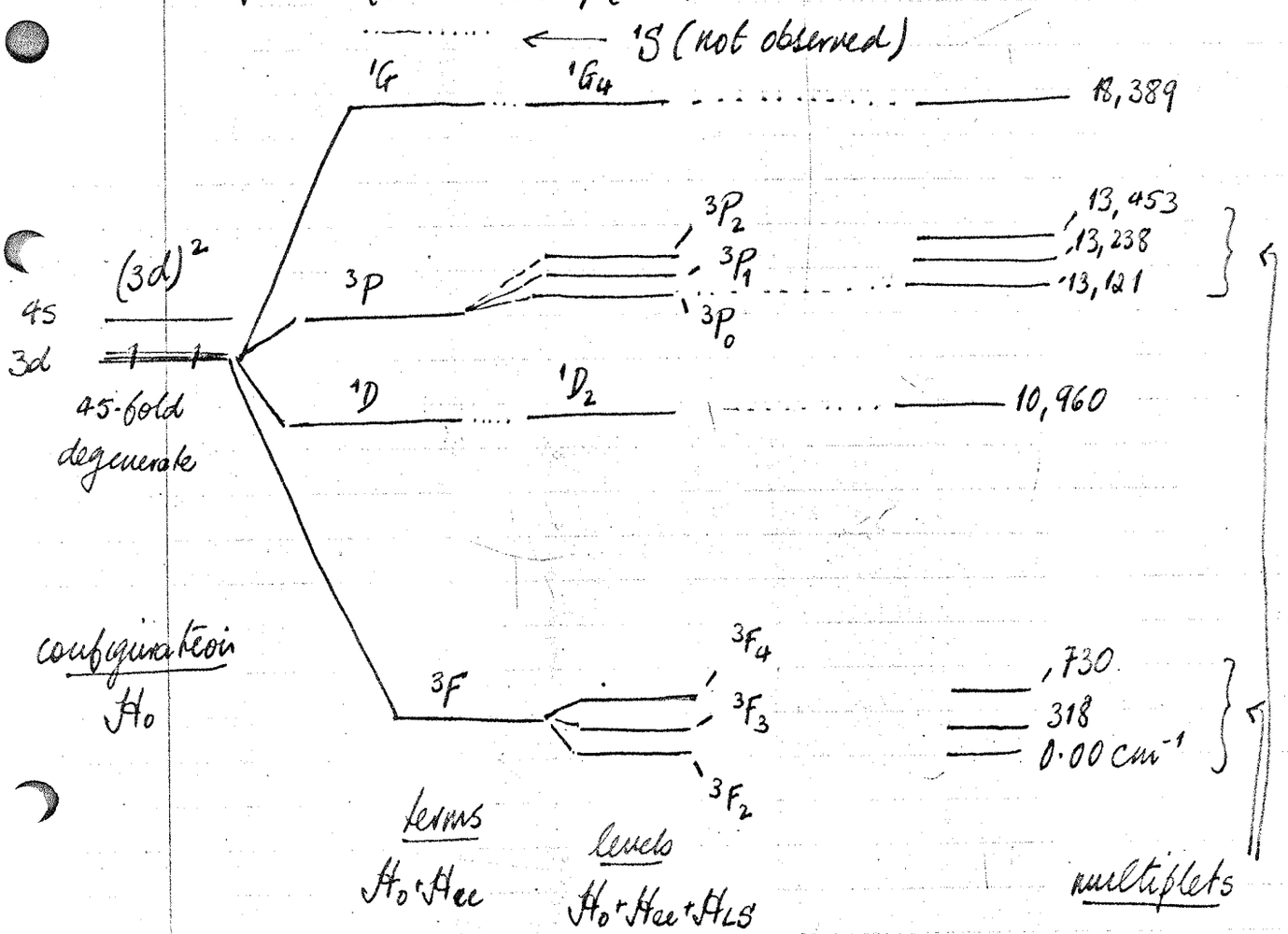
- This is the Landé interval rule discovered previously from experiment.

As a summary, let me give a complete example of an actually observed spectrum

The ~~F~~ vanadium ion V^{III} ~~E~~ The spectrum of the free ion has been observed – V^{III} also occurs in the complex ion $V(H_2O)_6^{3+}$

V ground state config^n: (closed shell) $4s^2(3d)^3$

V^{III} : (closed shell) $(3d)^2$



The nearest (observed) configuration to this is (3d)(4s). The lowest level of this 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}.

The lowest observed configuration that could interact with the V^{III} ground state is ~~E~~ $(3d)^2(4p)$, $^3F_2$ at 147,133 cm^{-1}. So ~~xxxxx~~ in this case we would be

perfectly justified in neglecting configuration interaction. /
[This is actually a rather favourable case].

Data: Moore, "Atomic Energy Levels", NBS.

Note the scheme of approximations employed:

$$\sum_{i=1}^{q} \underset{\sim}{\sigma}_i = \underset{\sim}{S} \; ; \; \sum_{i=1}^{q} \underset{\sim}{l}_i = \underset{\sim}{L} \; ; \; \underset{\sim}{S} + \underset{\sim}{L} = \underset{\sim}{J}$$

- We coupled the angular momenta $\underset{\sim}{\sigma}$ and $\underset{\sim}{l}$ of the individual electrons to $\underset{\sim}{S}$ and $\underset{\sim}{L}$, and then formed the resultant $\underset{\sim}{J}$.

This scheme obtained because $\mathcal{H}_{ee} \gg \mathcal{H}_{SL}$ - is called the RUSSELL-SAUNDERS or SL - coupling scheme.

If $\mathcal{H}_{SL} \gg \mathcal{H}_{ee}$, then it would be much better to consider first $\mathcal{H}_0 + \mathcal{H}_{SL}$, and then $\mathcal{H}_0 + \mathcal{H}_{SL} + \mathcal{H}_{ee}$.

