Multi-Electron Atoms II

***LS* Coupling** The basic idea of LS coupling or Russell-Saunders coupling is to assume that spin-orbit effects are small, and can be neglected to a first approximation. If there is no spin-orbit coupling, the total orbital angular momentum of the electrons is conserved as well as its 3rd component. These quantum numbers are denoted by L, M. In addition, the total spin of all the electrons is conserved as well as its 3rd component. These are denoted as S, M_s. With these choices of quantum numbers, configurations of an atom are denoted as ${}^{2S+1}L_J$, where J refers to the total angular momentum quantum number when spin and orbital angular momenta are added. The ground state configuration of a given atom can be stated in this form as long as the basic LS coupling scheme is valid. Without spin-orbit coupling, the various values of J which are possible for a given L and S will all have the same energy. When spin-orbit effects are included, these values will be split, and the lowest J value will be the lowest energy.

Central Field Approximation It has been a very useful approach to understanding the structure of atoms to make what is called the "Central Field Approximation." The idea here is to assume that in addion to its attraction to the nucleus, each electron experiences an average potential due to the other electrons. This potential is assumed to be spherically symmetric. Call it $S(r)$ for one electron. Then the starting or unperturbed Hamiltonian would be

$$H_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + S(r_i) \right). \tag{1}$$

The eigenstates of H_0 will be labeled by the same quantum numbers (n, l, m) as hydrogenic levels are, but once $S(r)$ is present, there is no longer the huge degeneracy present in a pure Coulomb potential. Instead, for a given value of the quantum number n, while the allowed values of l can generally still be restricted to $0, 1, \ldots, n-1$, the energy now depends on l as well as n, the smaller the value of l, the smaller the energy. This means for a given n, the $l = 0$ or s-state fills first, then $l = 1$ or p, followed by $l = 2$ or d, etc. This scheme works well for the atoms with moderate values of Z, but becomes more complex for atoms with higher Z, where for example the energy of an $n = 4, l = 0$ state can lie lower than a $n = 3, l = 2$ state. Nevertheless, under the central field approximation, the idea of electrons successively filling the various "shells" is very powerful. A shell here means all the available states for a given value of n and l. So for an $l = 0$ shell this is two electrons, for an $l = 1$ shell, it is six electrons, for an $l = 2$ shell it is ten electrons, etc.

Once the levels of the central field approximation are known, perturbation theory can give insight into the structure of the low lying levels of the atom. This means the relative placement of the ground state and the first few excited states. The perturbing potential is

$$H_1 = \sum_{i<j=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{j=1}^{N} S(r_i) \tag{2}$$

It is often true, as will be seen in the next example, that this splitting between the first few levels usually does not involve S directly.

Two electrons outside filled shells As a sample calculation, consider the column IVA of the periodic table, consisting of the elements carbon, silicon, germanium, tin, and lead. The electronic configuration of all of these elements has 2 $l = 1$ or 2 p electrons outside a core of filled shells. This is illustrated in the following table.

Z	$element$	$configuration$	$groundstate$
6	C	$(He)2s^2sp^2$	$^3P_0$
14	Si	$(Ne)3s^23p^2$	$^3P_0$
32	Ge	$(Ar)3d^{10}4s^24p^2$	$^3P_0$
50	Sn	$(Kr)4d^{10}5s^25p^2$	$^3P_0$
82	Pb	$(Xe)4f^{14}5d^{10}6s^26p^2$	$^3P_0$

For 2 electrons, the states allowed by the Pauli Principle are $^1D_2,^3P_0,^3P_1,^3P_2,^1S_0$. This list is easy to understand. With two $l = 1$ electrons, we may have $L = 2, 1, 0$. The states with $L = 2, 0$ are symmetric under interchange of the two electrons, so the Pauli Principle demands that the spin state be anti-symmetric, or $S = 0$. The states with $L = 1$ are anti-symmetric under interchange of the two electrons, so the Pauli Principle demands that the spin state be symmetric, or $S = 1$. From the table, we see that for all the elements in column IVA, the ground state has $L = 1, S = 1, J = 0$. To understand why $^3P_0$ is the ground state, we need to take account of the Coulomb repulsion between electrons, and spin-orbit coupling.

