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Angular Momentum in Quantum Mechanics

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In these lectures I shall describe how angular momenta are used to study atomic structure.

In the case of atomic hydrogen, we shall see that angular momentum theory is concerned with the angular part of wavefunctions.

The description of a N electron atom uses the coupling of N 1 electron states.

If you want to calculate physical quantities (eg transition probabilities) you have to calculate matrix elements between states. Angular momentum techniques allow you to calculate the angular part of the integrals. The key points are the introduction of tensor operators and the Wigner Eckart theorem. The very powerful techniques involved are often named "Racah methods". They have been developed in the paper:

Racah Phys Rev 62, 438 (1942)

Here is a list of references

A.R. Edmonds Angular Momentum in Quantum Mechanics (Princeton Univ Press NJ 1957)

U Fano G Racah Irreducible Tensorial Sets (Academic Press NY 1959)

B.R. Judd: Operator Techniques in Atomic Spectroscopy (Mc Graw-Hill NY 1963)

L.C. Biedenharn & Van Dam H: Q.T. of A.M. (Academic Press NY 1965) - Contain the reprints of the important papers in the theory

A Jucys & A Bandzaitis Teoria Momenta Kolichestva Dvijenia v Kvantovoi Mekhanike. (Vilnius 1965)

I Orbital Angular Momentum and Spin for one electron (atomic hydrogen)

For atomic hydrogen the Schrödinger equation is

$$\left.\begin{aligned} H|\psi\rangle &= E|\psi\rangle \\ \text{with} \quad H &= \frac{p^2}{2m} - \frac{e^2}{r} \end{aligned}\right\} \qquad (1)$$

We have made many approximations (Non relativistic QM, structureless nucleus)

The solutions of (1) are of the form

$$\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi) \qquad (2)$$
$$E = -\frac{1}{2n^2}\frac{me^4}{\hbar^2} \qquad n > \ell \geq |m|$$

where the spherical harmonics are defined by

$$Y_{\ell m}(\theta,\varphi) = (-)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}\, P_\ell^m(\cos\theta)\, e^{im\varphi}$$

and the Legendre functions by:

$$P_\ell^m(x) = \frac{(1-x^2)^{m/2}}{2^\ell\, \ell!}\, \frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell$$

The radial function $R_{n\ell}(r)$ can be expressed in terms of the associated Laguerre polynomials.

To understand the labels ℓ m we introduce the (orbital) angular momentum of the electron:

$$\vec{\ell} = \frac{1}{\hbar}(\vec{r} \wedge \vec{p}) \qquad (3)$$

It is the set of the 3 operators (ℓ_x, ℓ_y, ℓ_z).

The following commutation relations are basic to the theory:

$$[\vec{\ell}, f(r)] = 0 \qquad (4)$$

$$\left.\begin{aligned} [\ell_i, r_j] &= i\, e_{ijk}\, r_k \\ [\ell_i, p_j] &= i\, e_{ijk}\, p_k \\ [\ell_i, \ell_j] &= i\, e_{ijk}\, \ell_k \end{aligned}\right\} \qquad (5)$$

Labels $i, j, k \ldots$ represent x, y or z.

Vector $\vec{r} = (x\ y\ z)$ is written here as (r_x, r_y, r_z).

e_{ijk} is the full antisymmetric unit tensor of rank 3.

$$e_{xyz} = e_{yzx} = e_{zxy} = 1$$
$$e_{yxz} = e_{zyx} = e_{xzy} = -1$$

the 21 other elements are zero : $e_{xxy} = \ldots = 0$

In relations like (5) we sum over repeated elements.

So relations (5) read:

$$[l_x, x] = 0 \quad ; [l_x, y] = iz \quad \text{---}$$

An operator which like $f(r)$, commutes with $\vec{l}$ is called a <u>scalar</u>.

The commutation relations (5) have the same structure:

$$[l_i, V_j] = i\varepsilon_{ijk} V_k \qquad (6)$$

A set of 3 operators $\vec{V} = (V_x\ V_y\ V_z)$ verifying these relation is called a <u>vector</u> (operator).

<u>Exercices</u>: 1) Suppose $\vec{V}$ and $\vec{V'}$ are vector operators. Show that $\vec{V}\cdot\vec{V'} = V_x V'_x + V_y V'_y + V_z V'_z$ is a scalar and that $\vec{V}\wedge\vec{V'} = (V_x V'_y - V_y V'_x, V_y V'_z - V_z V'_y, V_z V'_x - V_x V'_z)$ is a vector. Suppose s_1 and s_2 are scalars. Show that $f(s_1, s_2)$ is equally a scalar.

2) Prove relations (4) and (5)

It can be shown (see eg Landau & Lifshitz Quantum Mechanics) that the eigenfunctions of the commuting operators $\vec{l}^2$, l_z have the form:

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

where $f(r)$ is an arbitrary function of r, l, m are integers such as $|m| \leq l$

The eigenvalues of $\vec{l}^2$ et l_z are $l(l+1)$ and m resp.

Now we can understand the rôle played by the angular momentum in solving atomic hydrogen. The hamiltonian H is a scalar, so $H, \vec{l}^2, l_z$ is a set of commuting operators. The eigenstates can be labeled with l, m and an additional quantum number n.

The usual notation replaces l by a letter:

l =	0	1	2	3	---
	s	p	d	f	---

To take the spin of the electron into account, we multiply (2) by a spin function (spinor).

The vector space of the spin functions is of dimension 2. It is convenient to introduce the spin operator

$$\vec{s} = \frac{1}{2}\vec{\sigma}$$

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

are the Pauli matrices.

The spin operator verifies the following commutation relations, similar to those of $\vec{l}$:

$$[s_i, s_j] = i\,\varepsilon_{ijk}\, s_k$$

As a basis of spin functions we can use $\chi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ which are eigenstates of s_z with the eigenvalue $+1/2$ and $-1/2$ respectively. The $\chi_{\pm 1/2}$ are also eigenstate of $\vec{s}^2$ with the eigenvalue $\frac{3}{4} = s(s+1)$ where $s = 1/2$.

We shall call a set of 3 hermitian operators $\vec{J} = (J_x, J_y, J_z)$ [$\varepsilon J_i^+ = J_i$] an Angular momentum if it verifies the following commutation relations:

$$[J_i, J_j] = i\,\varepsilon_{ijk}\, J_k \qquad (7)$$

Example: $\vec{l}$, $\vec{s}$, $\vec{j} = \vec{l} + \vec{s}$ (total angular momentum of the electron). Introducing two electrons 1 & 2: $\vec{l}_1 + \vec{l}_2$, $\vec{l}_1 + \vec{s}_2$ etc... are angular momenta.

It can be shown, considering the commutation relations (7) that the eigenvalue equations are given by:

$$J_z\,|\theta, J, M\rangle = M\,|\theta, J, M\rangle$$
$$\vec{J}^2\,|\theta, J, M\rangle = J(J+1)\,|\theta, J, M\rangle \qquad (8)$$

where $J = 0, 1/2, 1, 3/2, \ldots$

and $M = -J, -J+1, \ldots, J$ ($2J+1$ values for a given J)

The label θ is included to form a complete basis of states.

Furthermore the phases of the states can be chosen so that:

$$J_+\,|\theta, J, M\rangle = \sqrt{J(J+1) - M(M+1)}\;|\theta, J, M+1\rangle$$
$$J_-\,|\theta, J, M\rangle = \sqrt{J(J+1) + M(M-1)}\;|\theta, J, M-1\rangle \qquad (9)$$

where $J_\pm = J_x \pm i J_y$ are called ladder operators

Note that $\vec{J}$ applied to $|\theta, J, M\rangle$ does not change labels θ, J. and that any other state $|\theta, J, M'\rangle$ can be obtained by applying J_+ or J_- from $|\theta\, J\, M\rangle$. We say that the $2J+1$ states $|\theta\, J\, M\rangle$ (θ and J fixed) form an irreducible basis of the angular momentum $\vec{J}$

Exercices:

3) Prove eq(8) and (9)

4) Consider the harmonic oscillator in 2 dimensions ($\hbar=1$):
The hamiltonian is:
$H = \left(a_x^+ a_x + a_y^+ a_y + 1\right)\omega$ where $a_x^+ = \sqrt{\frac{\mu\omega}{2}}\, x - \frac{i}{\sqrt{2\mu\omega}} p_x$

Its eigenstates are $|s,t\rangle$ $s,t = 0,1,2\ldots$

$a_x^+ a_x |s,t\rangle = s|s,t\rangle$; $a_y^+ a_y |s,t\rangle = t|s,t\rangle$

Put $J_z = \frac{1}{2}\left(a_x^+ a_x - a_y^+ a_y\right)$, $J_+ = a_x^+ a_y$, $J_- = a_y^+ a_x$

Show that $\vec{J}$ is an angular momentum commuting with H and determine the eigenstates of $\vec{J}^2$ and J_z.

5) Consider the harmonic oscillator in 1 dimension.
$H = \left(a^+a + \frac{1}{2}\right)\omega$.

a) Put. $T_z = \frac{1}{2}a^+a + \frac{1}{4}$, $T_+ = \frac{ia^{+2}}{2}$, $T_- = \frac{ia^2}{2}$

Show that $\vec{T}$ verifies the commutation relations of an angular momentum.

Find the eigenstates of $\vec{T}^2$ and T_z.

Why are not these states of the form $|j,m\rangle$ with $m = -j, -j+1 \ldots j$?

b) Put $J_+ = \left(\sqrt{l+1-a^+a}\right)a^+$; $J_- = \left(\sqrt{l-a^+a}\right)a$; $J_z = a^+a - \frac{l}{2}$

Show that $\vec{J}$ verifies the commutation relations of an angular momentum for any value of l.

Consider the case l integer : what can be said of the eigenstates $|0\rangle, |1\rangle \ldots |l\rangle$ of H ? About the remaining eigenstates?

II Orbital Angular momentum and Spin for a N electron atom

1) The central field approximation

For a N electron atom the Schrödinger equation is:

$$H|\psi\rangle = E|\psi\rangle$$

with $$H = \sum_{i=1}^{N}\left(\frac{\vec{p}_i^{\,2}}{2m} - \frac{Ze^2}{r_i}\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{e^2}{r_{ij}} \qquad (10)$$

Effects not included in (10) due to the finite size and mass of the nucleus, the spins of the electrons, relativistic effects can be later introduced using perturbation theory.

We also study eq (10) with perturbation theory. We put :

$$H = H_0 + H_1$$

with $$H_0 = \sum_{i=1}^{N}\left(\frac{\vec{p}_i^{\,2}}{2m} + U(r_i)\right) = \sum_{i=1}^{N} h_i \qquad (11)$$

$U(r)$ is the mean potential energy seen by one electron (due to the nucleus and the other electrons).