$\mathcal{H}_0 + \mathcal{H}_{SL}$ commutes only with $\hat{\underset{\sim}{j}}_i^2$, and $\hat{j}_{zi}$:

$$\left.\begin{aligned} [\mathcal{H}_0 + \mathcal{H}_{SL}, \hat{\underset{\sim}{j}}_i^2] &= 0 \\ [\mathcal{H}_0 + \mathcal{H}_{SL}, \hat{j}_{zi}] &= 0 \end{aligned}\right\} \quad (53)/$$

$$i = 1, 2, \ldots\ldots, q$$

where $\underset{\sim}{j}_i = \underset{\sim}{l}_i + \underset{\sim}{\sigma}_i$ _____ (54)/

When we add on $\mathcal{H}_{ee}$, we get the same $\mathcal{H}_{tot}$ as before. This implies the following coupling scheme

$$\underset{\sim}{\sigma}_i + \underset{\sim}{l}_i = \underset{\sim}{j}_i \; ; \; \sum_{i=1}^{q} \underset{\sim}{j}_i = \underset{\sim}{J}$$

This is known as the (j-j) coupling scheme

It was thought that this kind of coupling is far less important than the LS scheme, and this is so for light atoms. However there has been a great deal of interest recently in the rare earth atoms and ions, both in the free gaseous state and in crystals, and in these cases one obtains the j-j scheme almost exclusively.

More generally, there is a continuous transition from the LS to the (j-j) scheme as we go to higher Z.

As an example, consider the case

(closed shell) $(np)^2$

- which is the usual example in text books to describe the LS-coupling method. We now assume that $H_{LS} \gg H_{ee}$ and treat this by the (j-j) scheme.

In this case one has $l_1 = l_2 = 1$, and $\sigma_1 = \sigma_2 = \frac{1}{2}$.

Hence for each electron, we may have

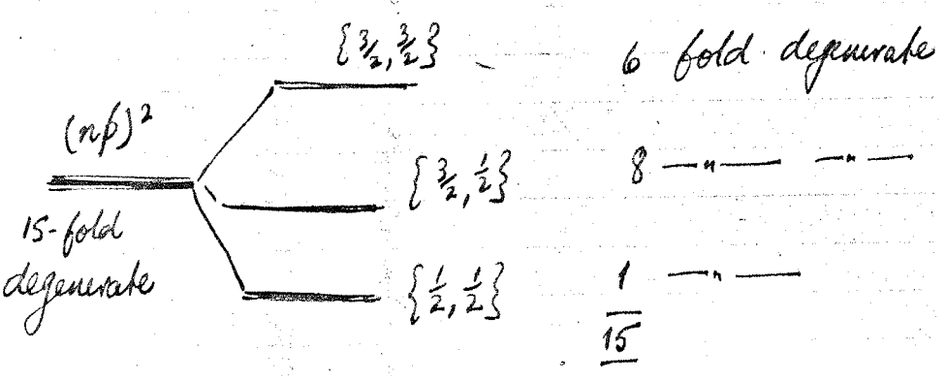
$j_1 = \frac{3}{2}$ or $\frac{1}{2}$;

$j_2 = \frac{3}{2}$ or $\frac{1}{2}$;

We will thus obtain 3 configurations:

$\{\frac{3}{2}, \frac{3}{2}\}$, $\{\frac{3}{2}, \frac{1}{2}\}$, $\{\frac{1}{2}, \frac{1}{2}\}$

so that the $(np)^2$ configuration will split into 3 levels:

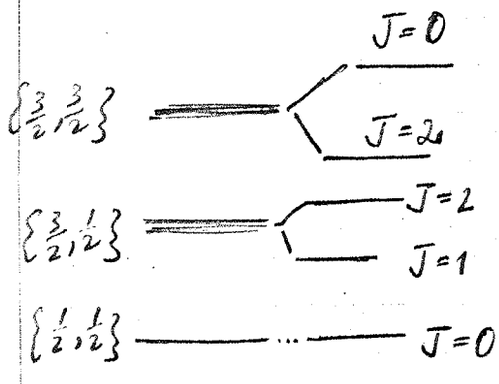


Levels $\{j_1, j_2\}$ are $\frac{1}{2}(2j+1)(2j)$ fold degenerate

[Pauli principle - $m_{j_1} \neq m_{j_2}$!!]

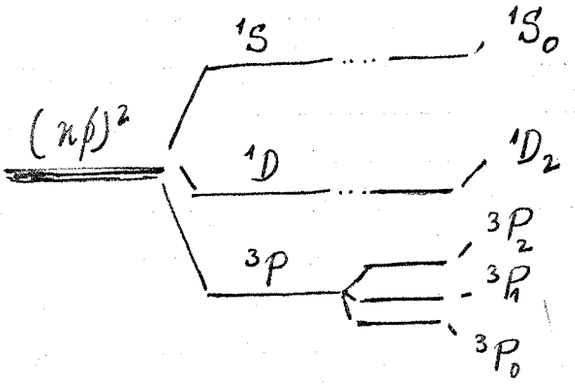
Otherwise $(2j_1+1)(2j_2+1)$ - fold degenerate

The introduction of the electron-electron interaction $\mathcal{H}_{ee}$, then gives rises to the levels



[J = 3, or 1 not allowed - Pauli principle]
↖ ↗ symmetric states.

