Atoms, Energy Levels and Spectroscopy

Energy Levels in Atoms (13.2, 13.3, 13.4, 13.5)
Coupling of Angular Momenta (13.7, 13.8)
Term Symbols and Selection Rules (13.9)
Russell-Saunders Coupling (13.9)

Examples
Hydrogen and Alkali Metal Atoms
Helium
Selection rules and other polyelectronic atoms

Supplementary Notes
Coupling of Angular Momenta
Hyperfine Splitting
Zeeman Interaction
Stark Effect
Atomic Spectroscopy

Electronic spectroscopy is the study of absorption and emission transitions between electronic states in an atom or a molecule.

Atomic spectroscopy is concerned with the electronic transitions in atoms, and is quite simple compared to electronic molecular spectroscopy. This is because atoms only have translational and electronic degrees of freedom, and sometime influenced by nuclear spin (molecules also have vibrations and rotations).

Recall (Lecture 5) that for hydrogen and hydrogen-like ions (i.e., He\(^+\), Li\(^{2+}\), Be\(^{3+}\), etc.) with a single electron and a nucleus with charge +Ze, the hamiltonian is:

\[
\mathcal{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}
\]

\(\mu = \frac{m_em_p}{m_e + m_p}\)  
reduced mass

\(e = 1.6021 \times 10^{-19} \text{ C}\)  
charge on an electron

\(r = \text{distance between } +e \text{ and } -e\)

\(\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ s}^2 \text{ kg}^{-1} \text{ m}^{-3}\)  
permittivity of free space

For a polyelectronic atom, the hamiltonian becomes:

\[
\mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}
\]

summed over \(i\) electrons. The new term describes coulombic repulsions between pairs of electrons which are distance \(r_{ij}\) apart (second term is coulombic attraction between nucleus and electrons)
SCF Method

The electron-electron repulsion term creates a many-body problem, in which the hamiltonian cannot be broken down into a sum of contributions from each electron - the result is that the Schroedinger equation cannot be solved exactly.

Methods of approximation have been devised, including that of Hartree, who replaces the electron repulsions with a sum of potential energy functions from separate electrons. This is known as the self-consistent field (SCF) method, under which the Schroedinger equation can be solved.

\[ \mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_i V(r_i) \]

The electron repulsions remove degeneracy of orbitals with different orbital angular momenta (like 3\(s\), 3\(p\), 3\(d\), which are degenerate in the H atom) - see next page

The atomic orbital (AO) energies vary with the principal quantum number \(n = 1, 2, 3, \ldots\) and the orbital angular momentum, \(\ell = 0, 1, 2, \ldots\) for \(s, p, d, \ldots\) orbitals.

Plots of the SCF Hartree-Fock radial distribution functions are shown for sodium - electron density is grouped into shells, as anticipated by early chemists!
Electron Configurations

The value of the orbital energy increases with the nuclear charge of the atom (the energy to remove an electron from the 1s orbital, the ionization energy, is 13.6 eV for He and 870.4 eV for Ne).

A comparison of the AO energy levels in a hydrogen-like atom/ion and a polyelectronic atom/ion are shown below:

The **aufbau** or building-up principle: electrons are “fed” into the orbitals in order of increasing energy until the electrons are used up - this gives the ground configuration of the atom.

The **Pauli-exclusion principle**: no two electrons may have the same set of quantum numbers: \( n, \ell, m_\ell, m_s \). Since \( m_\ell \) can have \( 2\ell + 1 \) possible values and \( m_s = \pm \frac{1}{2} \), each orbital characterized by \( n \) and \( \ell \) can have \( 2(2\ell + 1) \) electrons.
Configurations & States

Orbital: particular values of $n$ and $\ell$
Shell: all orbitals with same value of $n$
For $n = 1, 2, 3, 4, \ldots$ shells are labelled $K, L, M, N, \ldots$

A configuration describes the manner in which the electrons are distributed among the orbitals, but a given configuration may give rise to more than one state - the nature of the states depend on how the electrons couple with one another, resulting in states of different energies.

Trends in the periodic table:
alkali metals: outer $ns^1$ configuration, monovalent
alkaline earth metals: outer $ns^2$ configuration, divalent
noble gases: outer $np^6$ configuration, filled orbital sub-shell results in their characteristic chemical inertness
first transition series: characterized by filling of the $3d$ orbital ($3d$ and $4s$ are similar in energy, but their separation changes along the series).
Examples:
Cu has a $KLM4s^1$ or $KL3d^{10}4s^1$ ground configuration, the completely filled $3d^{10}$ orbital has an “innate stability”
Cr has a $KL3s^23p^63d^54s^1$ ground configuration, in some cases half-filled $d$-orbitals confer stability onto a particular configuration
lanthanides: filling of the $4f$ orbital is characteristic of the lanthanides, but since $4f$ and $5d$ are of similar energy, in some cases one electron will go into the $5d$ orbital
Angular Momenta & Magnetic Moments

An electron in an atom has two possible sources of angular momenta: orbital angular momentum and spin angular momentum. The orbital angular momentum vector for a single electron is given by:

\[ \ell(\ell + 1)\frac{1}{2}\hbar = \ell \hbar \]

where \( \ell = 0, 1, 2, \ldots \) (the quantity \([A(A+1)]^{1/2}\) happens so much in these discussions that we denote it as \(A^*\)).

The spin angular momentum vector for a single electron is:

\[ s(s + 1)\frac{1}{2}\hbar = s \hbar \]

where \( s = \frac{1}{2} \). For an electron with both types of angular momentum, there is a quantum number \( j \), assigned to the total angular momentum, which is a vector quantity:

\[ j(j + 1)\frac{1}{2}\hbar = j \hbar \]

\[ j = \ell + s, \ell + s - 1, \ldots, |\ell - s| \]

For one-electron atoms, where \( s = \frac{1}{2} \), \( j \) is not very useful (unless considering fine structure), but the quantum number \( J \) (for polyelectronic atoms) is very important.