Coulomb repulsion involving two electrons outside of filled shells Assume that the shells have been found by solving the Schrödinger equation for some average central potential. This potential includes the Coulomb attraction of each electron to the nucleus, plus some average potential due to all the “other” electrons on the electron being considered. We will not attempt to find this potential, but simply assume it exists and is spherically symmetric. What we are after are facts that can be understood about relative placements of energy levels, independent of the details of this central potential.

It is clear that repulsive interactions between electrons in filled shells will only affect the overall placement of the energies of the atom being considered, and will not differentiate between the possible ground states of our atoms with $2p$ electrons outside filled shells.

On the other hand, it is not as obvious that repulsive interactions between one of our p electrons and a filled shell could not affect the relative placement of energy levels. This turns out to be true, nevertheless, so it is the repulsive interactions of the electrons *outside* filled shells (in our case the $2p$ electrons) with each other that determines the relative placement of energy levels. We will obtain these results in two stages.

Interactions between a filled shell and an electron in an unfilled shell To keep a specific example in mind, consider in Si the interaction between a $3p$ electron and the $2p^6$ filled shell. Let us use the following notation: n, l, m, s refer to the quantum numbers of the electrons in the filled shell, where $m = -l, -l+1, \ldots, l$ is the eigenvalue of L_z, and $s = \pm 1/2$ is the eigenvalue of S_z. Summing over all electrons of the filled shell means summing over m and s. The electrons in the unfilled shell are denoted by n', l', m', s'. The total Coulomb potential between all the electrons is

$$V = \sum_{i<j=1}^{Z} V(\vec{r}_i - \vec{r}_j).$$

We are interested in terms in the matrix element $< A|V|A >$ which differentiate the various quantum numbers the electrons in the unfilled shell can have. Since V is a two body operator, any such terms will have the general form of Eq.(**??**), in particular, there will be a 'direct' term and an 'exchange' term. To simplify our writing we use i for r_i, $\vec{i}$ for $\vec{r}_i$, and $\hat{i}$ for $\hat{r}_i$. For a specific electron j in the unfilled shell, the direct term for the sum over all electrons in the filled n, l shell is

$$\sum_{i \in n,l} < a_i, a_j | \frac{e^2}{|\vec{i} - \vec{j}|} | a_i, a_j > \tag{3}$$

The wave function for the ith electron in the filled n, l shell is then

$$R_{nl}(i) Y_{lm}(\hat{i}) \chi_s, \tag{4}$$

while for the jth electron in the unfilled n', l' shell the wave function is

$$R_{n'l'}(j) Y_{l'm'}(\hat{j}) \chi_{s'}, \tag{5}$$

The direct term as defined in Eq.(3) is then explicitly,

$$\sum_{m,s} \int d^3\vec{i} d^3\vec{j} R^*_{nl}(i) Y^*_{lm}(\hat{i}) R_{nl}(i) Y_{lm}(\hat{i}) \frac{e^2}{|\vec{i} - \vec{j}|} R^*_{n'l'}(j) Y^*_{l'm'}(\hat{j}) R_{n'l'}(j) Y_{l'm'}(\hat{j}) (\chi^\dagger_s \chi_s)(\chi^\dagger_{s'} \chi_{s'}) \tag{6}$$

This expression simplifies greatly when we use the fact that

$$\sum_m |Y_{lm}(\theta, \phi)|^2 = \frac{2l+1}{4\pi}. \tag{7}$$

This means that the only dependence on $\hat{i}$ comes from the Coulomb potential itself. For the Coulomb potential, we use the expansion

$$\frac{1}{|\vec{r} - \vec{r'}|} = \sum_{k=0}^{\infty} \sum_{t=-l}^{l} \frac{4\pi}{2k+1} \left(\frac{r^k_<}{r^{k+1}_>}\right) Y_{kt}(\hat{r}) Y_{kt}(\hat{r}'), \tag{8}$$