The approximation of eq (10):

$$H_0|\psi_0\rangle = E_0|\psi_0\rangle \qquad (12)$$

is called the central field approximation. In this approximation H_0 is a separable hamiltonian. So we have to solve the one-electron equation :

$$h|\psi\rangle = \left[\frac{\vec{p}^2}{2m} + U(r)\right]|\psi\rangle = \varepsilon|\psi\rangle \qquad (13)$$

h commutes with the angular momentum $\vec{l}$ so the solutions of (13) are of the form

$$\psi_{nlm\,m_s} = \frac{R_{nl}(r)}{r}\, Y_{lm}(\theta,\varphi)\, \chi_{m_s} \qquad (14)$$

Of course, $R_{nl}(r)$ depends on the form of $U(r)$ and the energy ε_k ($k \equiv n\,l\,m\,m_s$) depends on n and l (but not on m and m_s). The state with given nl form a shell

We can find solutions of eq (12) by taking products of functions (14). For example for 2 electrons:

$$\psi_0 = \psi_{k_1}(1)\,\psi_{k_2}(2) \qquad (15)$$
$$E_0 = \varepsilon_{k_1} + \varepsilon_{k_2}$$

By permuting the electrons 1 and 2 we obtain another solution of eq (12) with the same energy:

$$\psi_0' = \psi_{k_1}(2)\,\psi_{k_2}(1) \qquad (16)$$

According to the exclusion principle of Pauli, the wave function must be ψ_1 totally antisymmetric in the

exchange of 2 electrons. So solutions (15) and (16) do not exist but their combination:

$$\psi = \psi_0 - \psi_0' = \frac{1}{\sqrt{2}}\left(\psi_{k_1}(1)\,\psi_{k_2}(2) - \psi_{k_1}(2)\,\psi_{k_2}(1)\right)$$

is an acceptable solution (if $k_1 \neq k_2$). The factor $\frac{1}{\sqrt{2}}$ is included to obtain a normalized solution if ψ_{k_1} and ψ_{k_2} are normalized.

In general for N electrons, we find acceptable solutions by using determinantal states:

$$\psi_0 = \{k_1, k_2, \ldots, k_N\} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix} \qquad (17)$$

$$E_0 = \varepsilon_{k_1} + \varepsilon_{k_2} + \cdots + \varepsilon_{k_N}$$

All $k_1 \ldots k_N$ are supposed different. When calculating the normalising integral $\int \psi_0^* \psi_0\, d1\, d2 \ldots dN$, we find $N!$ integrals of the form $\int \psi_k^*(1)\,\psi_{k'}^*(2) \ldots \psi_k(1)\,\psi_{k'}(2) \ldots d1\, d2 \ldots dN = 1$, the other like $\int \psi_k^*(1) \ldots \psi_{k'}(1) \ldots d1\, d2 \ldots dN$ disappearing. So ψ_0 is normalized.

The energy E_0 depends only on the quantum numbers nl:

$$E_0 = \varepsilon_{n_1 l_1} + \varepsilon_{n_2 l_2} + \dots + \varepsilon_{n_N l_N}$$

The vector space spanned by the states ψ_0 with given values of nl and varying values of m_ℓ m_s is called the configuration $(n_1 l_1)(n_2 l_2) \dots (n_N l_N)$.

Example: The lowest configuration of Nd^{+3} is:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^3 \quad (18)$$

The notation $2p^6$ means that $n=2, l=1$ appears 6 times in the configuration. Excepted $4f$, the electrons are in closed shells (eg the 6 states $m_\ell m_s = \bar{-1}, \bar{0}, \bar{1}, -\uparrow, 0\uparrow, 1\uparrow$ (m_s is indicated by + or − over m_ℓ) of shell $2p$ are used). So we can simplify notation and denote a state in configuration (18) by giving only the $m_s m_\ell$ values of shell $4f$. For example:

$$\{3\uparrow\ 1\uparrow\ -3\downarrow\}\ ;\ \{2\downarrow\ -1\downarrow\ 0\downarrow\}\ \text{etc}$$

What is the dimension of configuration (18)? This is the number of different triplets $m_s m_\ell$ in shell $4f$ [changing the order of k_i in state (17) gives the same state multiplied by ± 1]

So the dimension (degeneracy) of the configuration is $\frac{14 \times 13 \times 12}{3!} = 364$.

2) Terms

Now let us go back to the Schrödinger equation (10). Perturbation theory tells us that to find approximate solutions we have to diagonalise the restriction of the perturbation H_1 over the configuration. So we have to diagonalise the 364×364 matrix:

$$\begin{array}{|cccc|} \hline (\psi_1|H_1|\psi_1) & (\psi_1|H_1|\psi_2) & \dots & (\psi_1|H_1|\psi_{364}) \\ (\psi_2|H_1|\psi_1) & \dots & & \\ & & & \\ (\psi_{364}|H_1|\psi_1) & \dots & & (\psi_{364}|H_1|\psi_{364}) \\ \hline \end{array} \quad (19)$$

The eigenvalues of this matrix give the energy shifts.

Angular momenta theory permits:

a) to simplify the matrix by choosing the basis states $\psi_1 \dots \psi_{364}$

b) to calculate the angular part of the integral $(\psi_i|H_1|\psi_j)$ so that these integrals will be expressed in terms of radial integrals like $\int dr_1 dr_2 \, R_{4f}^2(r_1) R_{4f}^2(r_2) \frac{r_<^2}{r_>^3}$.

$r_< = \inf(r_1, r_2)$; $r_> = \sup(r_1, r_2)$

We introduce the orbital angular momentum

$$\vec{L} = \sum_{i=1}^{N} \vec{l}_i \qquad (20)$$

and the spin :

$$\vec{S} = \sum_{i=1}^{N} \vec{s}_i \qquad (21)$$

of the atom. It is easy to see that $\vec{L}$ and $\vec{S}$ are angular momenta.

For example :

$$[L_x, L_y] = \sum_{ij} [l_{ix}, l_{jy}] = \sum_{j=1}^{N} [l_{jx}, l_{jy}] = i \sum_{j=1}^{N} l_{jz} = iL_z$$

since l_{ix} and l_{jy} commute if $i \neq j$.

Why are these operators important?

The reason is that they commute with H_1 (and H).

In fact every term in the Hamiltonian H eq(10) is a scalar with respect to $\vec{L}$ and $\vec{S}$. For $\vec{S}$, this is because H is entirely in orbit space. To see it for $\vec{L}$ we remark that $\vec{p}_i$, $\vec{r}_i$, $\vec{r}_i - \vec{r}_j$ are vectors with respect to $\vec{L}$: For example $[L_x, r_{iy}] = [l_{ix}, r_{iy}] = i r_{iz}$. From this follows that $\vec{p}_i^{\,2}$, $\vec{r}_i^{\,2}$ and $r_{ij}^2 = (\vec{r}_i - \vec{r}_j)^2$ are scalars, and so are H_1 and H wich are functions of these scalars.

Now suppose we take a basis of configuration (18) of the form : $|\theta\, S M_S\, L M_L\rangle$ (22)

These states are linear combination of determinantal states and verify relations like (8) and (9) with respect to S et L. Since H_1 commute with $\vec{S}$ and $\vec{L}$, H_1 is diagonal with respect to $S M_S\, L M_L$. For example, if $M_S \neq M'_S$ we have :

$$\langle \theta\, S M_S\, L M_L | \underbrace{S_z H_1 - H_1 S_z}_{=0} | \theta' S' M'_S\, L' M'_L \rangle$$

$$= (M_S - M'_S) \langle \theta\, S M_S\, L M_L | H_1 | \theta' S' M'_S\, L' M'_L \rangle$$

and $\langle \theta\, S M_S\, L M_L | H_1 | \theta' S' M'_S\, L' M'_L \rangle = 0$

The only non zero matrix element of H_1 are then

$$\langle \theta\, S M_S\, L M_L | H_1 | \theta' S M_S\, L M_L \rangle$$

Moreover these matrix element are independant of M_S and M_L. To see this we use relation (9):

$$L_\pm |\theta\, S M_S\, L M_L\rangle = \sqrt{L(L+1) - M_L(M_L \pm 1)}\; |\theta\, S M_S\, L M_L \pm 1\rangle$$

and its conjugate : ($L_\pm^+ = L_\mp$

$$\langle \theta\, S M_S\, L M_L | L_\mp = \langle \theta\, S M_L\, L M_L \pm 1 | \sqrt{L(L+1) - M_L(M_L \pm 1)}$$

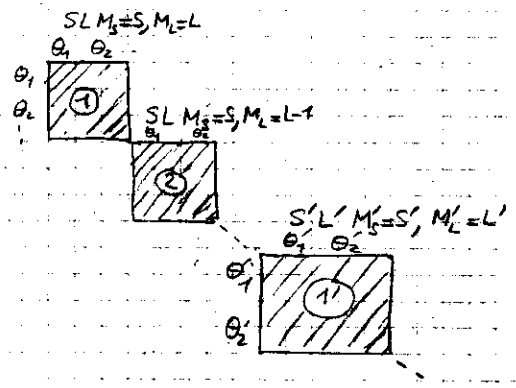
Then : $\langle \theta\, S M_S\, L M_L + 1 | \underbrace{L_+ H_1 - H_1 L_+}_{0} | \theta\, S M_S\, L M_L \rangle$

$$= \sqrt{L(L+1) - (M_L+1) M_L}\, \big(\langle \theta\, S M_S\, L M_L | H_1 | \theta\, S M_S\, L M_L \rangle -$$

$$\langle \theta\, S M_S\, L M_L + 1 | H_1 | \theta\, S M_S\, L M_L + 1 \rangle \big) = 0$$

The form of matrix (19) when we use the basis (22) is then much simpler than that using an arbitrary basis (like the one formed of determinantal states).

Its form is as follows:

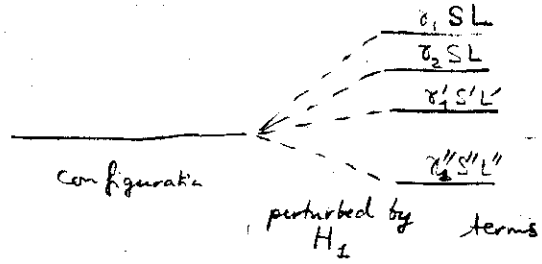


(23)

The matrix has a block form: we find non zero elements only in the submatrices ①, ② ... ①' ... . Moreover the $(2S+1)(2L+1)$ submatrices ① ② ... corresponding to the same values of S, L, with M_S and M_L taking all possible values are all identical.