In the case of LS coupling we obtain

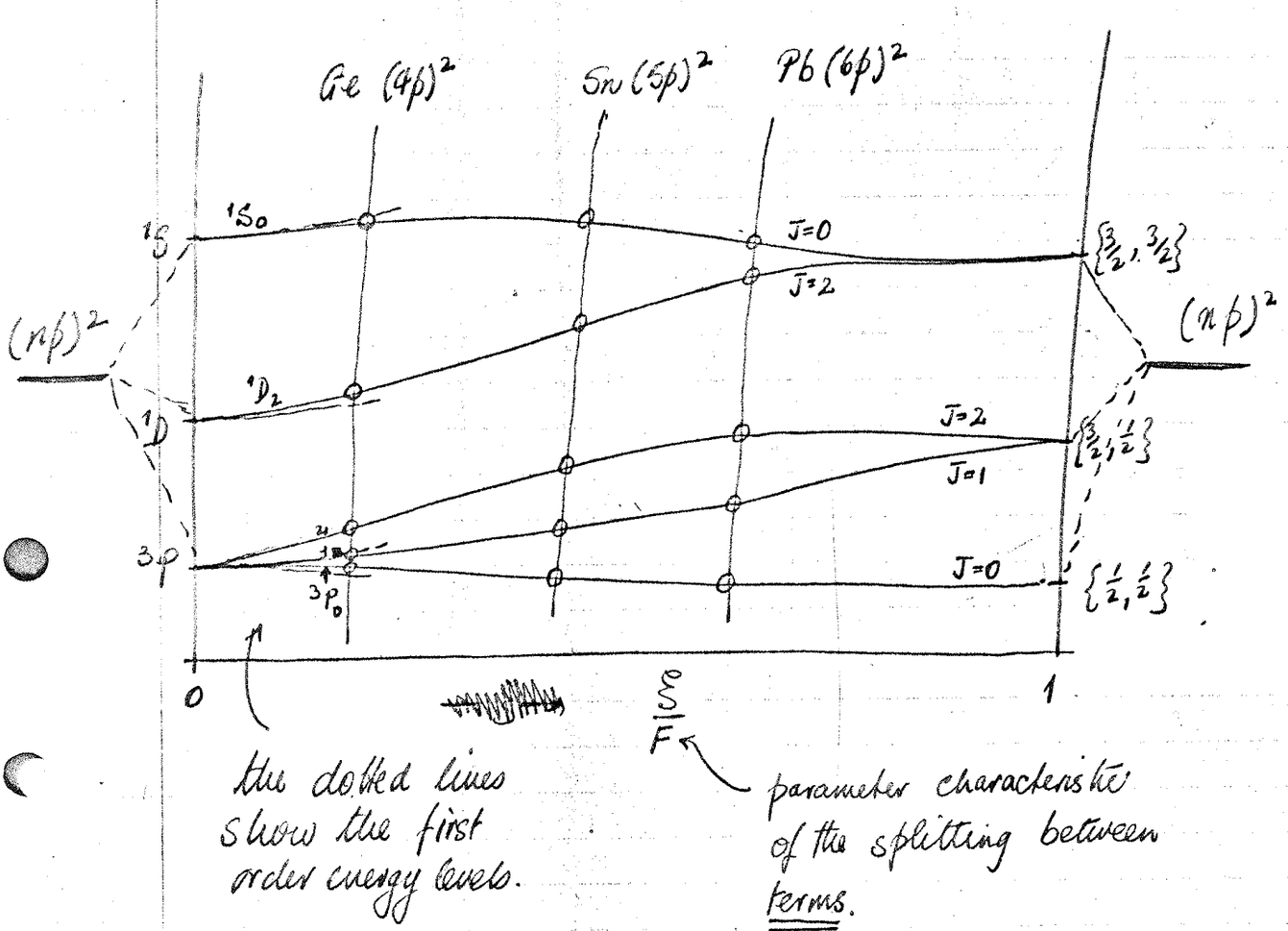


In this simple case, where we have 2 equivalent electrons, the spin-orbit coupling

$$\mathcal{H}_{LS} = \sum_{i=1}^{2} \xi(r_i)\, \hat{\sigma}_i \cdot \hat{l}_i$$

- contains only the one parameter ξ.

* We may thus plot the energy levels of $(np)^2$ as ξ increases from 0 to a value where $\mathcal{H}_{LS} \gg \mathcal{H}_{ee}$, and observe the transition from LS to (JJ) coupling. —



the dotted lines show the first order energy levels.

parameter characteristic of the splitting between terms.

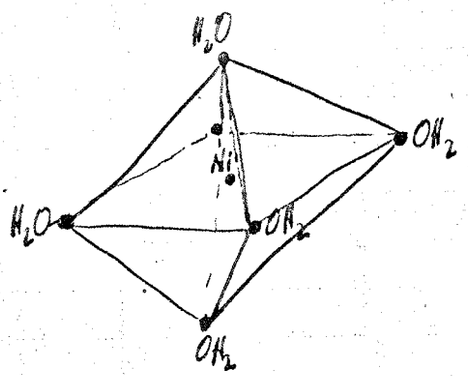
Note the progression towards (j-j) coupling with heavier elements. C $(2p)^2$ would be right over on the LHS of the diagram (almost pure LS coupling).

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 $NiSO_4 \cdot 7H_2O$, 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 molecules or ions - (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 ⊗ atom in the crystal, which we denote by $\mathcal{H}_{cryst}$, is thus given by

$$\mathcal{H}_{cryst} = \mathcal{H}_{tot.} + V_{cryst.} \qquad (55),$$

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 <u>free</u> 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

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

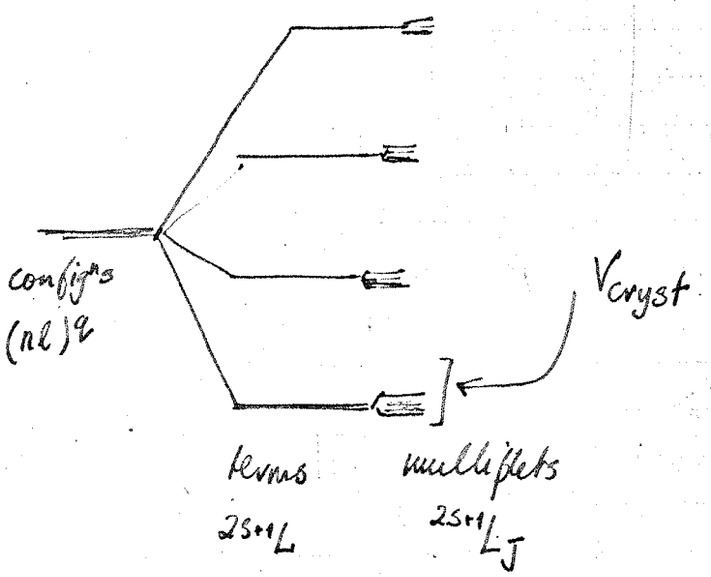
and then consider $\mathcal{H}_{ee}$ and $\mathcal{H}_{LS}$ as corrections.