where $r_>$ is the greater of r, r', etc for $r_<$. We used the summing indices k, t instead of the more usual l, m, since m, l already occur in our expression. Using Eq.(7) and substituting for the Coulomb potential from Eq.(8), we see that the integral over solid angle of $\vec{i}$ can be done immediately, and only the $k = 0, t = 0$ term in the sum survives. We finally have for the direct term involving the Coulomb interaction between the electrons in the filled nl shell and a single electron in the unfilled $n'l'$ shell,

$$2(2l+1)e^2 \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 |R_{nl}(r_1)|^2 (\frac{1}{r_>}) |R_{n'l'}(r_2)|^2, \tag{9}$$

where we called the integration variables r_1 and r_2 instead of r_i and r_j, and $r_>$ is the greater of r_1, r_2.

The most important feature of the result in Eq.(9) is that it is totally independent of m' and s'. This is actually easy to understand. The sum over the occupied shell must produce a spherically symmetric potential, and a spherically symmetric spin-independent potential cannot distinguish m' or s'. So, returning to our case where there are 2 $l = 1$ electrons outside of a set of filled shells, the direct Coulomb interaction of these electrons with those in filled shell will be the same whether the $l = 1$ electrons are in any of the states ${}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2, {}^1S_0$. Since it is spherically symmetric and independent of spin, this direct Coulomb term should really be included in the average central potential mentioned earlier.

Turning to the exchange term, for a specific electron j in the unfilled shell, the exchange term for the sum over all electrons in the filled n, l shell is

$$-\sum_{i \in n,l} < a_i, a_j | \frac{e^2}{|\vec{i} - \vec{j}|} | a_j, a_i > \tag{10}$$

Using the wave functions defined in Eqs.(4) and (5), the explicit form for the exchange term is

$$-\sum_{m,s} \int d^3\vec{i} d^3\vec{j} R^*_{nl}(i) Y^*_{lm}(\hat{i}) R_{n'l'}(i) Y_{l'm'}(\hat{i}) \frac{e^2}{|\vec{i} - \vec{j}|} R^*_{n'l'}(j) Y^*_{l'm'}(\hat{j}) R_{nl}(j) Y_{lm}(\hat{j}) (\chi_s^\dagger \chi_{s'}) (\chi_{s'}^\dagger \chi_s) \tag{11}$$

Substituting the expansion of the Coulomb potential from Eq.8), we will have two integrals to perform over solid angle, namely

$$\int d\Omega_i Y^*_{lm}(\hat{i}) Y_{kt}(\hat{i}) Y_{l'm'}(\hat{i}), \tag{12}$$

and

$$\int d\Omega_j Y^*_{l'm'}(\hat{j}) Y^*_{kt}(\hat{j}) Y_{lm}(\hat{j}). \tag{13}$$

(Note that we took the complex conjugate of the terms in spherical harmonics in Eq.8)¿ This is valid, since the sum is real.)

The integral of three spherical harmonics is well-known, and given by

$$\int d\Omega_i Y^*_{l_3 m_3}(\hat{i}) Y_{l_1 m_1}(\hat{i}) Y_{l_2 m_2}(\hat{i}) = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}} C(l_1, m_1, l_2, m_2; l_3, m_3) C(l_1, 0, l_2, 0; l_3, 0) \tag{14}$$

where the result vanishes unless $m_3 = m_1 + m_2$. The C's are Clebsch-Gordon coefficients. They occur in the addition of angular momentum. In Dirac notation, they are

$$C(l_1, m_1, l_2, m_2; l_3, m_3) \equiv < l_1, m_1, l_2, m_2 | l_3, m_3) >, \tag{15}$$

where in addition to $m_3 = m_1 + m_2$, the Clebsch-Gordon coefficient vanishes unless $l_3 \in |l_1 - l_2|, l_1 + l_2$. Using this result, we have for the integral of Eq.(13),

$$\int d\Omega_j Y^*_{l'm'}(\hat{j}) Y_{kt}(\hat{j}) Y_{lm}(\hat{j}) = \sqrt{\frac{(2k+1)(2l+1)}{4\pi(2l'+1)}} < k, t, l, m | l', m' >< k, 0, l, 0 | l', 0 > \tag{16}$$