To diagonalize matrix (23) we just have to diagonalize each block. We then find states $|\gamma S M_S L M_L\rangle$ which are still labeled with $S M_S L M_L$, and the energy of these states is independant of the M_S, M_L value. The vector space spanned by the $(2S+1)(2L+1)$ states $|\gamma S M_S L M_L\rangle$ for given γ, S, L is called $\underline{\text{term}}$ γSL. The usual notation is ^{2S+1}S, ^{2S+1}P, ^{2S+1}D ... for resp $L=0, 1, 2$ ...

We can represent the diagonalisation as follows:



The degeneracy of the configuration is (partially) lifted by the perturbation H_1

In the case of $4f^3$ the terms are

Quadruplets $(S=3/2)$: S D F G I

Doublets $(S=1/2)$: P D F G H I K L
D F G H

The evaluation of matrix (23) then consists in evaluating 4 2x2 matrices and 9 1x1 matrices.

To understand how one can find the terms of a given configuration, let us take the simpler configuration $2p^2$. A determinantal state $\{m_s m_\ell ; m'_s m'_\ell\}$ is an eigenvector of S_z and L_z with eigenvalues $M_S = m_s + m'_s$ and $M_L = m_\ell + m'_\ell$.

By considering these determinantal states, let us first the dimension of the subspaces of the configuration corresponding to given non negative values of M_S M_L :

M_S	M_L	D dimension of substate	states
1	1	1 :	$\{^{+}_{1}\ ^{+}_{0}\}$
1	0	1	$\{^{+}_{1}\ ^{+}_{-1}\}$
0	2	1	$\{^{+}_{1}\ ^{-}_{1}\}$
0	1	2	$\{^{+}_{1}\ ^{-}_{0}\}$ $\{^{+}_{0}\ ^{-}_{1}\}$
0	0	3	$\{^{+}_{1}\ ^{-}_{-1}\}$ $\{^{+}_{0}\ ^{-}_{0}\}$ $\{^{+}_{-1}\ ^{-}_{1}\}$

There is only one state with $M_S \geq 1$, $M_L \geq 1$. From this we deduce that ^3P is a term of the $2p^2$ configuration.

This term contains states with $M_S, M_L = (1,1), (1,0), (0,1)$ and $(0,0)$

M_S	M_L	E dimension of ^3P term	D−E
1	1	1	0
1	0	1	0
0	2	0	1
0	1	1	1
0	0	1	2

So it accounts for the dimensions of ($M_S M_L$) subspaces listed in column E. We still have to attribute the dimensions in column D−E to terms. Proceeding as above, we find the terms ^1D and ^1S.

Exercices 6) Express the $|^3P\ M_S M_L\rangle$ states of configuration $2p^2$ as linear combinations of determinantal states

7) Same question for the $|^1S, 0,0\rangle$ state of configuration $2p^2$

III Total angular momentum for a N electron atom

One of the most important effect not considered in the Schrödinger equation is the spin-orbit interaction :

$$\Lambda = \sum_{i=1}^{N} \xi(r_i)\, \vec{s}_i \cdot \vec{l}_i \qquad (24)$$

where $\xi(r) = \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{dU}{dr}$

If this interaction is small compared to H_1, we can consider Λ as a perturbation. In the same way as $\vec{L}, \vec{S}$ simplified the calculation of perturbation H_1, we introduce here the total angular momentum :

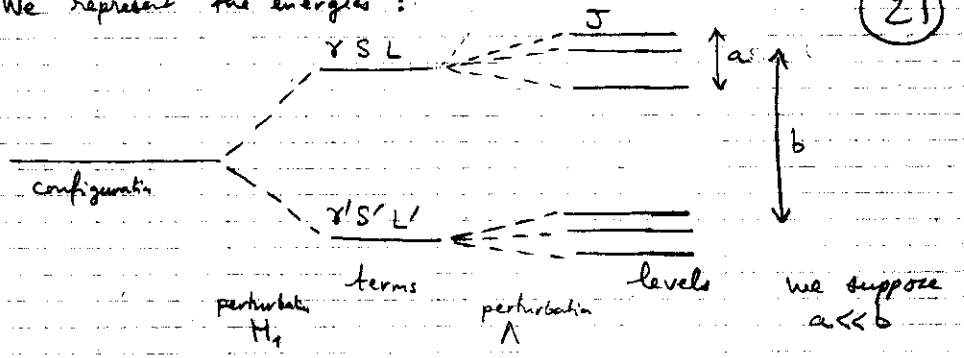
$$\vec{J} = \vec{S} + \vec{L}$$

It is easy to see that $\vec{s}_i$ and $\vec{l}_i$ are vectors with respect to $\vec{J}$. So Λ is a scalar with respect to J.

To calculate the perturbation due (within a given term) to Λ we shall use a basis $|J M\rangle$ instead of the basis $|M_S M_L\rangle$. (We will see later that we do not need any additional label to J is enough)

In the same way as before, it is possible to prove that the only non zero matrix elements are $\langle J M | \Lambda | J M \rangle$ and that they do not depend on M.

We represent the energies :



The degeneracy of a term is partially lifted.
We obtain <u>levels</u> which have a degeneracy of $(2J+1)$

Which are the J of a given term? How do we obtain the $|JM\rangle$ states from the $|M_S M_L\rangle$ states? We shall anser these very important questions now. However we we take a more general setting, by making the change : $E_{\theta J_1 J_2}$ spanned by the $(2J_1+1)(2J_2+1)$ states $|\theta J_1 M_1 J_2 M_2\rangle$

$$\vec{S} \longrightarrow \vec{J}_1$$
$$\vec{L} \longrightarrow \vec{J}_2$$

IV the coupling of two angular momenta

Let $\vec{J}_1$ and $\vec{J}_2$ be two independant angular momenta ; independant means that $[J_{1i}, J_{2j}] = 0$. We consider states of the form $|\theta J_1 M_1 J_2 M_2\rangle$ which are eigenstates of J_1^2, J_{1z}, J_2^2 and J_{2z}, and verify relations like (1) for $\vec{J}_1$ and $\vec{J}_2$.

From the independance of $\vec{J}_1$ and $\vec{J}_2$ it follows that $\vec{J} = \vec{J}_1 + \vec{J}_2$ is an angular momentum.

Acting with $\vec{J}$ on state $|\theta J_1 M_1 J_2 M_2\rangle$ does not change the labels θ, J_1 and J_2. So $\vec{J}$

So we can diagonalise J^2 and J_z within the subspace $E_{\theta J_1 J_2}$ spanned by the $(2J_1+1)(2J_2+1)$ states $|\theta J_1 M_1 J_2 M_2\rangle$ with fixed θ, J_1 and J_2. We want to find a basis of this subspace of the form $|\alpha J M\rangle$ satisfying relations (8) and (9).

To find the values of J we note that $|\theta J_1 M_1 J_2 M_2\rangle$ is an eigenstate of J_z with eigenvalue $M_1 + M_2$. So let us determine the dimension of the eigenspaces of J_z, within $E_{\theta J_1 J_2}$ corresponding to non negative values of M.

Let us take the example $J_1 = 2$, $J_1 = 1$

eigenvalue of J_z	dimension of eigenspace	eigenstates : values of (M_1, M_2)
3	1	(2,1)
2	2	(2,0) ; (1,1)
1	3	(2,-1) ; (1,0) ; (0,1)
0	3	(1,-1) ; (0,0) ; (-1,1)

To reproduce the dimensions in this table with $|JM\rangle$ states we have to take the values $J=3$, $J=2$ and $J=1$. Indeed we then have :

eigenvalue of J_z	dimension of eigenspace	eigenstates of J_z : values of $[J,M]$		
3	1	[3,3]		
2	2	[3,2]	[2,2]	
1	3	[3,1]	[2,1]	[1,1]
0	3	[3,0]	[2,0]	[1,0]

The method seen on this example can be generalised to any values of J_1, J_2. The result is that the J takes the values J_1+J_2, J_1+J_2-1, $J_1+J_2-2, \dots, |J_1-J_2|+1, |J_1-J_2|$ and that these values appear only <u>once</u>. When J has one of these values we say that J_1 J_2 J are triangular.
Since these values appear only once we can note the states as:
$|\theta\ J_1\ J_2\ J\ M\rangle$ with no additional label.

Let us now calculate these states in terms of the $|\theta\ J_1\ M_1\ J_2\ M_2\rangle$ states.

Let us work out the example of a ^5P term ($J_1 \equiv S_1 = 2$ $J_2 \equiv L = 1$)

The $M_1\ M_2$ states are noted as $|^5P\ M_S\ M_L\rangle$ and the JM states as $|^5P_J\ M\rangle$ [^5P_J the iiird notation for a level]

Suppose we want to find the state $|^5P_1\ 0\rangle$.
We first look for

$$|^5P_1\ 1\rangle = a\,|^5P\ 2\ -1\rangle + b\,|^5P\ 1\ 0\rangle + c\,|^5P\ 0\ 1\rangle$$

To find a, b, c we use the equation $J_+\,|^5P_1\ 1\rangle = 0$ because 1 is the greatest value of M in the $^5P_1$ level.

$$J_+\,|^5P\ 2\ -1\rangle = (S_+ + L_+)\,|^5P\ 2\ -1\rangle = L_+\,|^5P\ 2\ -1\rangle$$
$$= \sqrt{1.2-0}\ |^5P\ 2\ 0\rangle$$

$$J_+\,|^5P\ 1\ 0\rangle = \sqrt{2.3-1.2}\ |^5P\ 2\ 0\rangle + \sqrt{1.2-0}\ |^5P\ 1\ 1\rangle$$

$$J_+\,|^5P\ 0\ 1\rangle = \sqrt{2.3-0}\ |^5P\ 1\ 1\rangle$$

So $J_+\,|^5P_1\ 1\rangle = (a\sqrt{2}+2b)\,|^5P\ 2\ 0\rangle + (b\sqrt{2}+c\sqrt{6})\,|^5P\ 1\ 1\rangle$

and $a = -\sqrt{2}\,b$
$c = -b/\sqrt{3}$

The normalisation condition $|a|^2+|b|^2+|c|^2 = 1$ gives

$$\left(2+1+\tfrac{1}{3}\right)|b|^2 = 1 \quad \text{so} \quad b = -\sqrt{\tfrac{3}{10}}\,e^{i\varphi} \qquad \varphi \in \mathbb{R} \quad (25)$$

We take $\varphi = 0$ so :

$$|^5P_1\ 1\rangle = \sqrt{\tfrac{3}{5}}\,|^5P\ 2\ -1\rangle - \sqrt{\tfrac{3}{10}}\,|^5P\ 1\ 0\rangle + \sqrt{\tfrac{1}{10}}\,|^5P\ 0\ 1\rangle$$

To obtain $|^5P_1\ 0\rangle$ we apply the operator $J_- = S_- + L_-$

$$\sqrt{2-0}\ |^5P_1\ 0\rangle = \sqrt{\tfrac{3}{5}}\left\{\sqrt{2.3-2.1}\ |^5P\ 1\ -1\rangle\right\}$$
$$-\sqrt{\tfrac{3}{10}}\left\{\sqrt{2.3-0}\ |^5P\ 0\ 0\rangle + \sqrt{2-0}\ |^5P\ 1\ -1\rangle\right\}$$
$$+\sqrt{\tfrac{1}{10}}\left\{\sqrt{2.3-0}\ |^5P\ -1,1\rangle + \sqrt{2-0}\ |^5P\ 0,0\rangle\right\}$$
$$= \sqrt{\tfrac{3}{5}}\,|^5P\ 1\ -1\rangle - \frac{2}{\sqrt{5}}\,|^5P\ 0\ 0\rangle + \sqrt{\tfrac{3}{5}}\,|^5P\ -1,1\rangle$$

Then :

$$|^5P_1\ 0\rangle = \sqrt{\tfrac{3}{10}}\ |^5P\ 1\ -1\rangle - \sqrt{\tfrac{2}{5}}\ |^5P\ 0\ 0\rangle + \sqrt{\tfrac{3}{10}}\ |^5P\ -1\ 1\rangle$$

What we have obtained is a particular case of the development :

$$|\theta\, J_1\, J_2\, JM\rangle = \sum_{M_1 M_2} (J_1 M_1 J_2 M_2 \,|\, JM)\ |\theta\, J_1\, M_1\, J_2\, M_2\rangle \qquad (26)$$

The coefficients $(J_1 M_1 J_2 M_2 | JM)$ do not depend on θ as seen from the method of calculation used in our example.