~~This terminology.~~

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, $|\gamma L M_L S M_S\rangle$, 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

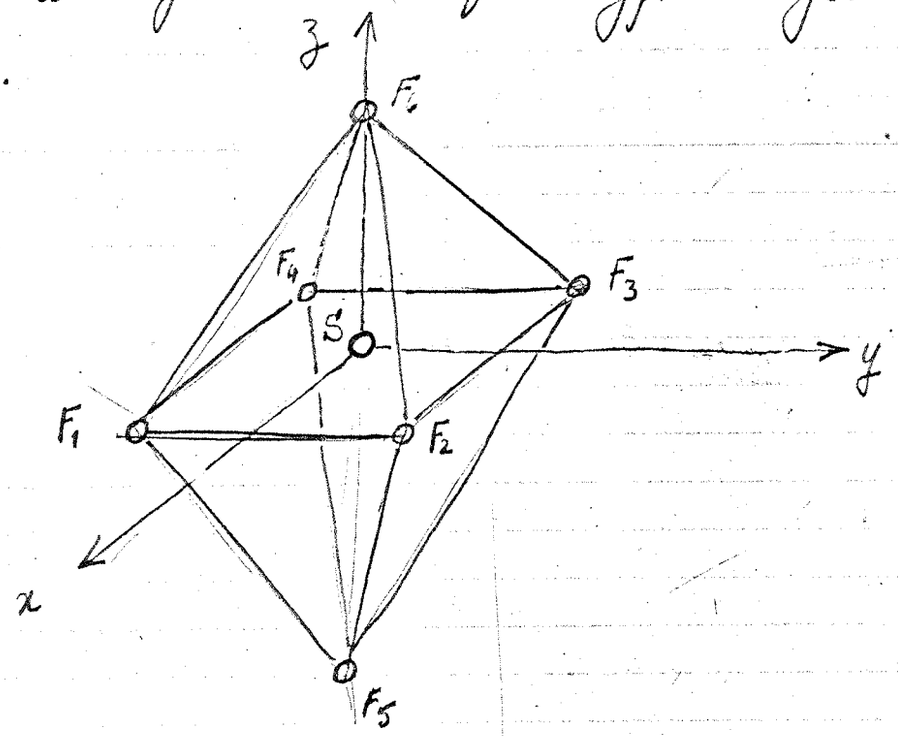
I have now defined the physical features of the situation, and the various assumptions underlying the crystal field model. We now proceed to discuss how one actually solves the problem. In the case of free atoms, recall that we used the spherical

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

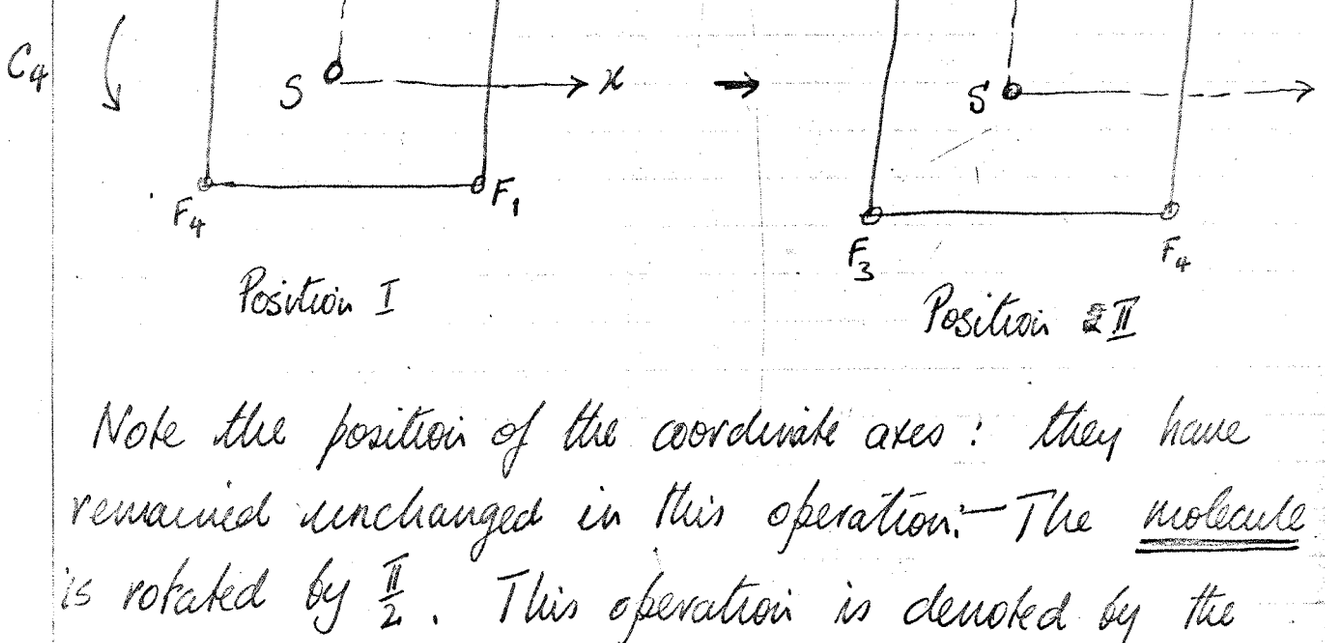


The 6 F atoms lie at the corners of an octahedron. Note that I have drawn in a set of Cartesian axes, with origin at the central S atom. It is important to note that these axes remain fixed in space – everything else is defined relative to these axes, such as the position of the 6 F atoms, the positions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

$$R_l R_k = R_q$$

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

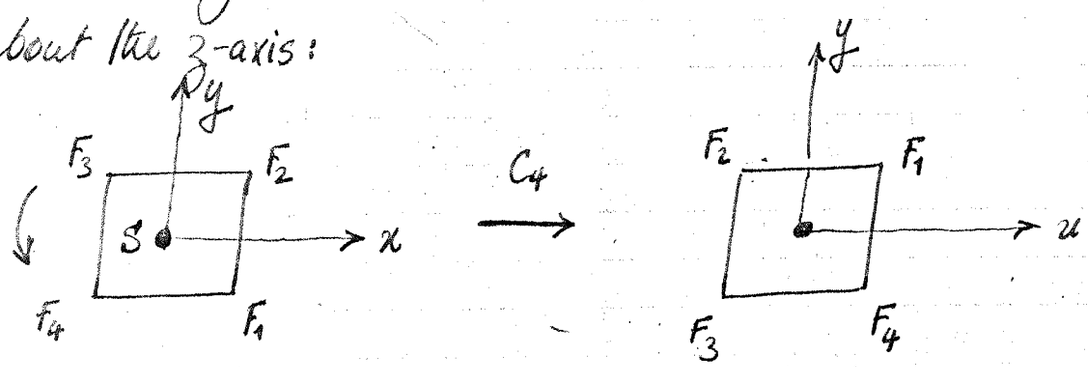
SF_6, G_7 is denoted by the symbol O_h.

