

Multi-Electron Atoms

Electron configuration notation (ground states)

H	1s	C	1s ² 2s ² 2p ²
He	1s ²	N	1s ² 2s ² 2p ³
Li	1s ² 2s	O	1s ² 2s ² 2p ⁴
Be	1s ² 2s ²	F	1s ² 2s ² 2p ⁵
B	1s ² 2s ² 2p	Ne	1s ² 2s ² 2p ⁶

Subshells s, p, d, f, ... correspond to orbital angular momentum $l = 0, 1, 2, 3, \dots$

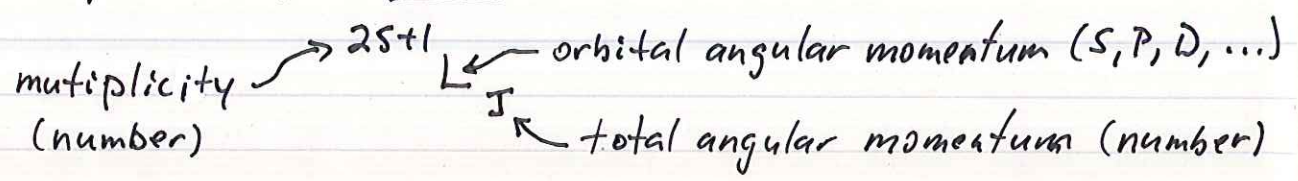
Electron configuration notation does not include information about m_l and m_s ($m_s = \pm \frac{1}{2}$).

Spectroscopic Notation

Total orbital angular momentum $\vec{L} = \sum_i \vec{l}_i$
 Total spin angular momentum $\vec{S} = \sum_i \vec{s}_i$
 Total angular momentum $\vec{J} = \vec{L} + \vec{S}$.

The state of the atom can be defined by the quantities L, S, J, M_J .

A spectroscopic term has the notation:

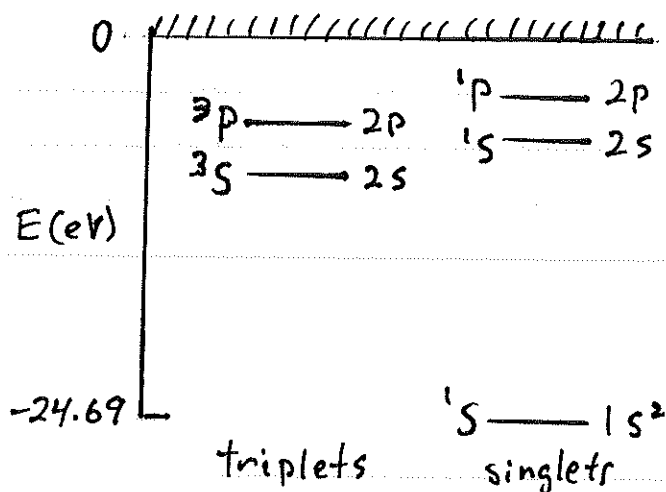


<u>Configuration</u>	<u>L</u>	<u>S</u>	<u>Term</u>	<u>Example</u>
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H	1s	0	$\frac{1}{2}$	$^2S_{1/2}$	ground state
He	1s ²	0	0	1S_0	ground state
He	1s 2s	0	0, 1	$^1S_0, ^3S_1$	excited state
He	1s 2p	1	0, 1	$^1P_1, ^3P_{2,1,0}$	excited state

Helium Atom

1. For a given principal quantum number n , triplet spin states have lower energy than singlet spin states,
2. For a given principal quantum number n , states of smaller orbital angular momentum L have lower energy.



For excited configurations only the excited electron is indicated, ignoring the remaining 1s electron.

