(continuation of notes from 2/5/08)   ①

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there would be 2 electrons in the same state. also, it

does not matter which electron is given spin up or down, so

$(m_{\ell_1}, m_{\ell_2}, m_{s_1}, m_{s_2}) = (1 \; 1 + \frac{1}{2} - \frac{1}{2})$ and $(1 \; 1 \; -\frac{1}{2} + \frac{1}{2})$ are the

same state. In rows 2,3,4,5 all with $m_{\ell_1} = 1$, $m_{\ell_2} = 0$, the

two m_ℓ values are distinct, so there is no restriction on the

m_s values, which run over all 4 combinations of $\pm \frac{1}{2}$. The

total number of states is 15, as expected.

The 15-dim'l space spanned by the states $|m\text{-sets}\rangle$

is invariant under orbital rotations generated by $\vec{L}$ and

spin rotations generated by $\vec{S}$, so it must be possible to

decompose it into invariant, irreducible subspaces characterized

by L, S. ~~For 2gy~~ Each L, S value occurs with some

multiplicity; if the multiplicity is >1, we need another index

(γ above) to resolve the degeneracies. In fact, for light atoms,

the largest multiplicity is 1, and γ is not needed; the first

atom for which$^{\text{a}}$ multiplicity >1 occurs is vanadium V.

Now get the allowed L, S values from the table above. First

look at the state with $M_L = 2$, $M_S = 0$. This must be the doubly

stretched state of a multiplet with $L = 2, S = 0$ (^1D). First,

since it is the only state with ~~2s~~ $M_L = 2$, $M_S = 0$, it is a

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nondegen. eigenstate of L_z, S_z.   But these commute with L^2, S^2, so it must be also an eigenstate of them, too. But with what eigenvalues?   It cannot be $L < 2$, because that would violate the rule $M_L \leq L$.   And it cannot be $L > 2$, e.g., $L=3$, because then we would see states with $M_L = 3$, and we do not. So it must be $L=2$. Similarly, we conclude $S=0$. So $|m\text{-set}\rangle$ #1 in the table is also the state

$$|L M_L S M_S\rangle = |2\ 2\ 0\ 0\rangle.$$

By applying lowering operators, $\overset{L-}{}$ we generate states with $L=2, M_L = 2,1,0,-1,-2$ (and $S, M_S = 0,0$).   Take the case

$$|L M_L S M_S\rangle = |2\ 1\ 0\ 0\rangle$$ which has $M_L = 1, M_S = 0$.   There are 2 m-sets in the table (rows 3,4) with $M_L = 1, M_S = 0$, spanning a 2D space, and the one with $|L M_L S M_S\rangle = |2\ 1\ 0\ 0\rangle$ is one vector in this space. ~~this vector orthogonal to it~~ ~~must be the stretched~~ Similarly, there are 3 m-sets with $M_L = 0, M_S = 0$ (rows 7,8,10) and $|L M_L S M_S\rangle = |2\ 0\ 0\ 0\rangle$ must be one vector in this 3D subspace.

Let's list the different M_L, M_S subspaces and their dimensions, with one check for each state generated by lowering the doubly stretched state ~~stretched~~ $|L M_L S M_S\rangle = |2\ 2\ 0\ 0\rangle$:   ($^1D$).

M_L	M_S	dim	^1D	^3P	^1S
2	0	1	✓		
1	1	1		✓	
1	0	2	✓	✓	
1	−1	1		✓	
0	1	1		✓	
0	0	3	✓	✓	✓
0	−1	1		✓	
−1	1	1		✓	
−1	0	2	✓	✓	
−1	−1	1		✓	
−2	0	$\underline{1}$	✓		
		15			

Now the state w. $M_L = 1$, $M_S = 1$ must also be an eigenstate of $L^2 S^2$ with $L=1$, $S=1$ (a ^3P state). It is a doubly stretched state that generates 9 states total when we apply L_- or S_-. Finally, the 3rd vector in the $M_L = 0$, $M_S = 0$ subspace must be an eigenvector of $L^2 S^2$ with $L=0$, $S=0$ (a ^1S state). Thus all 15 dim's are accounted for, and we get the same multiplets ^1D, ^3P, ^1S as before.