They are called Clebsch Gordan coefficients, or Vector coupling coefficients.

It is instructive to compare (26) with the relation :

$$|\theta\, J_1 J_2\, JM\rangle = \sum_{\substack{\theta' J_1' J_2' \\ M_1 M_2}} |\theta' J_1' M_1 J_2' M_2\rangle \langle \theta' J_1' M_1 J_2' M_2 | \theta\, J_1 J_2\, JM\rangle$$

$\equiv 1$ (closure relation)

We see that the elements of the transformation matrix have the form :

$$\langle \theta' J_1' M_1 J_2' M_2 | \theta\, J_1\, J_2\, JM\rangle = \delta_{\theta\theta'}\, \delta_{J_1' J_1}\, \delta_{J_2' J_2}\, (J_1 M_1 J_2 M_2 | JM) \qquad (27)$$

Exercices 8) Show that the condition $J_1\, J_2\, J$ triangular is equivalent to conditions : $J_1 + J_2 - J$, $J_1 - J_2 + J$, $-J_1 + J_2 + J$ non negative integers. (From that the condition is independant of the order of the 3 numbers $J_1 J_2 J$.)

9) Show the relation :

$$\sum_{J=|J_1-J_2|}^{J_1+J_2} (2J+1) = (2J_1+1)(2J_2+1)$$

What is the meaning of this relation ?

V Clebsch Gordan coefficients. 3j coefficients

We have seen how the Clebsch Gordan (CG) coefficients can be calculated. However, as in eq(25), we have to choose a phase. The generally accepted phase convention [called the Condon and Shortley phase convention, from their book Theory of Atomic Spectra (Cambridge Univ Press 1935)] consists in taking $(J_1\ M_{1\max}\ J_2\ M_2 \,|\, J\ J)$ positive where $M_{1\max}$ is the greatest value of M_1 $(= \max(J_1, J+J_2))$. With this convention the coefficients are real.

Note the following properties of the coefficients :

1) $(J_1 M_1 J_2 M_2 | JM) = 0$ if $M \neq M_1 + M_2$ or J_1, J_2, J non triangular

2) The inverse transformation of (26) can be written with CG coefficients :

$$|\theta\, J_1 M_1\, J_2 M_2\rangle = \sum_{JM} (J_1 M_1 J_2 M_2 | JM)\ |\theta\, J_1 J_2\, JM\rangle \qquad (28)$$

To prove this relation, use the conjugate of eq(27) to find the transformation matrix.

3) Orthogonality conditions. They are found by writing that states (26) or (28) are orthonormalised :

$$\sum_{M_1 M_2} (J_1 M_1 J_2 M_2 | JM)(J_1 M_1 J_2 M_2 | J'M') = \delta_{JJ'}\, \delta_{MM'} \qquad (29)$$

$$\sum_{JM} (J_1 M_1 J_2 M_2 | JM)(J_1 M_1' J_2 M_2' | JM) = \delta_{M_1 M_1'}\, \delta_{M_2 M_2'}$$

Putting $(JM | J_1 M_1 J_2 M_2) = (J_1 M_1 J_2 M_2 | JM)$ these relations have the form of closure relations.

Other properties of the CG coefficient are obtained by using an explicit algebraic expression of the coefficients. Such an expression can be found by generalizing the method of calculation that we have given, and keeping formal expressions with $J_1 M_1 J_2 M_2 J M$. (See the book of Judd). Other methods of finding such an expression depend on group theory [see Wigner: Group Theory (Academic Press NY (1959))].

The formal expressions obtained, which we will not derive (several expressions can be found: see the book of Jucys & Bandzaitis eq (13.1a)-(13.1d) and (17.10)).

are made more symmetric by defining the 3j coefficient:

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = (-)^{J_1 - J_2 - M_3} \frac{1}{\sqrt{2J_3+1}} (J_1 M_1 J_2 M_2 | J_3 - M_3)$$

This coefficient is zero if $M_1 + M_2 + M_3 \neq 0$.

One expression (obtained by Racah) has the form:

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = (-)^{J_1 - J_2 - M_3}$$

$$\times \sqrt{\frac{(J_1+J_2-J_3)!\,(J_1-J_2+J_3)!\,(-J_1+J_2+J_3)!\,(J_1+M_1)!\,(J_1-M_1)!\,(J_2+M_2)!\,(J_2-M_2)!\,(J_3+M_3)!\,(J_3-M_3)!}{(J_1+J_2+J_3+1)!}}$$

$$\times \sum_k \frac{(-)^k}{k!\,(J_1+J_2-J_3+k)!\,(J_1-M_1-k)!\,(J_2+M_2-k)!\,(J_3-J_2+M_1+k)!\,(J_3-J_1-M_2+k)!}$$

(30)

From this formula the following properties can be obtained:

1) $\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = \pm\sqrt{\frac{p}{q}}$ with p and q integers.

This property is used in the book:

Rotenberg, Bivins, Metropolis and Wooten: The 3j and 6j symbols (Mass Inst Technology Press 1959)

to tabulate the exact values of the 3j coefficient for which $J_1 \leq 8$, $J_2 \leq 8$, $J_3 \leq 8$.

2) The transposition of two columns introduces a phase factor $(-)^{J_1+J_2+J_3}$. For example:

$$\begin{pmatrix} J_2 & J_1 & J_3 \\ M_2 & M_1 & M_3 \end{pmatrix} = (-)^{J_1+J_2+J_3} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \quad (31)$$

Circular permutations of the columns do not change the value of the coefficient:

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = \begin{pmatrix} J_2 & J_3 & J_1 \\ M_2 & M_3 & M_1 \end{pmatrix} = \begin{pmatrix} J_3 & J_1 & J_2 \\ M_3 & M_1 & M_2 \end{pmatrix}$$

3) $$\begin{pmatrix} J_1 & J_2 & J_3 \\ -M_1 & -M_2 & -M_3 \end{pmatrix} = (-)^{J_1+J_2+J_3} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \quad (32)$$

4) There are other symmetries which modify the values of J and M (Regge). These symmetries (and symmetries (31)(32)) can be described by using a 3x3 matrix:

$$[M] = \begin{bmatrix} -J_1+J_2+J_3 & J_1-J_2+J_3 & J_1+J_2-J_3 \\ J_1+M_1 & J_2+M_2 & J_3+M_3 \\ J_1-M_1 & J_2-M_2 & J_3-M_3 \end{bmatrix} = \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}$$

The 9 entries of matrix M are non negative integers: they are linked by the condition that the sum of each line or column is a constant (M is a magic square).

With this notation the symmetries are:

$[M'] = (-)^{J_1+J_2+J_3}[M]$ if M' is obtained from M by transposing two columns or two lines

$[\tilde{M}] = [M]$ if $\tilde{M}$ is the transposed matrix of M.

(31)

exercise 10) Symmetry of atomic hydrogen.

a) Show that for the classical motion of a particle ($m=1$) in a Coulomb field : $\ddot{\vec{r}} = -\frac{\vec{r}}{r^3}$, the Lentz vector $\vec{A}' = \vec{l} \wedge \frac{d\vec{r}}{dt} + \hat{r}$ $\left(\hat{r} = \frac{\vec{r}}{r} \quad \vec{l} = \vec{r} \wedge \frac{d\vec{r}}{dt}\right)$ is a constant of motion.

b) Consider the same system in quantum mechanics (Atomic hydrogen, supposing a spinless electron. Put $\hbar = m = e^2 = 1$)
The hamiltonian is $H = \frac{p^2}{2} - \frac{1}{r}$ with bound eigenstates $|nlm\rangle$:

$$H|nlm\rangle = -\frac{1}{2n^2}|nlm\rangle \quad ; \vec{l}^2|nlm\rangle = l(l+1)|nlm\rangle ; l_z|nlm\rangle = m|nlm\rangle$$

Show that $\vec{A}'' = \frac{1}{2}(\vec{l} \wedge \vec{p} - \vec{p} \wedge \vec{l}) + \hat{r}$ commutes with H

c) The following relations are valid :

$$\vec{A}'' \wedge \vec{A}'' = -2iH\vec{l} \quad ; \quad \vec{l}.\vec{A}'' = \vec{A}''.\vec{l} = 0$$

and $(\vec{A}'')^2 = 1 + 2H(\vec{l}^2 + 1)$.

Consider only the subspace spanned by the bound states $|nlm\rangle$.
Put $\vec{A}'' = \sqrt{-2H}\,\vec{A}$; $\vec{f} = \frac{1}{2}(\vec{l} + \vec{A})$; $\vec{g} = \frac{1}{2}(\vec{l} - \vec{A})$
Show that $\vec{f}$ and $\vec{g}$ are two independant angular momenta.

d) By considering the relation $\vec{l}.\vec{A} = \vec{A}.\vec{l} = 0$ show that only certain values of f g can appear. Describe the $|n(n)\rangle$ in terms of f, g..