The integral of Eq.(12) is the complex conjugate of this,

$$\int d\Omega_i Y^*_{lm}(\hat{i}) Y^*_{kt}(\hat{i}) Y_{l'm'}(\hat{i}) = \sqrt{\frac{(2k+1)(2l+1)}{4\pi(2l'+1)}} < l', m' | k, t, l, m >< l', 0 | k, 0, l, 0 > \tag{17}$$

The index m is the L_3 value of an electron in the filled shell, and the index t is the index on the spherical harmonic that comes into the expansion of the Coulomb potential, Eq.(8). Both are summed over. The sum is easy to carry out, since in multiplying the results of the integrals Eqs.(16) and (17), we have the sum

$$\sum_{m,t} < l', m' | k, t, l, m >< k, t, l, m | l', m' >= 1. \tag{18}$$

The sum over m, t in Eq.(18) amounts to a sandwiching of the identity in $< l', m' | l', m' >$.

Putting all the pieces together, we have for the exchange contribution of Eq.(11)

$$-e^2 \frac{(2l+1)}{(2l'+1)} \sum_{k=0}^{\infty} | < k, 0, l, 0 | l', 0 > |^2 \int r_1^2 dr_1 r_2^2 dr_2 R^*_{nl}(r_1) R^*_{n'l'}(r_2) (\frac{r^k_<}{r^{k+1}_>}) R_{n'l'}(r_1) R_{nl}(r_2) \tag{19}$$

This term is also totally independent of m', and s'. While this exchange term could not be represented as a contribution to a spherically symmetric average potential, it shares the property that it cannot distinguish between the states ${}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2, {}^1S_0$. The conclusion so far is that the interaction of electrons in in the outer unfilled shell with electrons in the inner filled shells cannot decide between the various possibilities for the ground state of the atom.

Interactions between electrons in an unfilled shell Finally let us turn to the interactions of the electrons in the n', l' shell with themselves. Since n' and l' are fixed, these electrons all have the same radial wave function. It will turn out that the angular wave functions and angular integrals will be the determining factor in distinguishing states. We will consider the case of 2 electrons in an unfilled shell, with indices m'_1, s'_1 and m'_2, s'_2. We start with the direct Coulomb interaction. We may write down this term by eliminating the sum on m, s and making a few changes of indices in Eq.(6). We have

direct :

$$\int d^3\vec{i}d^3\vec{j}R^*_{n'l'}(i)Y^*_{l'm'_1}(\hat{i})R_{n'l'}(i)Y_{l'm'_1}(\hat{i})\tfrac{e^2}{|\vec{i}-\vec{j}|}R^*_{n'l'}(j)Y^*_{l'm'_2}(\hat{j})R_{n'l'}(j)Y_{l'm'_2}(\hat{j})(\chi^\dagger_{s'_1}\chi_{s'_1})(\chi^\dagger_{s'_2}\chi_{s'_2}) \tag{20}$$

The factor involving spinors is unity, so the main work will be to understand the angular integrals. Similarly, we can get the exchange term for this case by slight modifications of Eq.(11). We have

exchange :

$$-\int d^3\vec{i}d^3\vec{j}R^*_{n'l'}(i)Y^*_{l'm'_1}(\hat{i})R_{n'l'}(i)Y_{l'm'_2}(\hat{i})\tfrac{e^2}{|\vec{i}-\vec{j}|}R^*_{n'l'}(j)Y^*_{l'm'_2}(\hat{j})R_{n'l'}(j)Y_{l'm'_1}(\hat{j})(\chi^\dagger_{s'_1}\chi_{s'_2})(\chi^\dagger_{s'_2}\chi_{s'_1}). \tag{21}$$

Here the spinor factor vanishes unless $s'_1 = s'_2$. This is typical of an exchange contribution. An analogous result occurred in the exchange interaction between an electron in an unfilled shell and an electron in a filled shell. The sum on s in Eq.(11) picked out $s = s'$.