Term Diagrams

Config. -- Multiplet -- Term -- Level

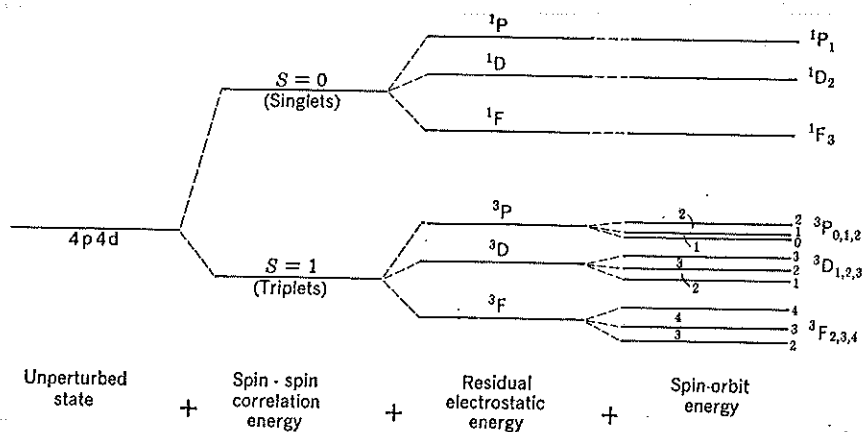


FIG. 8-1. Schematic diagram illustrating the fine-structure splitting of a level corresponding to a 4p and a 4d valence electron. The Landé-interval rule is illustrated in the spacings of the triplet levels.

3. If there is more than one electron in a partially filled shell, terms with larger L within a given multiplet have lower energy.

Identical Particles and Exchange Degeneracy

$$\left[\frac{\tilde{p}^2}{2m} + V \right] \psi = E \psi \quad \text{where } \tilde{p} = -i\hbar \nabla$$

Identical (indistinguishable) particles must feel the same potential V and appear the same way in the Hamiltonian. Consider two indistinguishable particles, 1 and 2

$$H = \frac{\tilde{p}_1^2}{2m} + \frac{\tilde{p}_2^2}{2m} + V(x_1) + V(x_2)$$

The solution to the Schrödinger Equation is

$$\psi_{ab} = \psi_a(x_1) \psi_b(x_2) \quad \text{with } E_{ab} = E_a + E_b$$

If we interchange the particles, the state

$$\psi_{ba} = \psi_b(x_1) \psi_a(x_2) \quad \text{has the same energy.}$$

This is called exchange degeneracy. Generalizing to N particles

$$\psi_a(x_1) \psi_b(x_2) \dots \psi_k(x_N). \quad \text{Exchange any pair,}$$

there could be $N!$ degenerate states. Any linear combination of these independent states could be an eigenfunction (solution) of the Hamiltonian, and can be classified as symmetric or antisymmetric...

Two indistinguishable particles and exchange symmetry

Two-particle states can be classified as

$$\psi_{ab}^+ = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) + \psi_b(x_1) \psi_a(x_2)] \quad \text{symmetric}$$

$$\psi_{ab}^- = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) - \psi_b(x_1) \psi_a(x_2)] \quad \text{antisymmetric}$$

$$\text{because } \psi_{ab}^+ = \psi_{ba}^+ \quad \text{and } \psi_{ab}^- = -\psi_{ba}^-$$

An electron also has spin, and its spin angular momentum is $\hbar/2$. The electron spin quantum number is $m_s = \pm 1/2$. The total wave function of an electron should be written as the product of spatial and spin wave functions, each of which is either symmetric or antisymmetric. For two electrons:

$$\text{Space } \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\Psi_a(x_1) \Psi_b(x_2) \pm \Psi_b(x_1) \Psi_a(x_2)]$$

$$\text{Spin } \chi(s_1, s_2) = \frac{1}{\sqrt{2}} [\chi_a(s_1) \chi_b(s_2) \pm \chi_b(s_1) \chi_a(s_2)]$$

Since spin is either + or -, there is one antisymmetric spin state and three symmetric spin states.

$$\chi(s_1, s_2) = \frac{1}{\sqrt{2}} [\chi_+(s_1) \chi_-(s_2) - \chi_+(s_2) \chi_-(s_1)] \quad \left. \begin{array}{l} \text{"singlet"} \\ \text{antisymmetric} \end{array} \right\}$$

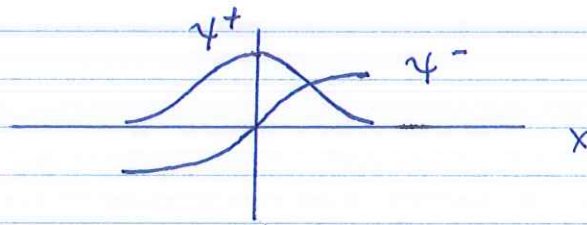
$$\chi(s_1, s_2) = \left\{ \begin{array}{l} \chi_+(s_1) \chi_+(s_2) \\ \frac{1}{\sqrt{2}} [\chi_+(s_1) \chi_-(s_2) + \chi_+(s_2) \chi_-(s_1)] \\ \chi_-(s_1) \chi_-(s_2) \end{array} \right\} \quad \left. \begin{array}{l} \text{"triplet"} \\ \text{symmetric} \end{array} \right\}$$

For Fermi-Dirac particles the total wave function $\Psi(x_1, x_2) \chi(s_1, s_2)$ must be antisymmetric with respect to the interchange of both space and spin coordinates, $x_1 \leftrightarrow x_2$ and $s_1 \leftrightarrow s_2$. If the spin wave function is antisymmetric, the spatial wave function must be symmetric, and vice-versa. Thus, triplet spin states have antisymmetric spatial wave functions, and singlet spin states have symmetric spatial wave functions.