(32)

VI Tensor operators. The Wigner–Eckart theorem

Definition : A tensor operator of rank K (K non negative integer), with respect to an angular momentum $\vec{J}$ is a set of $(2K+1)$ operators noted $T^{(K)}_q$

with $q = -K, -K+1, \ldots 0, 1 \ldots K+1$

satisfying the following commutation relations :

$$\left[J_z, T^{(K)}_q\right] = q\,T^{(K)}_q \qquad (33)$$

$$\left[J_\pm, T^{(K)}_q\right] = \sqrt{K(K+1) - q(q\pm1)}\; T^{(K)}_{q\pm1}$$

Note that these relations are very similar to the equations :

$$J_z|K\,q\rangle = q|K\,q\rangle$$

$$J_\pm|K\,q\rangle = \sqrt{K(K+1) - q(q\pm1)}\;|K\,q\rangle$$

We just have to make the replacement :

$|K\,q\rangle \rightarrow$ operator $T^{(K)}_q$

Acting with $\vec{J}_i \rightarrow$ acting with $\mathrm{ad}\,\vec{J}_i$

$(\mathrm{ad}\,A\;X = [J, X])$

Examples of tensor operators

a) A scalar s is a tensor of rank 0

b) Let $\vec{T}$ be vector operator.

Putting $T^{(1)}_{\pm 1} = \mp \frac{1}{\sqrt{2}} (T_x \pm i T_y)$

$$T^{(1)}_0 = T_z$$

relations (33) are verified.

So tensors of rank 1 are equivalent to vectors.

c) Let us consider the space of wavefunction of one electron (of the form $\psi(\vec{r})$) and take for $\vec{J}$ the orbital angular momentum $\vec{l}$. Consider the following operators:

$$C^{(k)}_q = \sqrt{\frac{4\pi}{2k+1}}\, Y_{kq}(\theta,\varphi) \qquad (34)$$

That is $C^{(k)}_q$ acts on $\psi(\vec{r})$ $\vec{r}=(r,\theta,\varphi)$ by multiplication.

The operators l_i are derivatives (for example $l_z = -i\frac{\partial}{\partial\varphi}$).

So we have :

$$l_i(Y_{kq}\cdot\psi) = Y_{kq}\, l_i(\psi) + \psi\, l_i(Y_{kq})$$

and in terms of the operators $C^{(k)}_q$:

$$[l_i, C^{(k)}_q]\,\psi = \psi \sqrt{\frac{4\pi}{2k+1}}\, l_i(Y_{kq})$$

Since $l_z(Y_{kq}) = q\, Y_{kq}$

and $l_\pm(Y_{kq}) = \sqrt{k(k+1)-q(q\pm1)}\; Y_{k\,q\pm1}$

we obtain that the $C^{(k)}_q$ form a tensor of rank k with respect to $\vec{l}$.

In the case $k=1$ we find

$$C^{(1)}_{\pm1} = \mp\frac{1}{\sqrt{2}}\frac{(x\pm iy)}{r}$$

$$C^{(1)}_0 = \frac{z}{r}$$

In the case $k=2$:

$$C^{(2)}_{\pm2} = \sqrt{\frac{3}{8}}\,\frac{(x\pm iy)^2}{r^2}$$

$$C^{(2)}_{\pm1} = \mp\sqrt{\frac{3}{2}}\,\frac{z(x\pm iy)}{r}$$

$$C^{(2)}_0 = \frac{3z^2-r^2}{2r^2}$$

These operators occur very often. For example the Coulomb interaction between two electrons at $\vec{r}_1$ and $\vec{r}_2$ can be put in the form:

$$\frac{e^2}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \sum_{q=-k}^{k} (-1)^q\, C^{(k)}_{-q}(1)\cdot C^{(k)}_q(2)$$

The importance of tensor operators stems from the Wigner-Eckart theorem, which simplifies the calculation of the matrix elements of tensor operators.

We want to calculate matrix elements like

$$(\theta\, J\, M \,|\, T^{(k)}_q \,|\, \theta'\, J'\, M') \qquad (35)$$

The idea of the calculation is that $T^{(k)}_q|\theta' J' M'\rangle$ is like a state $|\gamma k\, q\, J' M'\rangle$ from which follows that the dependence of matrix element (35) on $M\, q\, M'$ is given by a CG coefficient.

We first use $[J_z, T^{(k)}_q] = q\, T^{(k)}_q$

$$\langle \theta J M | J_z T^{(k)}_q - T^{(k)}_q J_z | \theta' J' M' \rangle = q \langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle$$

$$\Rightarrow (M - M' - q) \langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle = 0$$

So $\langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle = 0$ if $M \neq M' + q$

Then from: $[J_+, T^{(k)}_q] = \sqrt{k(k+1) - q(q+1)}\; T^{(k)}_{q+1}$ we get:

$$\sqrt{k(k+1) - q(q+1)}\; \langle \theta J M | T^{(k)}_{q+1} | \theta' J' M' \rangle$$

$$= \sqrt{J(J+1) - M(M-1)}\; \langle \theta J\, M-1 | T^{(k)}_q | \theta' J' M' \rangle$$

$$- \sqrt{J'(J'+1) - M'(M'+1)}\; \langle \theta J M | T^{(k)}_q | \theta' J' M'+1 \rangle \qquad (36)$$

We need a recurrence relation between CG coefficients:

Applying $J_- = J_{1-} + J_{2-}$ to:

$$|J_1 J_2 J M\rangle = \sum_{M_1 M_2} (J_1 M_1 J_2 M_2 | J M)\, |J_1 M_1 J_2 M_2\rangle$$

we get:

$$\sqrt{J(J+1) - M(M-1)}\; |J_1 J_2 J\, M-1\rangle = \sum_{M_1 M_2} \sqrt{J(J+1) - M(M-1)}\, (J_1 M_1 J_2 M_2 | J\, M-1) \underbrace{|J_1 M_1 J_2 M_2\rangle}_{+M_1}$$

$$= \sum_{M_1 M_2} (J_1 M_1 J_2 M_2 | J M) \Big[\sqrt{J_1(J_1+1) - M_1(M_1-1)}\; |J_1\, M_1 - 1\; J_2\, M_2\rangle$$

$$+ \sqrt{J_2(J_2+1) - M_2(M_2-1)}\; |J_1 M_1\, J_2\, M_2 - 1\rangle \Big]$$

$$= \sum_{M_1 M_2} \Big\{ (J_1\, M_1+1\; J_2\, M_2 | J M) \sqrt{J_1(J_1+1) - M_1(M_1+1)}$$

$$+ (J_1 M_1\, J_2\, M_2+1 | J M) \sqrt{J_2(J_2+1) - M_2(M_2+1)} \Big\}\, |J_1 M_1 J_2 M_2\rangle$$

So: $\sqrt{J_1(J_1+1) - M_1(M_1+1)}\; (J_1\, M_1+1\; J_2\, M_2 | J M)$

$$= \sqrt{J(J+1) - M(M-1)}\; (J_1 M_1\, J_2\, M_2 | J\, M-1)$$

$$- \sqrt{J_2(J_2+1) - M_2(M_2+1)}\; (J_1 M_1\, J_2\, M_2+1 | J M) \qquad (37)$$

We see that eq (36) and (37) are equivalent if we make the substitutions:

$$\begin{array}{ccc} k & \longleftrightarrow & J_1 \\ q & \longleftrightarrow & M_1 \\ J' & \longleftrightarrow & J_2 \\ M' & \longleftrightarrow & M_2 \end{array}$$

$$\langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle \longleftrightarrow (J_1 M_1 J_2 M_2 | J M)$$

But we have seen that relation (37) permits to calculate the CG coefficients. In the same way eq (36) permits to calculate the matrix elements of T^k_q for various $M\, q\, M'$ from one of them. Of course the result is the same as for eq (37):

$$\langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle = A\, (k\, q\, J' M' | J M)$$

where A is independant of $q M' M$.

This result is often written as: (Wigner-Eckart theorem)

$$\langle \theta J M | T^{(k)}_q | \theta' J' M' \rangle$$

$$= (-)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \theta J \| T^{(k)} \| \theta' J' \rangle \qquad (38)$$

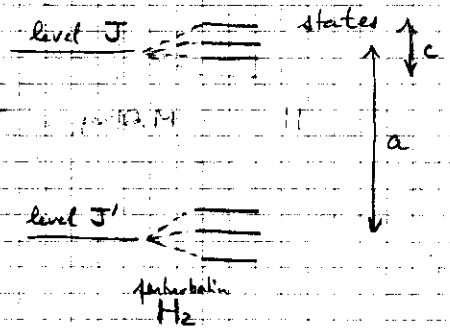
the last coefficient is called a reduced matrix element.

Example ① g- factor

When an atom is in a magnetic field $\vec{B}$ sufficiently weak, we must add a perturbation

$$H_2 = \frac{e\hbar}{2mc}\vec{B}.(\vec{L}+2\vec{S})$$

This perturbation lifts the degeneracy of the states of a given level $|\theta J M\rangle$



we suppose $c \ll a$

The energies are found by diagonalising the matrix $\langle \theta J M'|H_2|\theta J M\rangle$ [θ, J fixed]

So we need to calculate

$$\langle \theta J M'|L_q+2S_q|\theta J M\rangle = (-)^{J-M'}\begin{pmatrix} J & 1 & J \\ -M' & q & M\end{pmatrix}(\theta J\|L+2S\|\theta J) \quad (39)$$

since $\vec{L}$ and $\vec{S}$ are tensors of rank 1.

$\vec{J}$ is equally a tensor of rank 1. So:

$$\langle \theta J M'|J_q|\theta J M\rangle = (-)^{J-M'}\begin{pmatrix} J & 1 & J \\ -M' & q & M\end{pmatrix}(\theta J\|J\|\theta J) \quad (40)$$

In these equations $J_{\pm 1} = \mp\frac{1}{\sqrt{2}}J_\pm$ and $J_0 = J_z$

The reduced matrix element $(\theta J\|J\|\theta J) \neq 0$. In fact it can be shown that $(\theta J\|J\|\theta J) = \sqrt{J(J+1)(2J+1)}$

Dividing (39) by (40):

$$\langle \theta J M'|L_q+2S_q|\theta J M\rangle = g\langle \theta J M'|J_q|\theta J M\rangle$$

with $g = \dfrac{(\theta J\|L+2S\|\theta J)}{(\theta J\|J\|\theta J)}$

So to calculate the matrix elements of H_2 within one level we can replace H_2 by:

$$g\frac{e\hbar}{2mc}\vec{B}.\vec{J}$$

g is called the Landé factor.

② Selection rules

eq (38) tells us that the matrix element $\langle \theta J M|T^{(k)}_q|\theta' J' M'\rangle$ is zero if $M \neq q+M'$ or J K J' are not triangular.

Exercices

(11) Show that if $V^{(k)}$ and $W^{(k')}$ are tensor operators then $\left(V^{(k)} W^{(k')}\right)^{(\kappa)}_{q} = \sum_{mm'} (k\, m\, k' m' | \kappa\, q)\, V^{(k)}_{m} W^{(k')}_{m'}$

and $T^{(k)}_{q} = V^{(k)\dagger}_{-q} (-)^{k-q}$

are also tensor operators.