Notice that for determining which multiplets occur, we do not need to list any state with $M_L < 0$ or $M_S < 0$, since

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we are identifying multiplets by their doubly stretched members, that always have $M_L \geq 0$ and $M_S \geq 0$. This simplifies the table. For example, in the case of N (nitrogen, $1s^2 2s^2 2p^3$), the table is

	$m_{\ell 1}$	$m_{\ell 2}$	$m_{\ell 3}$	m_{s1}	m_{s2}	m_{s3}	M_L	M_S		L	S	
1	1	1	0	½	-½	½	2	½	✓	2	½	^2D
~~1~~	~~1~~	~~1~~	~~1~~	~~½~~	~~½~~	~~½~~						
2	1	1	-1	½	-½	½	●1	½	✓	1	½	^2P
3	1	0	0	½	½	-½	1	½	✓			
4	1	0	-1	½	½	½	0	3/2	✓	0	3/2	^4S
5	1	0	-1	½	½	-½	0	½	✓			
6	1	0	-1	½	-½	½	0	½	✓			
7	1	0	-1	-½	½	½	0	½	✓			

<u>Note:</u> State with all 3 m_ℓ's equal, $(m_{\ell 1}, m_{\ell 2}, m_{\ell 3}) = (1,1,1)$ or $(0,0,0)$ impossible, because you can't make the spin states distinct. So we start with $(m_{\ell 1}, m_{\ell 2}, m_{\ell 3}) = (110)$. In this state, m_{s1}, m_{s2} must be opposite since $m_{\ell 1} = m_{\ell 2}$, but m_{s3} can be anything ($\pm \frac{1}{2}$). However, we do not list the state with $m_{s3} = -\frac{1}{2}$, because it has $M_S < 0$. When all 3 m_ℓ's are distinct (e.g. $1, 0, -1$), then there are $8 = 2^3$ possibilities for m_s, but we only have 4 with $M_S > 0$ (e.g. rows $(3, 4, 5, 6)$. By looking for doubly stretched states we find the multiplets $^2D, {}^2P, {}^4S$ with dimensions $2 \times 5 = 10$, $2 \times 3 = 6$, $4 \times 1 = 4$. $10 + 6 + 4 = 20 = \binom{6}{3}$.

Continuing atomic structure...

Next case is O (oxygen) with config $1s^2 2s^2 2p^4$.   But it turns out that holes behave same way as electrons, insofar as computing allowed multiplets is concerned.   The 2p subshell has 6 slots; when we add 4 electrons, there remain 2 empty slots, or "holes". These behave like electrons for computing multiplets since a completely empty subshell and a completely full one both have $L = M_L = S = M_S = 0$.   Thus O (oxygen) has same multiplets as carbon.   Now it is easy to list the multiplets of the gnd state configurations of the first several elements:

Z	element	config	multiplets
1	H	$1s$	^2S
2	He	$1s^2$	^1S
3	Li	$1s^2 2s$	^2S
4	Be	$1s^2 2s^2$	^1S
5	B	$1s^2 2s^2 2p$	^2P
6	C	$1s^2 2s^2 2p^2$	$^3P, \, ^1D, \, ^1S$
7	N	$1s^2 2s^2 2p^3$	$^4S, \, ^2D, \, ^2P$
8	O	$1s^2 2s^2 2p^4$	$^3P, \, ^1D, \, ^1S$
9	F	$1s^2 2s^2 2p^5$	^2P
10	Ne	$1s^2 2s^2 2p^6$	^1S

When we go to heavier elements (more complicated configurations), it is possible that some multiplets occur more than once. This first happens with V (vanadium). In such cases there is more than one way to create multiplets of given L, S, and we need an extra

index, say, γ, in the specification of the unperturbed eigenstates :

$$| \gamma L M_L S M_S \rangle = \sum_{m\text{-sets}} (coefs) \, | m\text{-sets} \rangle$$

(still understood that we are working within a given configuration).

These calculations of allowed multiplets just tell us which L, S values occur in the given configuration of H_0. To do perturbation theory with H_1, we also need the coefs in the expansion above. These are generalizations of the C-G coefs and can be found with raising + lowering operators. Once that is done, we can do (degen) perturbation theory with H_1. We need to find the eigenvalues of

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

No primes are needed on L, M_L, S, M_S on the right because L^2, L_z, S^2, S_z all commute with H_1. In cases like C or N, where no multiplet occurs more than once, we don't need the γ index, and the energy shifts are just the diagonal elements of H_1. Evaluating these matrix elements would take us too far afield, but when you do it, some rules emerge about the energy shifts. Notice that the energy shifts due to H_1 depend on L and S, (i.e., which multiplet) but not on M_L, M_S (because of WE thm).