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.....

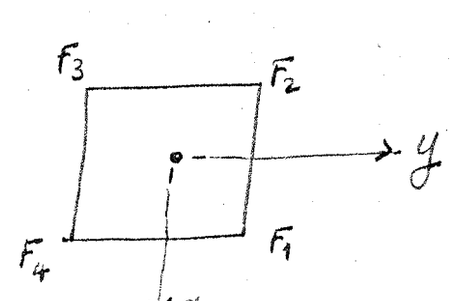
I will not go into the properties of individual point groups — but you should read about them. An excellent reference is Landau & Lifshitz "Quantum Mechanics", Chapter XII. I want to discuss the general properties of point groups and their relevance to quantum mechanics.

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.

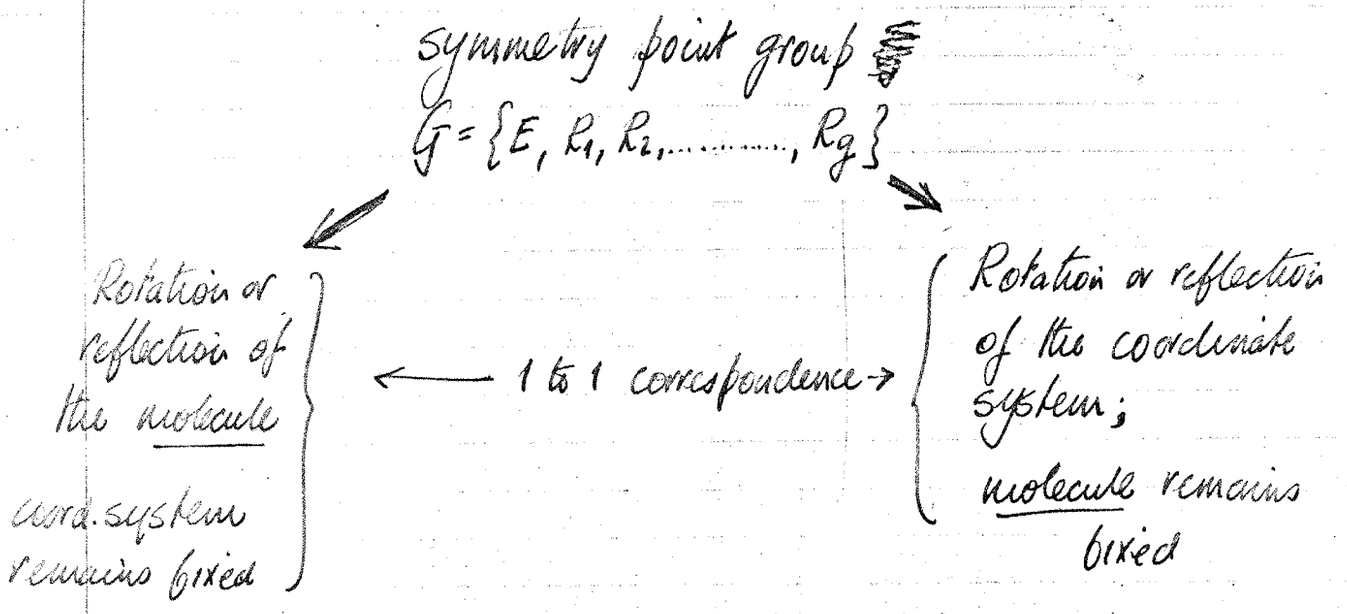
Consider again the rotation of the SF_6 molecule by $\frac{\pi}{2}$ about the z-axis:



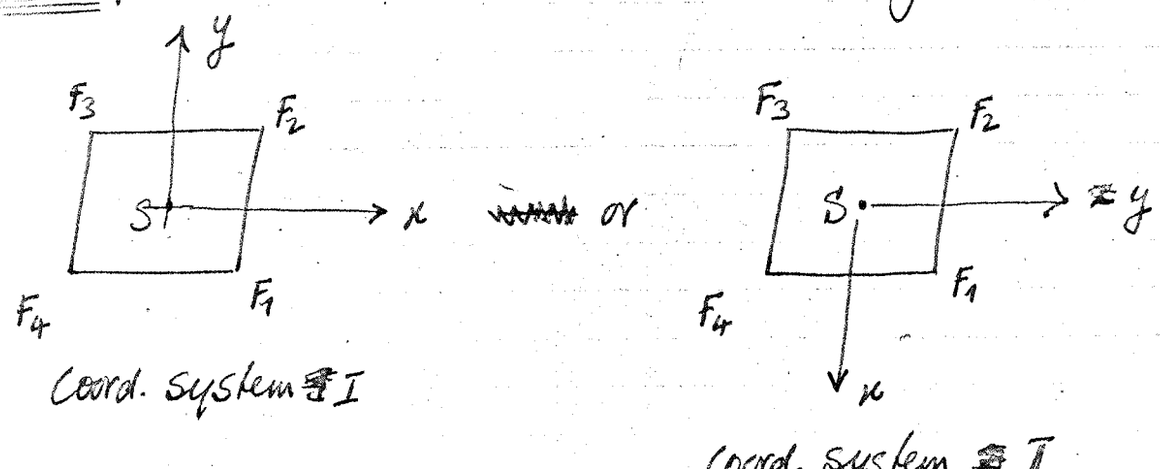
Exactly the same result is achieved by leaving the molecule alone, and rotating the coordinate system by $-\frac{\pi}{2}$:



— 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

coord. system Π. 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^n (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~~ ~~these~~ ~~different~~ 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^n (57) is brought out by considering what happens when $\mathcal{H}$ acts on a wave function Ψ^s_n, $\mathcal{H}\Psi^s_n$:—

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

operation R_k, interpreted as a coord. transformation

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

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

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

[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 $\hat{H}\bar{\Psi}_n^s = E_n\bar{\Psi}_n^s$

for any molecular system,

then in general

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

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

From eqn (58) above, have immediately that

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

↑ just a number.