If $k = k'$ Show that $V^{(k)} \cdot W^{(k)} = \sum_{q} (-)^{q} V^{(k)}_{q} W^{(k)}_{-q}$

is a scalar.

(12) a) Consider a system whose quantum states are restricted to $(2j+1)$ states of the form $|j\, m\rangle$ (Example : particle at rest of spin j).

Show that the operators :

$$T^{(L)}_{M} = \sum_{mm'} |j\, m\rangle\, (j\, m\, |\, j\, m'\, L\, M)\, \langle j\, m'|$$

are tensor operators.

Calculate $\mathrm{Tr}\left(T^{(L)}_{M}\, T^{(L')\dagger}_{M'}\right)$ and show that the set of the operators $T^{(L)}_{M}$ with $L = 0, 1, \ldots 2j$ and $-L \leq M \leq L$ form a basis of the space of the operators.

Suppose the system is in a state described by the density matrix : $\rho = \sum_{mm'} |j\, m\rangle\, \rho_{mm'}\, \langle j\, m'|$

Express ρ in terms of the $T^{(L)}_{M}$ and $t_{LM} = \mathrm{Tr}\left(\rho\, T^{L}_{M}\right)$

Calculate t_{LM} in terms of $\rho_{mm'}$.

Calculate $\mathrm{Tr}(\rho^2)$ in terms of the t_{LM}

b) Consider the example of a particle of spin $j = 3/2$ which is described by a density matrix of the form : $\rho = \dfrac{a\,|\alpha\rangle\langle\alpha| + b\,|\beta\rangle\langle\beta|}{a+b}$ with $\langle\alpha|\beta\rangle = 0$, $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, $0 < a, b < 1$

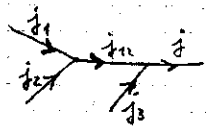
(melange of 2 pure states). Show that in this case $\mathrm{Tr}(\rho^2) \geq \frac{1}{2}$ and deduce that $t_{LM} \neq 0$ for at least one $L > 0$.

c) Consider the case of a particle of spin 1. Find conditions on t_{10} and t_{20} resulting from $0 \leq \rho_{mm} \leq 1$.

VII Recoupling of angular momenta. The 6j coefficient

The coupling of 3 angular momenta j_1 j_2 j_3 can be done by first coupling j_1 and j_2 to obtain j_{12} and then coupling j_{12} and j_3 to obtain j.

We can represent these couplings by:



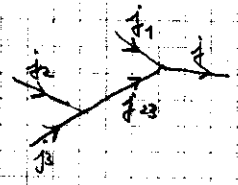
(G1)

The states so obtained are :

$$|(j_1 j_2) j_{12}\ j_3\ j m\rangle = \sum_{m_{12} m_3} |(j_1 j_2)\ j_{12}\ m_{12}\ j_3\ m_3\rangle (j_{12}\ m_{12}\ j_3 m_3 | j m)$$

$$= \sum_{m_1 m_2 m_3} |j_1 m_1\ j_2 m_2\ j_3 m_3\rangle \sum_{m_{12}} (j_1 m_1\ j_2 m_2 | j_{12} m_{12})(j_{12}\ m_{12}\ j_3 m_3 | j m) \qquad (41)$$

In this expression the coefficient $\sum_{m_{12}} (\quad | \ m_{12})(m_{12} \quad | \ )$ is called a coupling coefficient : it is the generalisation of CG coefficients. Note that it depends on an intermediate momentum j_{12}. In general, coupling N+2 angular momenta necessitates N intermediate momenta. Note that these momenta can be choosen in several ways. In the case of the coupling of 3 momenta, we can begin with coupling j_2 and j_3 to form j_{23}, and then j_1 and j_{23}, as represented in the graph:



(G2)

The states are noted :

$$|j_1 (j_2 j_3) j_{23}\ j m\rangle = \sum_{m_1 m_{23}} |j_1 m_1 (j_2 j_3) j_{23}\ m_{23}\rangle (j_1 m_1\ j_{23} m_{23} | j m)$$

$$\sum_{m_1 m_2 m_3} |j_1 m_1\ j_2 m_2\ j_3 m_3\rangle \sum_{m_{23}} (j_2 m_2\ j_3 m_3 | j_{23} m_{23})(j_1 m_1\ j_{23} m_{23} | j m) \qquad (42)$$

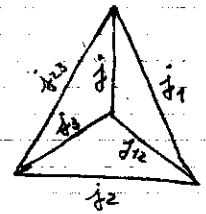
Each of these states is a linear combination of the $|(j_1 j_2) j_{12}\ j_3\ j m\rangle$ (with the same $j m$) :

$$|j_1 (j_2 j_3) j_{23}\ j m\rangle = \sum_{j_{12}} C(j_1 j_2 j_3\ j_{23} j_{12}\ j m)\ |(j_1 j_2) j_{12}\ j_3\ j m\rangle$$

Applying $J_\pm$ to this equality we see that the coefficients $C(j_1 j_2 j_3\ j_{23} j_{12}\ j m)$ do not depend on m. So we write : $C(j_1 j_2 j_3\ j_{23} j_{12}\ j m) = \sqrt{(2j_{12}+1)(2j_{23}+1)}\ (-)^{j_1+j_2+j_3+j} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}$

which defines the 6j symbol. It is a recoupling coefficient.

This recoupling can be represented by the graph :



(G3)

This graph is obtained by joining the corresponding free branches of (G1) and (G2). It gives the triangular conditions in the 6j coefficients : Each vertex of the graph gives a condition. In the symbol they appear as :

The 6j have symmetry properties :

1) Two columns can be exchanged without changing the value of the symbol (no phase factor appears)

$$\left\{ \leftrightarrow \quad \cdot \right\}$$
$$\left\{ \leftrightarrow \quad \cdot \right\}$$

2) The value of the 6j is not changed by exchanging the momenta in two columns :

$$\left\{ \updownarrow \updownarrow \quad \cdot \right\}$$

These symmetries are those of figure G3 if it is viewed as a regular tetrahedron

Exercices 13) Express the 6j coefficient in terms of 3j coefficient

14) Atomic helium : approximate symmetry.

The hamiltonian, eq(40), is written as :

$$H = h_1 + h_2 + H_1$$

where $h_i = \frac{p_i^2}{2m} - \frac{Z'e^2}{r_i}$ is an hydrogenic hamiltonian ($i = 1,2$)

Configurations $2s^2$ and $2p^2$ ($n=2$ complex) which have almost equal energies are strongly mixed by H_1. A numerical calculation (done for $Z' = 1.6875$) gives the ^1S eigenstates of H :

$$|\psi_1\ {}^1S\rangle = 0.829\ |2s^2\ {}^1S\rangle + 0.481\ |2p^2\ {}^1S\rangle + \dots$$
$$|\psi_2\ {}^1S\rangle = -0.399\ |2s^2\ {}^1S\rangle + 0.664\ |2p^2\ {}^1S\rangle + \dots \qquad (43)$$

The aim of this exercice is to show that eq (43) can be interpreted by replacing H_1 by a diagonalisable approximation.

We restrict the operators to the $n=2$ complex and use for electrons 1 and 2 the parabolic states of exercice 10 : $|f_{m_1} f_{m_1'}\rangle$ and $|f_{m_2} f_{m_2'}\rangle$ with $f = \frac{n-1}{2} = \frac{1}{2}$. We shall consider only ^1S states : for these states the wavefunction factors in an antisymmetric spin part $\chi(1,2) = \chi_{1/2}(1)\,\chi_{-1/2}(2) - \chi_{1/2}(2)\,\chi_{-1/2}(1)$ and a symmetric orbital part.

Put $|FGLM\rangle = \sum_{\substack{m_1 m_1' m_2 m_2' \\ m_3 m_3'}} |\underbrace{f_{m_1} f_{m_1'}}_{\text{electron 1}}\ \underbrace{f_{m_2} f_{m_2'}}_{\text{electron 2}}\rangle$

$$\times (f_{m_1} f_{m_2} | F m_3)\,(f_{m_1'} f_{m_2'} | G m_3')\,(F m_3\ G m_3' | LM)$$

and $|\varphi_0\rangle = \chi(1,2)\ |F=0, G=0, L=0, M=0\rangle$

$|\varphi_1\rangle = \chi(1,2)\ |F=1, G=1, L=0, M=0\rangle$

a) Express $|\varphi_0\rangle$ and $|\varphi_1\rangle$ in terms of $|2s^2\,{}^1S\rangle$ and $|2p^2\,{}^1S\rangle$

b) We replace H_1 by $H_{1\,appr} = \alpha(\vec{A}_1 - \vec{A}_2)^2$ where $\vec{A}_i = \vec{r}_i - \vec{q}_i$ are the modified Lenz vectors of electron i. Designate by π_2 the inversion: $\vec{r}_2 \to -\vec{r}_2$.

Show that the states $\pi_2 |FGLM\rangle$ are eigenstates of $h_1 + h_2 + H_{1\,appr}$, L^2, and L_z. Compare $\pi_2|\varphi_0\rangle$ and $\pi_2|\varphi_1\rangle$ with eq (43).

Answers of some exercises

① It is convenient to use the following relations:

$$e_{ijk}\, e_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}$$

$$e_{ijk}\, e_{ijl} = 2\delta_{kl}$$

If $\vec{V}$ and $\vec{V}'$ are vector operators then:

a) $[l_i, \vec{V}\cdot\vec{V}'] = [l_i, V_j V'_j] = [l_i, V_j]\, V'_j + V_j [l_i, V'_j]$

we have used the relation $[ab, c] = a[b,c] + [a,c]b$

$$[l_i, \vec{V}\cdot\vec{V}'] = i e_{ijk} V_k V'_j + i e_{ijk} V_j V'_k$$
$$= i(\underbrace{e_{ijk} + e_{ikj}}_{0}) V_k V'_j = 0$$

So $\vec{V}\cdot\vec{V}'$ is a scalar.

b) $[l_i, (\vec{V}\wedge\vec{V}')_j] = [l_i, e_{jkl} V_k V'_l]$

$$= e_{jkl}\left(V_k [l_i, V'_l] + [l_i, V_k] V'_l\right)$$
$$= e_{jkl}\, i e_{ilm} V_k V'_m + e_{jkl}\, i e_{ikm} V_m V'_l$$
$$= i(\delta_{jm}\delta_{kl} - \delta_{ji}\delta_{mk}) V_k V'_m + i(\delta_{ji}\delta_{lm} - \delta_{jm}\delta_{li}) V_m V'_l$$
$$= i\, V_i V'_j - i\delta_{ji}\, \vec{V}\cdot\vec{V}' + i\,\delta_{ji}\,\vec{V}\cdot\vec{V}' - i\, V_j V'_i$$
$$= i(V_i V'_j - V_j V'_i) = i e_{ijk} (\vec{V}\wedge\vec{V}')_k$$

So $\vec{V}\wedge\vec{V}'$ is a vector operator.

c) If s_1 and s_2 commute with $\vec{l}$, so do $s_1^\alpha s_2^\beta$. Supposing $f(s_1, s_2)$ can be expressed as a series $f(s_1, s_2) = \sum c_{\alpha\beta} s_1^\alpha s_2^\beta$ it is clear that $f(s_1, s_2)$ commutes with $\vec{l}$.