As in previous examples, both the direct and exchange terms break up into radial integrals and angular integrals. If we substitute the expansion of the Coulomb potential from Eq.(8), the radial integral part of both expressions becomes

$$\frac{4\pi e^2}{2k+1}\int r_i^2 dr_i r_j^2 dr_j |R_{n'l'}(r_i)|^2 |R_{n'l'}(r_j)|^2 \frac{(r_<)^k}{(r_>)^{k+1}} \tag{22}$$

Turning to the angular integrals, for the direct term we have

$$\left(\int d\Omega_i Y^*_{l'm'_1}(\hat{i})Y_{kt}(\hat{i})Y_{l'm'_1}(\hat{i})\right)\left(\int d\Omega_j Y^*_{l'm'_2}(\hat{j})Y^*_{kt}(\hat{j})Y_{l'm'_2}(\hat{j})\right). \tag{23}$$

For the exchange term we have

$$\left(\int d\Omega_i Y^*_{l'm'_1}(\hat{i})Y_{kt}(\hat{i})Y_{l'm'_2}(\hat{i})\right)\left(\int d\Omega_j Y^*_{l'm'_2}(\hat{j})Y^*_{kt}(\hat{j})Y_{l'm'_1}(\hat{j})\right). \tag{24}$$

To evaluate these integrals, we use Eqs.(14) and (15). For the direct integral of Eq.(23), we have

$$\frac{(2k+1)(2l'+1)}{4\pi(2l'+1)} < k0l'm'_1|l'm'_1 >< k0l'0|l'0 >^2< k0l'm'_2|l'm'_2 > \tag{25}$$

For the exchange angular integral of Eq.(24), we have

$$\frac{(2k+1)(2l'+1)}{4\pi(2l'+1)}\left(< k, m_1'-m_2', l'm_2'|l'm_1' >< k0l'0|l'0 >\right)^2 \tag{26}$$

Next, we will put all the pieces together. Since we are only interested in *relative* spacings of the levels $^1D_2, ^3P_0, ^3P_1, ^3P_2, ^1S_0$, we will lump all factors that are independent of l' into a constant, denoted as A_k. The sum of direct and exchange interactions of the unfilled shell electrons from Eqs.(20) and (21) can then be written as

$$\sum_{k=0}^{\infty} A_k < k0l'0|l'0 >^2 \left(< k0l'm_1'|l'm_1' >< k0l'm_2'|l'm_2' > -\delta_{s_1',s_2'} < k, m_1'-m_2', l'm_2'|l'm_1' >^2\right) \tag{27}$$

Now let us make use of the fact that $l' = 1$. The Clebsch-Gordon coefficient $< k0l'0|l'0 >$ is for the addition of angular momentum k to $l' = 1$ to get a resulting angular momentum $l' = 1$. The allowed values of k are then $k = 0, 1, 2$, so the apparently infinite sum on k is really finite. Furthermore there is a general property of Clebsch-Gordon coefficients that can be used to eliminate $k = 1$. The Clebsch-Gordon coefficient $< l_1 0 l_2 0|l_3 0 >$ vanishes unless $l_1 + l_2 + l_3$ is *even*. This follows from parity considerations. So in our case, the sum over k collapses to $k = 0$ and $k = 2$ terms. Furthermore, the $k = 0$ term cannot distinguish between our states. This is clear intuitively. The $k = 0$ term is spherically symmetric, so it cannot shift the states of different L apart. At a more detailed level, the $k = 0$ term in Eq.(27) is $A_0(1 - \delta_{m_1',m_2'}\delta_{s_1',s_2'})$. If we set $m_1' = m_2' = 1$ and $s_1' = 1/2, s_2' = -1/2$, we have projected on ^1D, and we obtain A_0. If we set $m_1' = 1, m_2' = 0$, along with $s_1' = s_2' = 1/2$, we have projected on ^3P, and we again obtain A_0. Finally, if we set $m_1' = m_2' = 0$, along with $s_1' = 1/2, s_2' = -1, 2$, we again get A_0. This combination does not directly give ^1S, but instead gives the combination $(2/3)(^1D) + (1/3)(^1S)$. (This will be explained below.) But since we already have that ^1D gives A_0, it follows that ^1S is also A_0. The conclusion is that the $k = 0$ term does not distinguish among $^1D_2, ^3P_0, ^3P_1, ^3P_2, ^1S_0$.