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

i.e. Ψ_n^s and $(R_k \Psi_n^s)$ 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 $\bar{\imath}$-fold degenerate
i.e. let there be $\bar{\imath}$ wave functions

$$\Psi_{n1}^s, \Psi_{n2}^s, \ldots\ldots, \Psi_{n\bar{\imath}}^s$$

all belonging to the energy level E_n

$$E_n \text{ ——— } \Psi_{n1}^s, \Psi_{n2}^s, \ldots\ldots, \Psi_{n\bar{\imath}}^s.$$

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

Then by equn (59), the functions

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

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

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

This equation is more usually written as

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

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

~~Likewise we see that the operation symmetry operations R_k of the point symmetry group of~~

If we let the symmetry operation R_k act on all the degenerate eigenfunctions $\bar{\Psi}_{n1}, \bar{\Psi}_{n2}, \ldots, \bar{\Psi}_{n\bar{\imath}}$, ~~successively~~ 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:

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

- 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>:

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

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

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

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

so that

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

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

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

Applying R_Q directly to $\bar{\psi}_{n\mu}$, we have,

$$R_Q \bar{\psi}_{n\mu} = \sum_{\lambda=1}^{\tau} D_{\lambda\mu}(R_Q)\, \bar{\psi}_{n\lambda}$$

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,

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

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:

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

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

$$\{ \overline{2}\Psi_{n1}, \overline{2}\Psi_{n2}, \ldots\ldots, \overline{2}\Psi_{n\bar{\imath}} \}$$

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

$$\overline{\Phi}_{nr} = \sum_{\mu=1}^{\bar{\imath}} a_{\mu r}\, \overline{2}\Psi_{n\mu} \qquad \text{---------- (64)}$$

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

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

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

By the same 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 $\underset{\sim}{A}^{-1} = \underset{\sim}{A}^{\dagger} \quad [= (\underset{\sim}{A}^{*})' \;\; !!]$.

Hence (64) can easily be inverted:

$$\overline{2}\Psi_{n\mu} = \sum_{r=1}^{\bar{\imath}} (a)^{-1}_{r\mu}\, \overline{\Phi}_{nr} \qquad \text{- always true,}$$

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

---------- (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:

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

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

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

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

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

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

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

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

i.e.

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

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 ~~in~~ 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

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

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

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

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

- 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,

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

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:

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

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

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

i.e. & the first set ~~etc~~ 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 ℓ-dimensional representation Γ would have been reduced to 3 reps. of smaller dimensions.

This never happens. We can never find a transf^{m} $\hat{A}$ 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

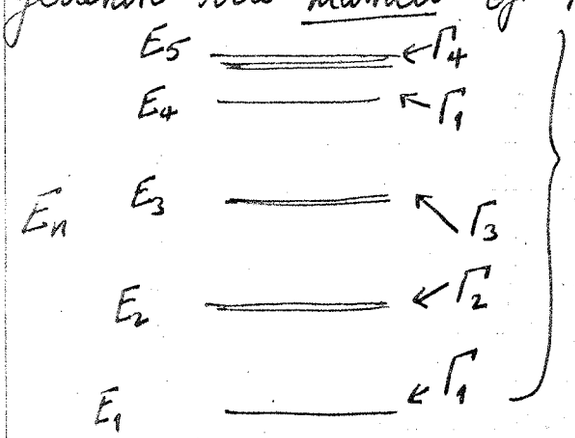
Thus, if the Hamiltonian of an atomic or molecular system is invariant under all operations of a group G:

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

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

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

The set of wave fn's $\{\Psi_{n1}, \ldots\ldots, \Psi_{n\ell}\}$ 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 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 ~~the~~ V to $\mathcal{H}^\circ$ usually "lowers" the symmetry of the system — ~~since~~ ~~[illegible]~~ i.e. $\mathcal{H}$ will be invariant under some group G,

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

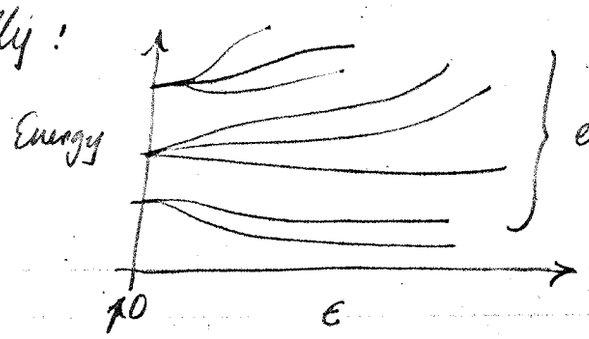
which is smaller than the group G° — G is usually a subgroup of G°; thus:

$$G^\circ : \{\underbrace{E, R_1, R_2, \ldots\ldots, R_g}_{G}, R_{g+1}, \ldots\ldots, R_{g_0}\}$$

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 ~~[illegible]~~ matrices of the ~~corresponding~~ 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 — ~~and~~ 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:



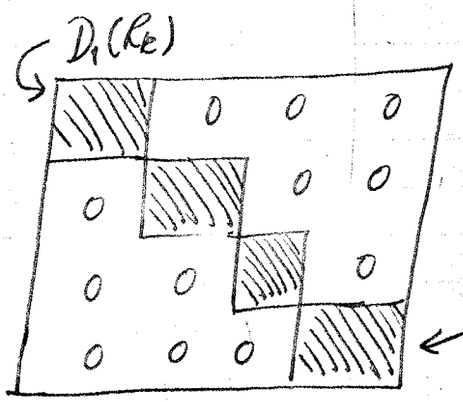
energy levels of $\mathcal{H}^\circ$

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

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

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)', 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:

$$\{\underbrace{\underset{\sim}{D}^\circ(E), \underset{\sim}{D}^\circ(R_1), \underset{\sim}{D}^\circ(R_2), \ldots \underset{\sim}{D}^\circ(R_g)}, \underset{\sim}{D}^\circ(R_{g+1}), \ldots\ldots, D^\circ(R_{g_0})\}$$

This set of matrices forms a reducible rep. of G.