(47)

② a) From $[r_i, f(r)] = 0$

and $[p_i, f(r)] = -i\hbar \left[\frac{\partial}{\partial r_i}, f(r)\right]$

$= -i\hbar \frac{\partial f(r)}{\partial r_i} = -i\hbar \frac{r_i}{r} \frac{df}{dr}$

We get $[l_i, f(r)] = \frac{1}{\hbar} e_{ijk} [r_j p_k, f(r)]$

$= \frac{1}{\hbar} e_{ijk} r_j [p_k, f(r)] = -i e_{ijk} r_j \frac{r_k}{r} \frac{df}{dr} = 0$

b) $[l_i, r_j] = \frac{1}{\hbar} e_{ikl} [r_k p_l, r_j]$

$= \frac{1}{\hbar} e_{ikl} r_k [p_l, r_j] = \frac{1}{\hbar} e_{ikl} r_k (-i\hbar \delta_{lj})$

$= -i e_{ikj} r_k = i e_{ijk} r_k$

c) $[l_i, p_j] = \frac{1}{\hbar} e_{ikl} [r_k p_l, p_j] = \frac{1}{\hbar} e_{ikl} [r_k, p_j] p_l$

$= \frac{1}{\hbar} e_{ikl} i\delta_{kj} p_l = i e_{ijl} p_l$

d) We have just shown that $\vec{r}$ and $\vec{p}$ are vector operators so $\vec{l} = \frac{1}{\hbar} \vec{r} \wedge \vec{p}$ is a vector operator (from exercice 1)

③ See Landau & Lifschitz Quantum Mechanics §27

④ An easy calculation shows $J_i^+ = J_i$ $(i = x, y, z)$, and:

$[J_z, J_\pm] = \pm J_\pm$

$[J_+, J_-] = 2 J_z$

(48)

which is equivalent to relations (7)

Putting $n_x = a_x^+ a_x$ $n_y = a_y^+ a_y$

we find:

$\vec{J}^2 = J_+ J_- + J_z^2 - J_z = \left(\frac{n_x + n_y}{2} + 1\right) \frac{n_x + n_y}{2} = \frac{1}{4}(H+1)(H-1) = \frac{1}{4}(H^2 - 1)$

and $J_z = \frac{n_x - n_y}{2}$. Note that $[H, \vec{J}] = 0$

So $|s\,t\rangle$ is an eigenstate of J^2 and J_z

with eigenvalues $j(j+1) = \left(\frac{s+t}{2} + 1\right) \frac{s+t}{2}$ (ie $j = \frac{s+t}{2}$)

and $m = \frac{s-t}{2}$

Remark: Here the wave functions $\psi_{st}(x, y)$ are genuine functions, not spinors, even for j half integer.

An irreducible basis of $\vec{J}$ is formed of the $|s\,t\rangle$ state with a given value of $s+t$, ie of energy.

(5) a) An easy calculation shows:

$$[T_z, T_\pm] = \pm T_\pm \qquad [T_+, T_-] = 2T_z$$

(49)

Note that $H = \omega T_z$ does not commute with $\vec{T}$

$$\vec{T}^2 = T_+T_- + T_z^2 - T_z = -\frac{3}{16}$$

So the eigenstates $|n\rangle$ of H are eigenstates of T^2 and T_z and are not of the form $|jm\rangle$. This is because $\vec{T}$ is not hermitian:

$$T_x^+ = \frac{1}{2}(T_+ + T_-)^+ = -T_x$$
$$T_y^+ = -T_y$$
$$T_z^+ = T_z$$

and $\vec{T}^2$ has a negative eigenvalue.

b) From $a(a^+a) = (a^+a+1)a$ we have for an arbitrary function of $H = a^+a + 1/2$:

$$af(H) = f(H+1)a$$
$$a^+f(H) = f(H-1)a^+$$

So $[J_+, J_z] = \sqrt{l+1-a^+a}\left(a^+a - \frac{l}{2} - 1\right)a^+ - \sqrt{l+1-a^+a}\left(a^+a - \frac{l}{2}\right)a^+ = -J_+$

$[J_-, J_z] = J_-$

$[J_+, J_-] = \sqrt{l+1-a^+a}\sqrt{l+1-a^+a}\,a^+a - \sqrt{l-a^+a}\sqrt{l-a^+a}\,aa^+$

$= (l+1-a^+a)a^+a - (l-a^+a)(a^+a+1) = 2J_z$

$\vec{J}^2 = \frac{l}{2}\left(\frac{l}{2}+1\right)$. If l is integer states $|n\rangle$ and $|n'\rangle$ are not connected by $\vec{J}$ if $n \le l$ and $n' \ge l$.

Over $|0\rangle$ --- $|l\rangle$ $\vec{J}$ is hermitian. These states are $|j,m\rangle$ states with $j = l/2$

Over $|l+1\rangle, |l+2\rangle$ --- J_x and J_y are antihermitian: an infinite number of states corresponding to the same eigenspace of $\vec{J}^2$ are connected by the operators $J_\pm$

(6) We need the following formula, where W_i is an operator acting on electron i:

$$\left(\sum_{i=1}^N W_i\right)\{k_1, k_2 \cdots k_N\} = \{Wk_1, k_2 \cdots k_N\} + \{k_1, Wk_2 \cdots k_N\} + \cdots$$

(50)

$$+ \{k_1, k_2 \cdots Wk_N\}.$$

To show this formula we develop the determinant [P permutations of electrons; $(-)^P$ parity of permutation]

$$\left(\sum_{i=1}^N W_i\right)\sum_P \frac{(-)^P}{\sqrt{N!}}\psi_{k_1}(P(1))\,\psi_{k_2}(P(2)) \cdots \psi_{k_N}(P(N))$$

$$= \sum_P \frac{(-)^P}{\sqrt{N!}}\left(\sum_{i=1}^N W_{P(i)}\right)\psi_{k_1}(P(1))\,\psi_{k_2}(P(2)) \cdots \psi_{k_N}(P(N))$$

$$= \sum_P \frac{(-)^P}{\sqrt{N!}}(W\psi_{k_1})(P(1))\,\psi_{k_2}(P(2)) \cdots \psi_{k_N}(P(N))$$

$$+ \sum_P \frac{(-)^P}{\sqrt{N!}}\psi_{k_1}(P(1))\,(W\psi_{k_2})(P(2)) \cdots \psi_{k_N}(P(N))$$

$$+ \cdots = \{W\psi_{k_1}, \psi_{k_2} \cdots \psi_{k_N}\} + \{\psi_{k_1}, W\psi_{k_2}, \ldots\} + \cdots$$

From: $|^3P\ 1,1\rangle = \{1^+\ 0^+\}$ we get acting with $L_- = l_{1-} + l_{2-}$:

$$\sqrt{1.2-1.0}\,|^3P\ 1,0\rangle = \sqrt{1.2-1.0}\,\{0^+\ 0^+\} + \sqrt{1.2-0.(-1)}\,\{1^-\ -1^+\}$$

So $|^3P\ 1,0\rangle = \{1^-, -1^+\}$ (the problem was to find the phase)

Acting on $|^3P\ 1,1\rangle$ with $S_- = s_{1-} + s_{2-}$ we obtain:

$$\sqrt{2}\,|^3P\ 0,1\rangle = \{1^-\ 0^+\} + \{1^+\ 0^-\} \quad \text{so} \quad |^3P\ 0\ 1\rangle = \frac{1}{\sqrt{2}}\left(\{1^-\ 0^+\} + \{1^+\ 0^-\}\right)$$

From: $S_-|^3P\ 1,0\rangle = \sqrt{2}\,|^3P\ 0,0\rangle = \{1^-, -1^+\} + \{1^+, -1^-\}$

we get $|^3P\ 0,0\rangle = \frac{1}{\sqrt{2}}\left(\{1^-, -1^+\} + \{1^+, -1^-\}\right)$

(7) Two methods: a) Find a linear combination of determinants $\{^{+}_{1}\ ^{-}_{1}\}$, $\{^{+}_{0}\ ^{-}_{0}\}$ and $\{^{+}_{-1}\ ^{-}_{1}\}$ which is orthogonal to $|^3P,0,0\rangle$ (calculated in exercice 6) and $|^1D,0,0\rangle$ (which can be calculated in the same way)

b) Put:

$$|^1S,0,0\rangle = a\{^{+}_{1}\ ^{-}_{1}\} + b\{^{+}_{0}\ ^{-}_{0}\} + c\{^{+}_{-1}\ ^{-}_{1}\}$$

and determine a, b, c from $S_+|^1S\ 0\ 0\rangle = L_+|^1S,0,0\rangle = 0$ and the normalisation condition

(10) Ref Hughes Proc Phys Soc (1967) 91, 810
Wulfman in Group theory and its appl ed EM Loebl vol 2 (1971)

c) $\vec{f}$ and $\vec{g}$ verify the relations:

$$[f_i, g_j] = 0$$

$$[f_i, f_j] = i\varepsilon_{ijk} f_k$$

$$[g_i, g_j] = i\varepsilon_{ijk} g_k$$

$$f_i^+ = f_i \qquad g_i^+ = g_i$$ (on the subspace of bound states)

d) H is a scalar with respect to $\vec{f}$ and $\vec{g}$, so there is a basis of bound eigenstates of H of the form:

$|\alpha\ f\ m_1\ g\ m_2\rangle$ (eigenvectors of $\vec{f}^2$, f_z, $\vec{g}^2$, g_z

Relation $\vec{l}\cdot\vec{A} = \vec{A}\cdot\vec{l}$ implies $\vec{f}^2 = \vec{g}^2$. So only states with $f = g$ appear.

Relation $(\vec{A}'')^2 = 1 + 2H(\vec{l}^2 + \mathbb{1})$ implies that the energy of state $|\alpha\ f\ m_1\ g=f\ m_2\rangle$ is $\frac{-1}{2(2f+1)^2}$

Comparing the number of states with a given energy $\frac{-1}{2n^2}$ we obtain that $f=g$ takes the values $0, \frac{1}{2}, 1, \frac{3}{2}$ ... and that these values appear only once (ie label α is not needed). Remarking that $\vec{l} = \vec{f} + \vec{g}$ The $|nlm\rangle$ states are obtained from the $|f\ m_1\ f\ m_2\rangle$ states by coupling:

$$|^n l\, m\rangle = \sum_{m_1 m_2} (f\ m_1\ f\ m_2 | l\, m)\ |f\ m_1\ f\ m_2\rangle$$

with $f = g = \frac{n-1}{2}$

The $|f\ m_1\ f\ m_2\rangle$ states are the parabolic states.