We also see that the singlet (antisymmetric) spin state of two electrons has total spin 0, while the triplet (symmetric) spin state can have total spin -1, 0, or +1.

An antisymmetric state vanishes when $a = b$. Two particles cannot be in the same state if their total wave function is antisymmetric. This is the Pauli exclusion principle.

Note that in a symmetric potential $V(x)$ the Hamiltonian is symmetric. One can then show that all bound states in a symmetric potential are either symmetric (even) ψ^+ or antisymmetric (odd) ψ^- .



Note that any function can be expressed as a sum of symmetric and antisymmetric parts.

$$\psi^+(x) = \psi^+(-x) \quad \text{even}$$

$$\psi^-(x) = -\psi^-(-x) \quad \text{odd}$$

$$\psi(x) = \psi^+(x) + \psi^-(x)$$

$$\text{where } \psi^+(x) = \frac{\psi(x) + \psi(-x)}{2} \quad \text{symmetric}$$

$$\text{and } \psi^-(x) = \frac{\psi(x) - \psi(-x)}{2} \quad \text{antisymmetric}$$

If the spatial wave function is symmetric, the electrons are, on average closer together, and their mutual repulsion raises the energy of the state relative to the antisymmetric wave function. But a symmetric spatial state must have an antisymmetric spin state, which is a singlet in the case of two electrons. So the singlet state has higher energy than the triplet state.

ground state $2p^2$

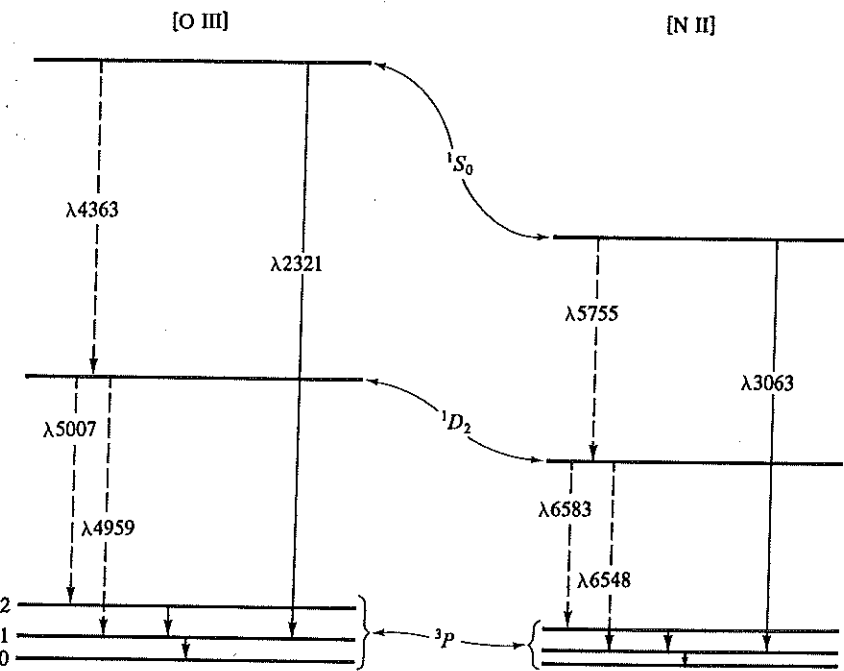
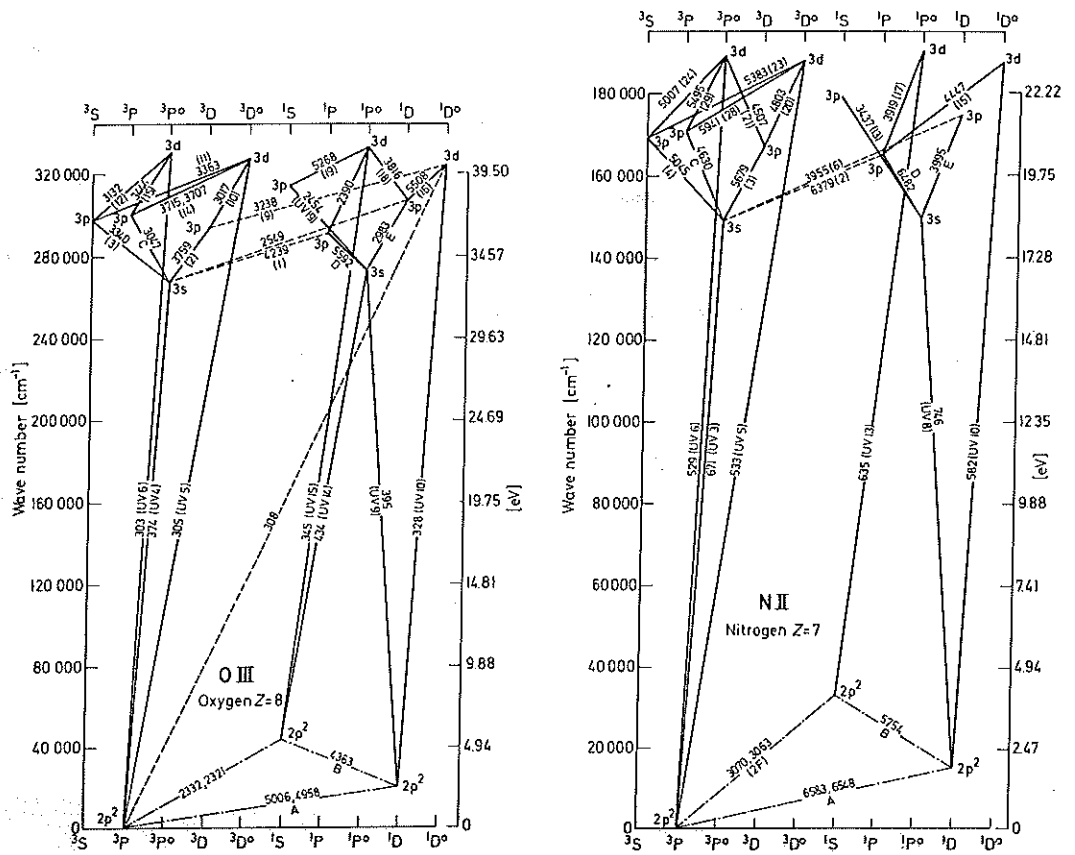