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

$$\underset{\sim}{A}^\dagger \underset{\sim}{D}^\circ(R_k) \underset{\sim}{A} = \underbrace{\underset{\sim}{D}_1(R_k) + \underset{\sim}{D}_2(R_k) + \ldots\ldots + D_N(R_k)}$$

irred. reps. of G

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

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

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

$\bar{\Psi}^s_{n\mu}$: eigenf"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. Then can immediately see in eqn" (69) [p. 107], that the characters are related by:

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

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

This is the core of the method for crystal field theory. The group G° 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.

Hevia, Appendix B.

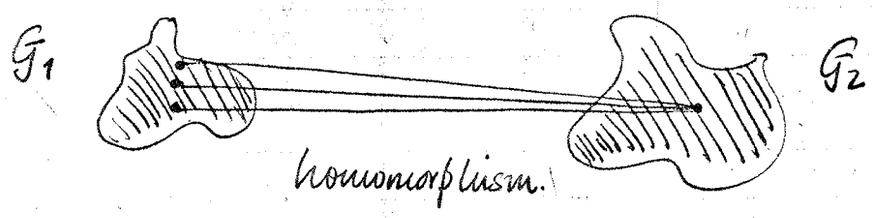
Definition: Two groups G_1 and G_2 are homomorphic if some element of G_2 can be associated with every element of G_1, such that if

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

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.

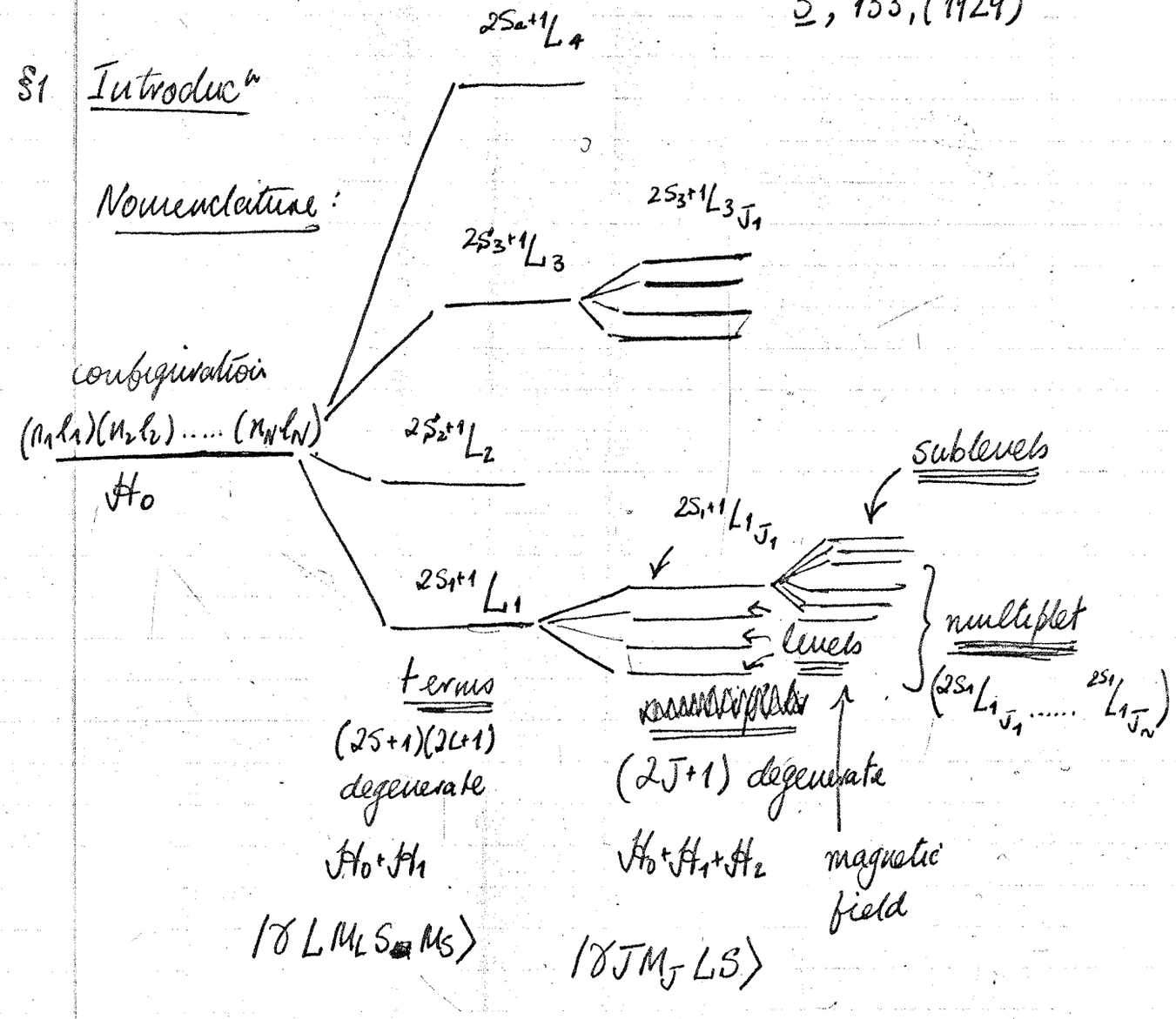
Miss Morgan. - Maths. & Phys.
- Translation of Bethe's article.