(12) a) To show that $T^{(L)}_M$ are tensor operators compare the matrix elements $\langle jm | T^{(L)}_M | j m' \rangle$ with the Wigner-Eckart theorem.

$$\mathrm{Tr}\left[T^{(L)}_M \left(T^{(L')}_{M'}\right)^+ \right] = \sum_{mm'} (jm \,|\, j m' \, LM)(jm \,|\, j m' \, L'M')$$

Use (3j) and the orthogonality conditions to find:

$$\mathrm{Tr}\left[T^{(L)}_M \left(T^{(L')}_{M'}\right)^+ \right] = \delta_{LL'} \delta_{MM'} \frac{2j+1}{2L+1}$$

The operators form a space of dimension $(2j+1)^2$. For two operators A, B of matrixes $A_{mm'}$ and $B_{mm'}$ We can define an hermitian product by $(A,B) = \sum_{mm'} A^*_{mm'} B_{mm'} = \mathrm{Tr}\, B A^+$

So the $T^{(L)}_M$ are orthogonal for this hermitian product. Since they are $(2j+1)^2$ in number, the $T^{(L)}_M$ form a basis of the operator space. In particular the density matrix can be decomposed as:

$$\rho = \sum_{LM} \alpha_{LM} T^{(L)}_M$$

Then $\mathrm{Tr}\left(T^{(L)}_M \rho\right) = t_{LM} = \alpha^*_{LM} \frac{2j+1}{2L+1}$ $\quad (\rho^+ = \rho)$

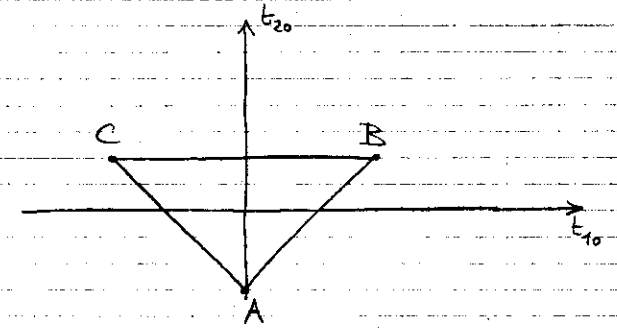
So $\rho = \sum_{LM} \frac{2L+1}{2j+1} t^*_{LM} T^{(L)}_M$ $\quad$ (A)

$$t^*_{LM} = \sum_{mm'} \rho_{mm'} (jm \,|\, j m' \, LM)$$

$$\rho_{mm'} = \sum_{LM} \frac{2L+1}{2j+1} (jm \,|\, j m' \, LM)\, t^*_{LM} \quad (\text{Put } T^{(L)}_M = \text{definition in (A)})$$

$$\mathrm{Tr}(\rho^2) = \mathrm{Tr}\,\rho\rho^+ = \sum_{LML'M'} \frac{(2L+1)(2L'+1)}{(2j+1)^2} t^*_{LM} t_{LM'} \mathrm{Tr}\left(T^L_M \left(T^{L'}_{M'}\right)^+\right) = \sum_{LM} \frac{(2L+1)}{2j+1} |t_{LM}|^2$$

c)



(t_{10}, t_{20}) must be inside the triangle ABC

with $A \begin{cases} t_{10} = 0 \\ t_{20} = -\sqrt{\frac{2}{5}} \end{cases}$ $\quad B \begin{cases} t_{10} = \frac{1}{\sqrt{2}} \\ t_{20} = \frac{1}{\sqrt{10}} \end{cases}$ $\quad C = \begin{cases} t_{10} = -\frac{1}{\sqrt{2}} \\ t_{20} = \frac{1}{\sqrt{10}} \end{cases}$

This is seen using ($t_{00} = 1$ from $\mathrm{Tr}\,\rho = 1$):

$$\rho_{11} = \frac{1}{3}\left(1 + \frac{3}{\sqrt{2}} t_{10} + \frac{5}{\sqrt{10}} t_{20}\right)$$

$$\rho_{00} = \frac{1}{3}\left(1 - 5\sqrt{\frac{2}{5}}\, t_{20}\right)$$

$$\rho_{-1-1} = \frac{1}{3}\left(1 - \frac{3}{\sqrt{2}} t_{10} + \frac{5}{\sqrt{10}} t_{20}\right)$$

(13) We have :

$$C = \langle -- j_{12}\ j_m | -- j_{23}\ j_m \rangle = \frac{1}{[j]} \sum_m \langle -- j_{12}\ j_m | -- j_{23}\ j_m \rangle$$

with $[j] = 2j+1$

Using (41) and (42) :

$$C = \sqrt{[j_{12}][j_{23}]} \sum_{\substack{m_1 m_2 m_3 \\ m_{12} m_{23} m}} (-)^{j_1 - j_2 + m_{12} + j_{12} - j_3 + m_1 + j_2 - j_3 + m_{23} + j - j_{23} + m}$$

$$\begin{pmatrix} j_1 & j_2 & j_{12} \\ m_1 & m_2 & -m_{12} \end{pmatrix} \begin{pmatrix} j_{12} & j_3 & j \\ m_{12} & m_3 & -m \end{pmatrix} \begin{pmatrix} j_2 & j_3 & j_{23} \\ m_2 & m_3 & -m_{23} \end{pmatrix} \begin{pmatrix} j_1 & j_{23} & j \\ m_1 & m_{23} & -m \end{pmatrix}$$

So

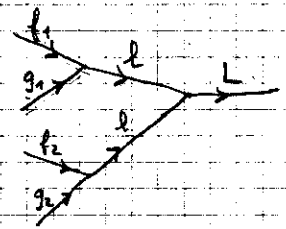
$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} = \sum_{\text{all } m} (-)^{j_3 + j + j_{23} + m_3 + m_{23} + m}$$

$$\times \begin{pmatrix} j_1 & j_2 & j_{12} \\ m_1 & m_2 & m_{12} \end{pmatrix} \begin{pmatrix} j_{12} & j_3 & j \\ m_{12} & m_3 & -m \end{pmatrix} \begin{pmatrix} j_3 & j_2 & j_{23} \\ -m_3 & m_2 & m_{23} \end{pmatrix} \begin{pmatrix} j_1 & j & j_{23} \\ m_1 & m & -m_{23} \end{pmatrix}$$

(14) Ref Wulfman (see Exercise 10)

Sinanoğlu & Herrick J Chem Phys 62, 886 (1975)

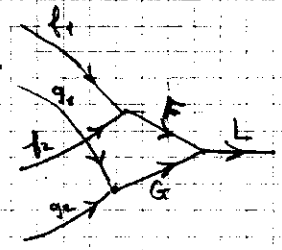
a) The $|(nl)^2\ SeL\rangle$ (orbital part of the) states are obtained by the coupling (1^{st} + 2^{nd} part)



They are eigenstates of $\vec{l}_1^{\,2}, \vec{l}_2^{\,2}, \vec{L}^2, L_z$

with $\vec{l}_1 = \vec{f}_1 + \vec{g}_1$; $\vec{l}_2 = \vec{f}_2 + \vec{g}_2$

The $|FGLM\rangle$ states are obtained by the coupling :



They are eigenstates of $\vec{F}^2, \vec{G}^2, \vec{L}^2, L_z$

with $\vec{F} = \vec{f}_1 + \vec{f}_2$, $\vec{G} = \vec{g}_1 + \vec{g}_2$; $\vec{L} = \vec{F} + \vec{G} = \vec{l}_1 + \vec{l}_2$

By performing a recoupling between these states, we find $|\varphi_0\rangle$ and $|\varphi_1\rangle$ in terms of $|2s^2\ {}^1S\rangle$ and $|2p^2\ {}^1S\rangle$.

The result is :

$$|\varphi_0\rangle = \frac{1}{2} |2s^2\ {}^1S\rangle + \frac{\sqrt{3}}{2} |2p^2\ {}^1S\rangle$$

$$|\varphi_1\rangle = \frac{\sqrt{3}}{2} |2s^2\ {}^1S\rangle - \frac{1}{2} |2p^2\ {}^1S\rangle$$

Note that these states are also eigenstates of :

$$(\vec{A}_1 + \vec{A}_2)^2 = (\vec{F} - \vec{G})^2 = 2\vec{F}^2 + 2\vec{G}^2 - (\vec{F} + \vec{G})^2 = 2\vec{F}^2 + 2\vec{G}^2 - \vec{L}^2$$

We dont take $H_{1\text{appr}}$ proportional to $(\vec{A}_1 + \vec{A}_2)^2$ but to $(\vec{A}_1 - \vec{A}_2)^2$ [In the paper of Sinanoğlu and Herrick it is explained why this $H_{1\text{appr}}$ produces a repulsion between the two electrons]

b) From the definition of $\vec{A}_2$: $\pi_2 \vec{A}_2 \pi_2 = -\vec{A}_2$

$\pi_2 \vec{l}_2 \pi_2 = \vec{l}_2$

So $\vec{L} \pi_2 = \pi_2 \vec{L}$

$H_{1appr} \pi_2 = \alpha \pi_2 (\vec{A}_1 + \vec{A}_2)^2$

and $H_{1appr} \pi_2 |FGLM\rangle = \alpha \left[2F(F+1) + 2G(G+1) - L(L+1) \right] \pi_2 |FGLM\rangle$

From $\pi_2 |2s\rangle_2 = |2s\rangle_2$ and $\pi_2 |2p\rangle_2 = -|2p\rangle_2$ (the parity of nl is $(-)^l$)

We have :

$|\varphi'_0\rangle = \pi_2 |\varphi_0\rangle = \frac{1}{2} |2s^2\, {}^1S\rangle - \frac{\sqrt{3}}{2} |2p^2\, {}^1S\rangle$

$|\varphi'_1\rangle = \pi_2 |\varphi_1\rangle = \frac{\sqrt{3}}{2} |2s^2\, {}^1S\rangle + \frac{1}{2} |2p^2\, {}^1S\rangle$

In terms of these states, eq(43) reads :

$|\psi_1\, {}^1S\rangle = -0.002 |\varphi'_0\rangle + 0.958 |\varphi'_1\rangle + \dots$

$|\psi_2\, {}^1S\rangle = 0.757 |\varphi'_0\rangle - 0.024 |\varphi'_1\rangle + \dots$

So φ'_0 and φ'_1 are good approximations of ψ_2 and ψ_1 resp (more precisely of the components of ψ_2 and ψ_1 within the $n=2$ complex).