FIGURE 3.1 Energy-level diagram for lowest terms of [O III], all from ground $2p^2$ configuration, and for [N II], of the same isoelectronic sequence. Splitting of the ground $3P$ term has been exaggerated for clarity. Emission lines in the optical region are indicated by dashed lines, and by solid lines in the infrared and ultraviolet. Only the strongest transitions are indicated.

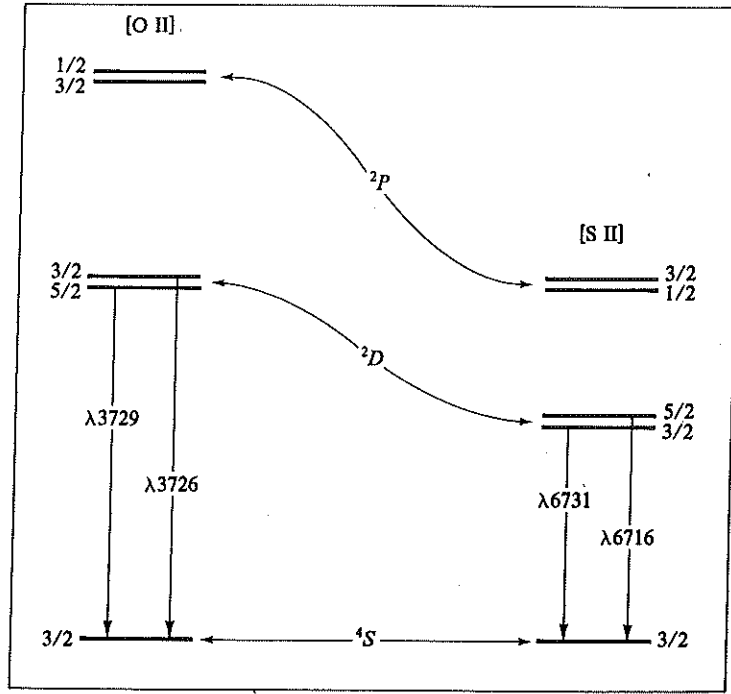
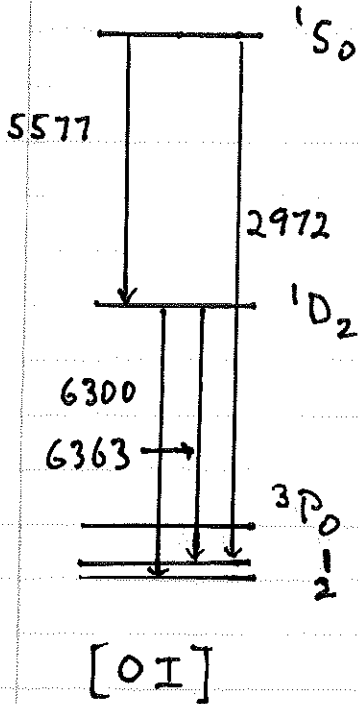