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^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." 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^{n}s 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 <u>Group Theoretical Solution</u>

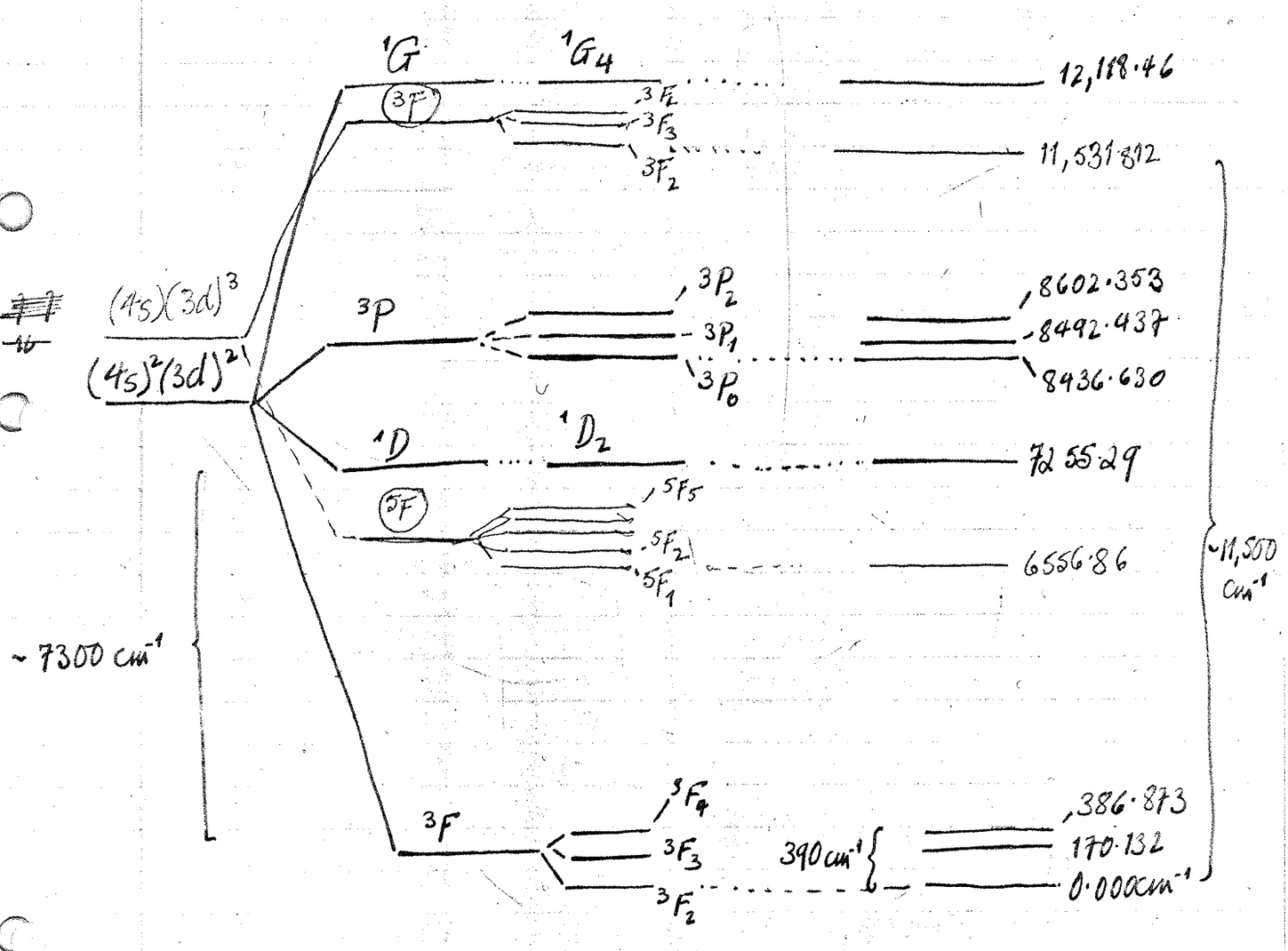
§2

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.

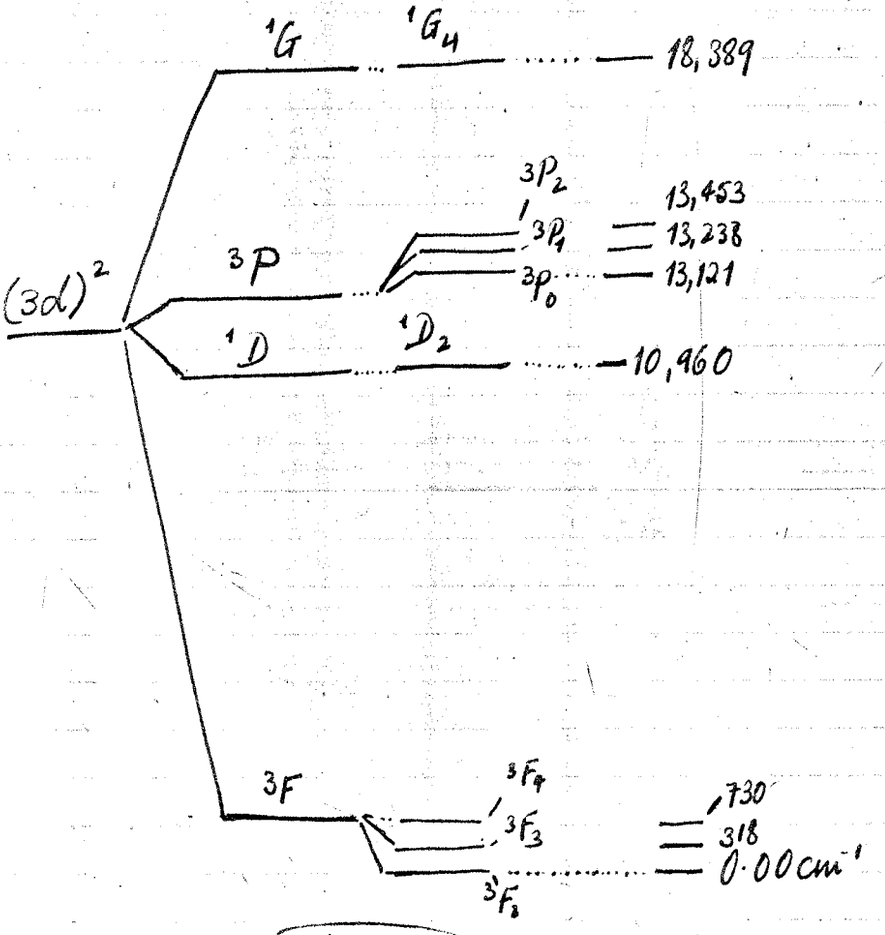


The nearest configuration that can interact with $(4s)^2(3d)^2$ is $(4s)(3d)^3$ - as this gives $^3F_2$, $^3F_3$, $^3F_4$ levels which can interact with the ground state multiplet

Free ion

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

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



4s
3d

The nearest observed 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}

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