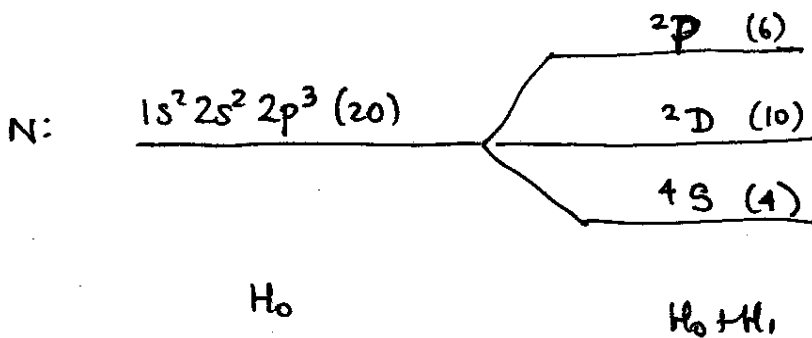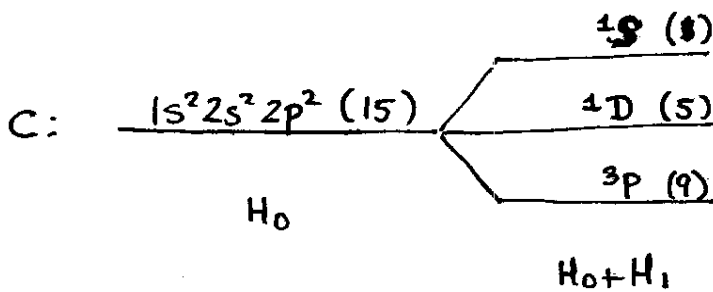The following rules (semi empirical) govern the ordering of the

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energy shifts.   (Hund's rules:)

1.   The lowest multiplet has the highest S

2.   For given S, the lowest multiplet has the highest L.

The physics of rule #1 is familiar: higher S means more symmetric spin states, which means more antisymmetric spatial states, which means lower Coulomb energy.   This is what made the triplet state lower in energy than the singlet states in helium, and it also lies behind ferromagnetism   (align spins, lower Coulomb energy).   We won't try to justify rule 2 physically.

These rules allow us to order the multiplets in C and N:

^1S (1)

C: $1s^2 2s^2 2p^2$ (15)

^1D (5)

^3P (9)

H_0

$H_0 + H_1$

^2P (6)

N: $1s^2 2s^2 2p^3$ (20)

^2D (10)

^4S (4)

H_0

$H_0 + H_1$

Now consider H_2 (the spin-orbit term). This term
itself is an approximation, since it pretends that each electron
moves in a central force potential. Even in the HF appx, this
neglects the exchange (nonlocal) potential. We will just summarize
some results.

First, H_2 does not commute with $\vec{L}$ or $\vec{S}$, but with $\vec{J} = \vec{L} + \vec{S}$.
So we couple $\vec{L} + \vec{S}$ to get eigenbasis of J^2, J_z:

$$| \gamma\, L\, S\, J\, M_J \rangle = \sum_{M_L M_S} | \gamma\, L\, M_L\, S\, M_S \rangle \underbrace{\langle L S\, M_L M_S | J M_J \rangle}_{CG\ coef.}$$

just like in Hydrogen. Then one can show

$$\langle L S J M_J | \sum_i \xi(r_i)\, \vec{L}_i \cdot \vec{S}_i | L S J M_J \rangle$$

$$= A \ \langle L S J M_J | \vec{L} \cdot \vec{S} | L S J M_J \rangle \qquad A = const.$$