FIGURE 5.2 Energy-level diagrams of the $2p^3$ ground configuration of [O II] and $3p^3$ ground configuration of [S II].

ground state $2p^3$



ground state $2p^4$

When the p subshell is more than half full, as in $O I$ which has configuration $1s^2 2s^2 2p^4$, the term diagram is the same as for $O III$ $1s^2 2s^2 2p^4$, except that the J levels in the $3P$ term are inverted.

That is, terms with n electrons in the p subshell are the same as terms with $6-n$ electrons, except for inversion of the J levels.

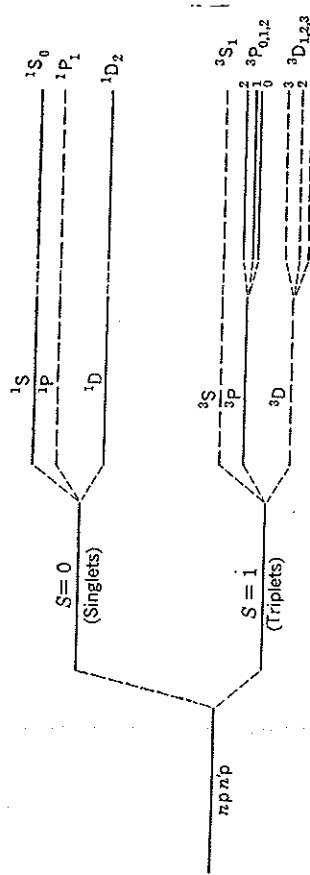


Fig. 8-3. Schematic illustration of the LS fine-structure splitting of a configuration involving two p electrons. The dashed levels are missing from the multiplet if the electrons are equivalent ($n = n'$).

valence electrons are involved. This complexity is somewhat reduced, of course, if some of these are in the same subshell. Electrons which are in the same subshell are called *equivalent electrons*; the exclusion principle must always be taken into account in analyzing the fine structure of a configuration involving equivalent electrons.

In case a subshell is more than half filled with electrons, the application of the exclusion principle leads to the important result that *the combinations of L and S available to these electrons are exactly the same as if only a number of electrons equal to the number of unoccupied substates in the subshell were actually present.* (Thus if five electrons were in a certain p subshell, the number of L and S combinations would be exactly the same as for *one* electron in this subshell, namely, $S = \frac{1}{2}$ and $L = 1$.) The most complicated fine structure therefore is associated with those elements having approximately *half-filled* subshells.

As an illustration of the effect of the exclusion principle upon the fine structure of a level, the fine-structure splitting is compared schematically in Fig. 8-3 for two equivalent and for two nonequivalent p electrons. The levels missing from the fine structure for the equivalent electrons are shown dotted.

This figure indicates that the 3D , 3S , and 1P terms that are found in the fine structure of a configuration of two nonequivalent p electrons are missing from the corresponding multiplet for equivalent electrons. These terms are eliminated because of the exclusion-principle requirement that no two electrons may have the same set of quantum numbers n, l, m_l , and m_s and because *only physically distinguishable states can be counted.*

The general case of any number of equivalent electrons is best treated by the use of group theory, but unfortunately this method is beyond the scope of the present work. We can, however, deal with the particular case illustrated in Fig. 8-3 by a more elementary method. Let us tabu-

late the various possible values of m_{l1} , m_{s1} , m_{l2} , and m_{s2} for the two electrons, first treating them as nonequivalent (Table 8-1). We then take account of the exclusion principle and the indistinguishability of the electrons by striking out those states for which $m_{l1} = m_{l2}$ and $m_{s1} = m_{s2}$, and by eliminating duplication of indistinguishable states. Thus states 1, 4, 17, 20, 33, and 36 are removed by the first criterion, and such