We are finally left with understanding the $k = 2$ term in Eq.(27). A useful aid in this is the extensive table given in the Wikipedia website "Table of Clebsch-Gordon coefficients." The notation there is $< j_1 m_1 j_2 m_2|j_1 j_2 j m >$, which we have denoted as $< j_1 m_1 j_2 m_2|j_3 m_3 >$. Glancing at Eq.(27) for $k = 2$, in the notation of the Wikipedia table, we have $j_1 = 2, j_2 = 1, j = 1$. From the table, we have

$$< k0l'0|l'0 >=< 2010|10 >= -\sqrt{\frac{2}{5}}. \tag{28}$$

The square of this factor occurs in Eq.(27) and can be absorbed into A_2. The terms that will distinguish our states all occur inside the large parenthesis in Eq.(27). Let us take each state in turn. In the notation $^S L_J$, when there is more than one possibility for J, since we are not (yet) taking into account spin orbit coupling, these will all have the same energy. For our case, this means $^3P_0, ^3P_1, ^3P_2$ all have the same energy.

We now take each case in turn. The results do not depend on the value of L_3 or S_3. At the present level, without spin orbit coupling, all of L^2, L_3, S^2, S_3 are conserved. This makes it easy to project out the quantities we want by choosing L_3 and S_3 appropriately.

- ${}^1D_2$ To insure $L = 2$, we take $m'_1 = m'_2 = 1$. The Pauli principle will be satisfied if $s'_1 = 1/2, s'_2 = -1/2$. Our term is then

$$A_2 < 2011|11 >^2 = A_2(\sqrt{\frac{1}{10}})^2 = \frac{A_2}{10} \tag{29}$$

- ${}^3P_{2,1,0}$ We can guarantee that $S = 1$ if we take $s'_1 = s'_2 = 1/2$. The Pauli principle is satisfied if we take $m'_1 = 1, m'_2 = 0$. Our term is then

$$A_2(< 2011|11 >< 1010|10 > - < 2110|11 >^2) \tag{30}$$

$$= A_2 \left(\sqrt{\frac{1}{10}})(-\sqrt{\frac{2}{5}}) - (-\sqrt{\frac{3}{10}})^2 \right) = -\frac{A_2}{2}$$

- ${}^1S_0$ This case is slightly tricky. If we choose $m'_1 = m'_2 = 0$, we get $L_3 = 0$, but both $L = 2$ and $L = 0$ are included. To get what we want, we use the fact that

$$|m'_1 = 0, m'_2 = 0 >= \sqrt{\frac{2}{3}}|L = 2, M = 0 > + \sqrt{\frac{1}{3}}|L = 0, M = 0 > . \tag{31}$$

Setting $m'_1 = m'_2 = 0$, and $s'_1 = 1/2, s'_2 = -1/2$, we get

$$A_2 < 2010|10 >^2 = A_2(\sqrt{\frac{2}{5}})^2 = \frac{2A_2}{5}.$$

Using Eq.(31), we have

$$\frac{2A_2}{5} = (\frac{2}{3})({}^1D_2) + (\frac{1}{3})({}^1S_0) \tag{32}$$

Using ${}^1D_0 = A_2/10$, we finally have

$${}^1S_0 = A_2. \tag{33}$$

At this point, we can write formulas for the energies of the various states. We denote by E_0 all contributions to the energy which do not distinguish the states ${}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2, {}^1S_0$. We have

$$p^2 \left\{ \begin{array}{lcl} E({}^1S) & = & E_0 + A_2 \\ E({}^1D) & = & E_0 + A_2/10 \\ E({}^3P) & = & E_0 - A_2/2 \end{array} \right. \tag{34}$$

Neither E_0 nor A_2 are known without a full, detailed calculation. However, we can still check the above by taking a ratio of energy differences. From Eq.(34), we have

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = \frac{3}{2}. \tag{35}$$

This value may be compared with experimental results for several atoms. The following table is taken from *Condon and Shortley*, p. 198.