$$= \frac{A}{2} \Big[J(J+1) - L(L+1) - S(S+1) \Big].$$

So energy is ↑ fn of J if $A > 0$, ↓ fn of J if $A < 0$. In fact,
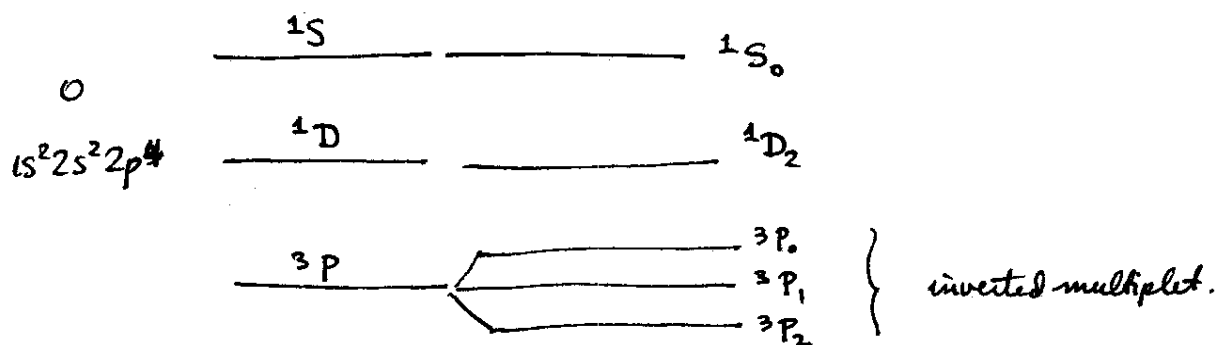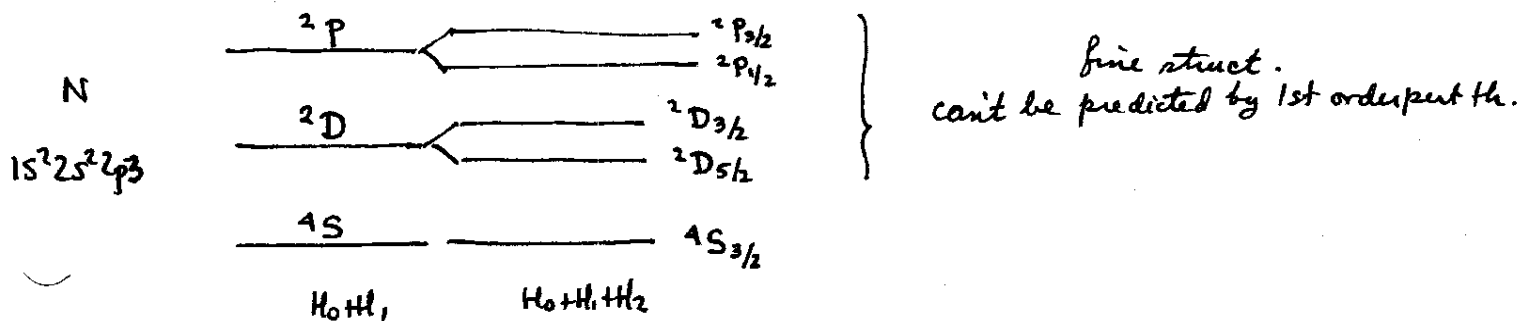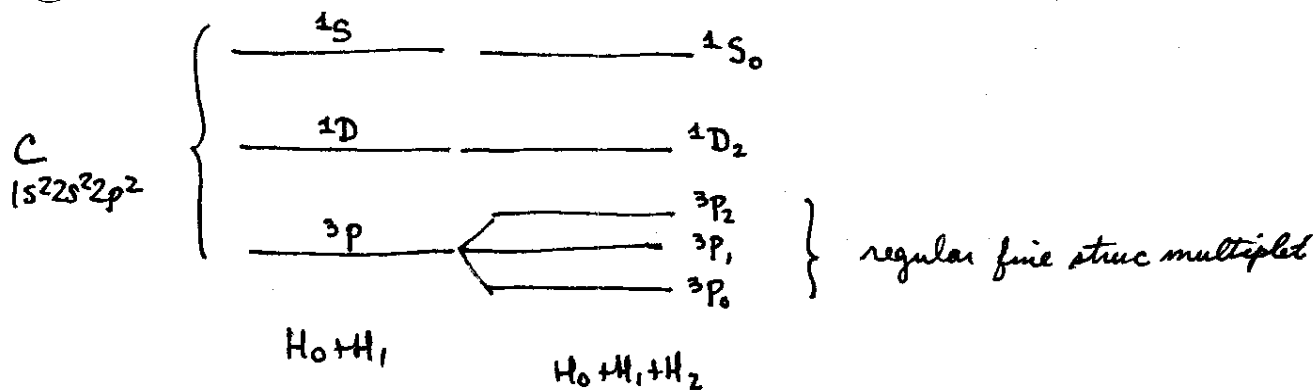
$\ \ \ \ < \frac{1}{2}$ filled subshells $\quad A > 0 \quad$ ("regular" multiplet)

$\ \ \ \ > \frac{1}{2}$ filled subshells $\quad A < 0 \quad$ ("inverted" multiplet).

$\ \ \ \ = \frac{1}{2}$ filled $\qquad\qquad A = 0 \quad$ (must go on to 2nd order pertn th).

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With J values, levels of C, N, O are:

C
$1s^2 2s^2 2p^2$

^1S ———————— $^1S_0$

^1D ———————— $^1D_2$

^3P —————— $\Big\{$ $^3P_2$ $^3P_1$ $^3P_0$ $\Big\}$ regular fine struc multiplet

$H_0 + H_1$ $H_0 + H_1 + H_2$

N
$1s^2 2s^2 2p^3$

^2P —————— $\Big\{$ $^2P_{3/2}$ $^2P_{1/2}$

^2D —————— $\Big\{$ $^2D_{3/2}$ $^2D_{5/2}$

^4S ———————— $^4S_{3/2}$

$\Big\}$ fine struct. can't be predicted by 1st order pert th.

$H_0 + H_1$ $H_0 + H_1 + H_2$

O
$1s^2 2s^2 2p^4$

^1S ———————— $^1S_0$

^1D ———————— $^1D_2$

^3P —————— $\Big\{$ $^3P_0$ $^3P_1$ $^3P_2$ $\Big\}$ inverted multiplet.

Subscript is J-value, e.g. $^3P_2$ means $S=1, L=1, J=2$.

Diagrams not to scale, in particular, fine structure splitting $\ll$ splitting between multiplets, which is on order of $\approx$ ~~100~~. 1-3 ev. or so.