TABLE 8-1. m_{l1} AND m_{s1} VALUES FOR TWO EQUIVALENT p ELECTRONS

m_{l1}	m_{s1}	m_{l2}	m_{s2}	Label	m_{l1}	m_{s2}	Label
+1	$+\frac{1}{2}$	+1	$+\frac{1}{2}$	OUT	+	+	11
	+		-	1	+	-	12
	-		+	1	-	+	13
+1	+	0	-	OUT	-	-	14
	+		+	2	+	+	6
	+		-	3	+	-	8
	-		+	4	-	+	7
	-		-	5	-	-	9
+1	+	-1	+	6	+	+	11
	+		-	7	+	-	13
	-		+	8	-	+	12
	-		-	9	-	-	14
0	+	+1	+	2	+	+	OUT
	+		-	4	+	-	15
	-		+	3	-	+	15
	-		-	5	-	-	OUT
0	+	0	+	OUT	+	+	OUT
	+		-	10	+	-	OUT
	-		+	10	-	+	OUT
	-		-	OUT	-	-	OUT

pairs of states as 2 and 3, 5 and 13, 6 and 15, etc., are labeled with new numbers 1, 2, 3, etc. For two equivalent p electrons, only the fifteen combinations of $M_L = m_{l1} + m_{l2}$, $M_s = m_{s1} + m_{s2}$, and $M_J = M_L + M_s$ shown in Table 8-2 are possible. We must now compare these states with the states expected in the LS multiplet: 1S_0 , 1P_1 , 1D_2 , 3S_1 , ${}^3P_{0,1,2}$, ${}^3D_{1,2,3}$. Of these, we can immediately see that the 3D_3 state cannot be present, since this would require M_J values of $+3$ and -3 . This in turn rules out the presence of 3D_2 and 3D_1 , since if one possible combination of a given L and S is present, all must be. On the other hand, state 2 requires the presence of an LS term with $L \geq 1$ and $S \geq 1$. Of the available combinations, this requires that ${}^3P_{0,1,2}$ be present. Furthermore, state 1 can come only from an LS term having $L \geq 2$ and $S \geq 0$; from this we conclude that the 1D_2 term must be present.

Multi-electron Atoms - Perturbation Theory

For atoms with more than one electron, the Hamiltonian can be written as the sum of various terms of decreasing magnitude

$$H = - \sum_i \frac{Ze^2}{r_i} + \sum_i \frac{\tilde{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{r_{ij}} + H_{\text{spin-orbit}} + H_{\text{hfs}} + \dots$$

If the energy levels and wavefunctions corresponding to the large terms in the Hamiltonian are known, then the small terms, such as spin-orbit and hyper-fine splitting can be treated as perturbations.

For example, in first-order perturbation theory, write

$$\begin{aligned} H &= H_0 + \alpha H_1 & \text{where } H_1 \ll H_0 \\ E &= E_0 + \alpha \Delta E & \Delta E \ll E_0 \\ \psi &= \psi_0 + \alpha \psi_1 & \psi_1 \ll \psi_0 \end{aligned}$$

and imagine increasing α from 0 to 1. Then use Schrödinger equation and separate terms of the same order in α .

$$H\psi = E\psi$$

$$(H_0 + \alpha H_1)(\psi_0 + \alpha \psi_1) = (E_0 + \alpha \Delta E)(\psi_0 + \alpha \psi_1)$$

$$(H_0 - E_0)\psi_0 + \alpha [(H_1 - \Delta E)\psi_0 + (H_0 - E_0)\psi_1] + \alpha^2 [\dots] = 0$$

$$\text{So } (H_0 - E_0)\psi_0 = 0$$

$$(H_1 - \Delta E)\psi_0 + (H_0 - E_0)\psi_1 = 0$$

Multiply by ψ_0^* and integrate over volume

$$\int [\psi_0^* H_1 \psi_0 - \Delta E \psi_0^* \psi_0 + \psi_0^* H_0 \psi_1 - E_0 \psi_0^* \psi_1] d^3r = 0$$

Now by the properties of quantum mechanical operators

$$\int \psi_0^* H_0 \psi_1 d^3r = \int \psi_1 (H_0 \psi_0)^* d^3r = \int E_0 \psi_0^* \psi_1 d^3r$$

$$\Rightarrow \boxed{\int \psi_0^* H_1 \psi_0 d^3r = \Delta E}$$

Spin-orbit coupling (L-S) = Fine Structure splitting of levels

The electron in its rest frame sees a magnetic field due to the orbiting nucleus of

$$\vec{B}' = -\frac{\vec{v} \times \vec{E}}{c} \quad \text{where } \vec{E} = -\vec{F} = \frac{1}{e} \frac{d\psi}{dr}$$