Atom	*Configuration*	$(E(^1S) - E(^1D))/(E(^1D) - E(^3P))$
Theory	np^2	1.50
C I	$2p^2$	1.13
N II	$2p^2$	1.14
O III	$2p^2$	1.14
Si I	$3p^2$	1.48
Ge I	$4p^2$	1.50
Sn I	$5p^2$	1.39
La II	$6p^2$	18.43
Pb I	$6p^2$	0.62

(36)

The agreement between theory and experiment is qualitatively correct and even semi-quantitative except for *La II* and *Pb I*, where the whole notion of $L - S$ coupling breaks down. The alternative to ignoring spin-orbit coupling as in the $L-S$ scheme, is to include the spin-orbit coupling and try to treat the electrostatic repulsion of the electrons as small. This is known as $J - J$ coupling, and is discussed at length in *Condon and Shortley.*

Ground State Configurations including Spin-Orbit Without going into as much detail as just done for the IVA column of the Periodic Table, it is possible to figure out the ground state configuration for most atoms using a few simple arguments which are quantum mechanical in origin. These are known as "Hund's Rules," after the German physicist Friedrich Hund, who formulated them in 1927. We will illustrate them for the second row of the Periodic Table; the elements $Li, Be, B, C, N, O, F, Ne$. Using the central field approximation, these elements all have a filled $1s^2$ shell, often denoted as a He shell. For the electrons outside of this filled shell the following table gives the electronic configuration of the unfilled shell, and the ground state configuration.

Z	*element*	*configuration*	*ground state*
3	Li	$(He)2s$	$^2S_{1/2}$
4	Be	$(He)2s^2$	$^1S_0$
5	B	$(He)2s^22p$	$^2P_{1/2}$
6	C	$(He)2s^22p^2$	$^3P_0$
7	N	$(He)2s^22p^3$	$^4S_{3/2}$
8	O	$(He)2s^22p^4$	$^3P_2$
9	F	$(He)2s^22p^5$	$^2P_{3/2}$
10	Ne	$(He)2s^22p^6$	$^1S_0$

A closed shell, meaning all states with a given n, l, has zero values for $L^2, S^2, J^2, L_3, S_3, J_3$. This is easy to show and is explored in the next Exercise.

Exercise 1 Consider as a specific case, a filled p shell, i.e. one with 6 electrons, all with the same radial wave function, and all having $l = 1$. Show that such a state has $L^2 = S^2 = J^2 = 0$. This can be done using the definition of a state satisfying the Pauli Principle,(Eq.(**??**) in the previous notes) along with raising and lowering operators for spin and orbital angular momentum.

Now let us examine ground states of the atoms listed in the table above. Lithium has one electron outside of a Helium core, so it certainly has $S = 1/2$ and getting the electron close to the nucleus says this electron should have $L = 0$. So Lithium has ${}^2S_{1/2}$ as its ground state. Beryllium is similar to Helium, so its ground state is ${}^1S_0$. Boron has one p electron outside of filled shells, so it certainly has $S = 1/2$, and $L = 1$. The rule for adding $\vec{L}$ and $\vec{S}$ to get $\vec{J}$ would permit $J = 3/2, 1/2$. But just as in hydrogen, the lower J value is favored by spin-orbit coupling so Boron has the ground state ${}^2P_{1/2}$. Next we have Carbon. From the previous notes, we know that we have $S = 1, L = 1$. These could add up to $J = 2, 1, 0$, but spin-orbit coupling will favor $J = 0$, so the ground state of Carbon is ${}^3P_0$. Nitrogen is our first case with more than two electrons in an unfilled shell. The allowed values of spin are $3/2, 1/2, 1/2$. The $S = 3/2$ state is totally symmetric. This would require a totally antisymmetric spacial wave function. This is good, since a totally antisymmetric wave function will be best at keeping the electrons apart, and therefore minimizing the Coulomb repulsion. A totally antisymmetric state of three p electrons has $L = 0$. (See the next exercise.) We have then that the ground state of Nitrogen is ${}^4S_{3/2}$.