The electron's orbital angular momentum is

$$\vec{l} = -m\vec{v} \times \vec{r} \quad \text{quantized } \vec{l} = \sqrt{l(l+1)} \hbar$$

$$\text{So } \vec{B}' = \frac{\vec{l}}{cemr} \frac{d\psi}{dr}$$

The electron has magnetic moment proportional to its spin \vec{l}_s

$$\vec{\mu} = -g \frac{e}{2mc} \vec{l}_s \quad \vec{l}_s = \sqrt{s(s+1)} \hbar, \quad s = \frac{1}{2}$$

$$g = 2.00232$$

The spin-orbit energy (H_{so} term in Hamiltonian) is

$$U = -\frac{1}{2} \vec{\mu} \cdot \vec{B} \quad \text{or} \quad H_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{d\psi}{dr} \vec{l} \cdot \vec{l}_s$$

$$\text{Summed over all electrons } H_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{d\psi}{dr} \vec{L} \cdot \vec{L}_s$$

$$\text{Total angular momentum operator } \vec{J} = \vec{L} + \vec{S}$$

$$\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

$$\text{where } |L-S| \leq J \leq L+S$$

The change in energy corresponding to H_{so} is, in 1st order perturbation theory

$$\Delta E_{fs} = \int \psi_0^* H_{so} \psi_0 d^3r$$

$$\text{so } \Delta E_{fs} = \frac{1}{2} C [J(J+1) - L(L+1) - S(S+1)]$$

$$\text{where } C = \hbar^2 \int \psi_0^* \frac{1}{2m^2c^2} \frac{1}{r} \frac{d\psi}{dr} \psi_0 d^3r$$

The spacing between adjacent levels in a term refers to holding L and S fixed, and changing J by 1.

$$\begin{aligned} \text{So } E_{J+1} - E_J &= \frac{1}{2} C [(J+1)(J+2) - J(J+1)] \\ &= C(J+1) \end{aligned}$$

This is the Landé interval rule — The spacing between two adjacent levels in a term is proportional to the larger of the two J values involved. This rule is very helpful in determining the J values from observation.

Addition of angular momentum — Since the total J must satisfy $\vec{J} \cdot \vec{J} = J(J+1)\hbar^2$, and its z -component must be $J_z = m_J \hbar$, the number of J values in any term is equal to the smaller of $(2L+1)$ and $(2S+1)$. J must lie within the range:

$$L - S \leq J \leq L + S \quad \text{if } L \geq S$$

$$S - L \leq J \leq L + S \quad \text{if } L \leq S$$

If the constant C above is positive, higher J levels within a term have higher energy. This is called normal ordering, and it occurs when a ^{sub}shell is less than half full. Inverted ordering occurs when a ^{sub}shell is half-filled or more.

The exclusion principle acts to eliminate some combinations of L and S if a subshell is more than half full. If a subshell is more than half full, the terms available are exactly the same as if the number of electrons were equal to the number of unoccupied states. That is, terms for p^2 are the same as for p^4
 " " p^1 " " " " " " p^5

Spin-Orbit (Fine Structure) splitting of Hydrogenic Atoms

The s-o energy perturbation of a level specified by n, J, L, S , is

$$\Delta E_{fs} = \frac{\alpha^2 hc R Z^4}{n^3} \left[\frac{J(J+1) - L(L+1) - S(S+1)}{L(L+1)(2L+1)} \right]$$

where $R = \frac{2\pi^2 \mu e^4}{ch^3} = 109737.312 \text{ cm}^{-1}$ is the Rydberg constant (I.P. of hydrogen)

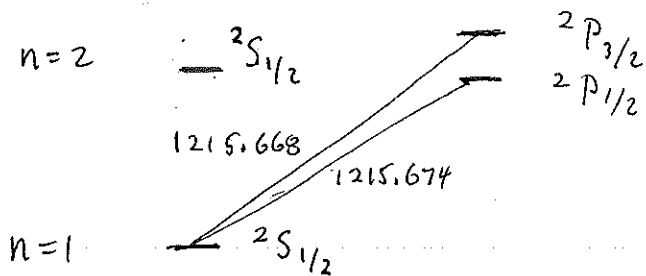
$\mu = \frac{m_e M}{m_e + M}$ is the reduced mass ($M = \text{nuclear mass}$)

The energies of the principal states of a hydrogenic atom are

$$E_n = -\frac{hcR Z^2}{n^2}$$

Then $\Delta E_{fs} \propto \frac{\alpha^2 Z^2 E_n}{n}$ where $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.0}$ is the "fine structure constant"

Example: $1s \rightarrow 2p$ transition of hydrogen (Ly α) 1215.7 \AA



For each level, the perturbation is

$$\Delta E_{fs} = \alpha^2 \frac{hcR}{n^3} \left[\frac{J(J+1) - L(L+1) - S(S+1)}{L(L+1)(2L+1)} \right]$$

where $hcR = 13.6 \text{ eV}$

$${}^2P_{3/2} \quad \Delta E_{fs} = \alpha^2 \cdot \frac{13.6}{8} \left[\frac{3/2(5/2) - 2 - 1/2(3/2)}{1 \cdot 2 \cdot 3} \right] \text{ eV} = \frac{\alpha^2 \cdot 13.6}{48} \text{ eV}$$

$${}^2P_{1/2} \quad \Delta E_{fs} = \alpha^2 \cdot \frac{13.6}{8} \left[\frac{1/2(3/2) - 2 - 1/2(3/2)}{1 \cdot 2 \cdot 3} \right] \text{ eV} = -\frac{\alpha^2 \cdot 13.6}{24} \text{ eV}$$

The net splitting is then $(\Delta E_{fs})_{3/2} - (\Delta E_{fs})_{1/2} = \left(\frac{1}{137}\right)^2 \frac{13.6}{16}$

$$= 4.5 \times 10^{-5} \text{ eV}$$

To calculate the splitting in wavelength:

$$\lambda = \frac{hc}{E} \Rightarrow \Delta\lambda = \frac{hc}{E^2} \Delta E = \frac{\lambda^2}{hc} \Delta E$$

$$= \frac{(1215.7 \times 10^{-8})^2 \cdot 4.5 \times 10^{-5} \text{ eV} \cdot 1.602 \times 10^{-12} \text{ erg/eV}}{6.63 \times 10^{-27} \cdot 3 \times 10^{10}} = 5.4 \times 10^{-11} \text{ cm} = 0.0054 \text{ \AA}$$

Fine structure splitting in non-hydrogenic atoms

Na I	3s → 3p	5890, 5896 \AA
C IV	2s → 2p	1548.2, 1550.8 \AA
N V	2s → 2p	1238.8, 1242.8 \AA
O VI	2s → 2p	1031.9, 1037.6 \AA

These examples are "almost" hydrogenic atoms in the sense that they have filled inner principal quantum states, and one "extra" electron in the highest principal quantum state. Their fine-structure splitting can be approximated using hydrogenic formulae, assuming that the inner-shell electrons shield the outer one.

Example: O VI (1031.9, 1037.6) $1s^2 2s \rightarrow 1s^2 2p$
 Effective nuclear charge $Z_{\text{eff}} \approx 8 - 2 = 6$

$$\Delta E_{fs} \propto \frac{\alpha^2 Z_{\text{eff}}^2}{n} E_n \quad \text{where } E_n = \frac{13.6 Z_{\text{eff}}^2}{n^2} \approx 122.4 \text{ eV}$$

$$\Delta E_{fs} ({}^2P_{3/2}) = \frac{\alpha^2 \cdot 6^4 \cdot 13.6}{48} \quad \Delta E_{fs} ({}^2P_{1/2}) = -\frac{\alpha^2 \cdot 6^4 \cdot 13.6}{24}$$

$$\Delta E_{fs} ({}^2P_{3/2}) - \Delta E_{fs} ({}^2P_{1/2}) = 0.0587 \text{ eV} \quad (6^4 \text{ times that of H I})$$

$$\Delta\lambda = \frac{\lambda^2 \Delta E}{hc} = \frac{(1035.4 \times 10^{-8})^2 \cdot 0.0587 \cdot 1.6 \times 10^{-12}}{6.63 \times 10^{-27} \cdot 3 \times 10^{10}} = 5.1 \times 10^{-8} \text{ cm} = 5.1 \text{ \AA}$$

This is very close to the actual splitting of 5.7 \AA. The difference can be explained as incomplete shielding, Z_{eff} is slightly larger than 6. For this reason the actual I.P. = 138 eV, not 122 eV.