Exercise 2 Show that three $l = 1$ electrons with the same radial wave function have $L = 0$ if the spacial wave function is totally antisymmetric.

Turning to Oxygen, we now have four p electrons. This looks complicated, but not if we regard it as *a completely filled shell minus 2 electrons.* This a first example of the concept of *hole*, or the absence of an electron. Pursuing this, we think of Oxygen as two holes outside of filled shells. By the same reasoning we used in Carbon, minimizing the Coulomb repulsion will say that the ground state should have $S = 1, L = 0$. The ground state of Oxygen is ${}^3P_2$. What happened to the spin-orbit coupling rule of favoring the lowest J value? The answer is that holes have positive charge, opposite to electrons, but feel the same magnetic field as electrons. So for holes, the spin magnetic moment wants to *align* with the orbital angular momentum, so the highest value of J is favored. The same argument applies to Fluorine, which has one hole outside of filled shells, so $S = 1/2, L = 1$. The largest J is again favored by spin-orbit coupling so the ground state of Fluorine is ${}^2P_{3/2}$. Finally, for Neon, the whole p shell is filled and its ground state is then ${}^1S_0$.

Constructing Anti-symmetric Angular Wave Functions For filling the outermost shell of an atom, it is invariably advantageous to minimize the Coulomb repulsion between the electrons in this shell. The way to do this is to take a totally symmetric state for the spins of the electrons in the unfilled shell, and a totally anti-symmetric spacial wave functions for these same electrons. Since by being in a certain shell, the electrons all have the same radial wave function, anti-symmetry in space then involves the angular wave function. The best way to illustrate how to do this is with examples.

- **3 electrons in a p shell** The electrons all have $l = 1$, so the only quantum number to play with is $m = 1, 0, -1$. We can build a state by writing

  $$|A >= \frac{1}{\sqrt{3!}}(\sum_P (-1)^p P|10-1>) \tag{37}$$

  $$= \frac{1}{\sqrt{6}}(|10-1> -|01-1> +|0-11> -|-101> +|-110> -|1-10> .$$

  This state certainly has $L_3 = 0$. Applying L_+, it is easy to show that $L_+|A >= 0$, which proves $L = 0$.

- **3 electrons in a d shell** Here we again can only play with $m = 2, 1, 0, -1, -2$. Suppose we take the biggest M we can get, consistent with anti-symmetry. This is done with the three m values $2, 1, 0$. Then we write

  $$|A >= \frac{1}{\sqrt{3!}}\sum_P (-1)^p P|210> . \tag{38}$$

  This state clearly has $L_3 = 3$. We show that $L = 3$ by again using the raising operator and showing that $L_+|A >= 0$.

- **4 electrons in a d shell** Again we have only $m = 2, 1, 0, -1, -2$. Following the same method, we can build an antisymmetric state for four electrons out of $m = 2, 1, 0, -1$. We write

  $$|A >= \frac{1}{\sqrt{4!}}\sum_P (-1)^p P|210-1> . \tag{39}$$

  This state has $L_3 = 2$, and we show it has $L = 2$ by again showing that $L_+|A >= 0$.

- **5 electrons in a d shell** Here we use $m = 2, 1, 0, -1, -2$. This case is very similar to three electrons in a p shell. We have

  $$|A >= \frac{1}{\sqrt{5!}}\sum_P (-1)^p P|210-1-2> . \tag{40}$$

  The state has $L_3 = 0$ and is shown to have $L = 0$ by showing $L_+|A >= 0$.

- **4-6 electrons in p shell or $6-10$ electrons in d shell** To treat these cases, regard the system as a *filled* shell minus a certain number of *holes*. So for example 4 electrons in a p shell is better treated as 2 holes in a p shell. To minimize the repulsion between holes, the same arguments apply, so symmetric spin and anti-symmetric spacial wave function is chosen. However, since holes act like *positive* charges, the sign of spin-orbit coupling is reversed and the state with *maximum* J is favored instead of the usual case of the minimum value of J.