If the nucleus has a non-zero spin quantum number \( I \), there may be a coupling from nuclear spin angular momentum:

\[ I(I + 1)\frac{1}{2}\hbar = I \hbar \]

Since the nucleus is so large compared to the electron, this angular momentum is considerably smaller, so can normally be neglected - however, if looking at fine structure, this additional angular momentum results in hyperfine splitting in atomic spectra.
Angular Momenta & Magnetic Moments, 2

A charge \(-e\) circulating in an orbit is equivalent to current flowing through a circular wire. The latter causes a magnetic field perpendicular to the plane of the loop:

while the former results in a magnetic moment.

The magnetic moment \(\mu_\ell\) from orbital angular momentum is opposite direction to the orbital angular momentum vector, \(\ell\). The classical picture of the electron spinning about its own axis gives a magnetic moment \(\mu_s\) in the opposite direction to the spin angular momentum vector \(s\).

\(\mu_\ell\) and \(\mu_s\) may be parallel or antiparallel, and can be regarded as tiny classical bar magnets that interact.
Singlet & Triplet States

He: \(1s^12s^1\) excited configuration (ground: \(1s^2\)), so electrons do not have to be paired since they are in different orbitals. According to Hund’s rules, the state of the atom with spins parallel lies lower in energy than the state in which they are paired (though both states are allowed).

Parallel and antiparallel spins differ in overall angular momentum. When they are paired, zero net spin, called the singlet state:

\[
\sigma_-(1,2) = 2^{-1/2} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right]
\]

The spin angular momenta of two parallel spins add together for non-zero total spin, this is the triplet state:

\[
\begin{align*}
\sigma_+(1,2) &= 2^{-1/2} \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right] \\
\alpha(1)\alpha(2) &= \beta(1)\beta(2)
\end{align*}
\]

In the singlet state, the anti-parallel pair of spins are precisely anti-parallel, and the resultant vector is zero.

In the triplet state, the parallel pair of spins are not precisely parallel; rather, the angle between the spin angular momentum vectors is always constant, so all three arrangements have the same total spin angular momentum.
Coupling of Angular Momenta

The interaction of $\mu_\ell$ and $\mu_s$ (like small classical bar magnets) is referred to as coupling of angular momenta. The larger the magnetic moments involved, the greater the size or strength of the coupling.

The coupling of two vectors $\mathbf{a}$ and $\mathbf{b}$ produces a resultant vector $\mathbf{c}$. If these vectors represent angular momenta, then $\mathbf{a}$ and $\mathbf{b}$ undergo precession around $\mathbf{c}$. The rate of precession (or precession frequency) increases as the strength of the coupling increases.

Normally, $\mathbf{c}$ precesses about some arbitrary direction in space, unless in the presence of an electric or magnetic field (Stark and Zeeman effects, respectively), in which case space quantization may be observed.

The spin of one electron can interact with:
(a) spins of other electrons
(b) its own orbital motion ($ls$ or $jj$- coupling, often important only for few states of heavy atoms)
(c) orbital motion of other electrons (very small)
Russell-Saunders Coupling

If we make the approximation that (i) the coupling between the spin of an electron and its orbital momentum can be neglected (no $jj$-coupling), but that (ii) coupling between orbital momenta is significant and (iii) coupling between spin momenta is weak but appreciable, then this is the opposite extreme to $jj$-coupling known as the **Russell-Saunders coupling approximation**, and provides a useful way of describing the states of most atoms.

**Non-equivalent electrons** are those which have different values of $n$ or $\ell$: e.g., $3p^1 3d^1$ or $3p^1 4p^1$ configurations have non-equivalent electrons, but $2p^2$ electrons are equivalent.

Consider the coupling of orbital angular momenta of two non-equivalent electrons, which is known as **$\ell\ell$ coupling**.

For example, the He atom with excited configuration $2p^1 3d^1$, where the $2p$ and $3d$ electrons are labelled 1 and 2 so that $\ell_1 = 1$ and $\ell_2 = 2$, which have vectors with magnitudes of $2^{1/2} \hbar$ and $6^{1/2} \hbar$, respectively. These vectors couple to give a resultant $L$ of magnitude:

$$[L(L + 1)]^{1/2} \hbar = L \hbar$$

The values of the total orbital angular momentum number $L$ are limited, since the relative orientations of $\ell_1$ and $\ell_2$ are limited to the **Clebsch-Gordan series**:

$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, ..., |\ell_1 - \ell_2|$$

In this example, $L = 3, 2$ or 1 and magnitude of $L$ is $12^{1/2} \hbar$, $6^{1/2} \hbar$ or $2^{1/2} \hbar$ (see next page).
Coupling

One can calculate the possible values of the magnitude of $L$ and then construct vector diagrams showing this coupling:

The terms of the atoms are labelled as $S, P, D, F, G, ...$ for $L = 0, 1, 2, 3, 4, ...$ (capital letters are for multielectron atoms). So the $2p^13d^1$ configuration gives rise to $P, D$ and $F$ terms (Figure a). If a third electron is present, then coupling in a third vector to any of the $L$ in the figure above will give terms arising from three non-equivalent electrons.

For a filled sub-shell (e.g., $2p^6$ or $3d^{10}$), $L = 0$.

Space quantization of the total orbital angular momentum produces $2L + 1$ components, $M_L = L, L-1, ..., -L$. In a filled sub-shell, $\sum_i (m_\ell)_i = 0$ (sum over all electrons in sub-shell). Since $M_L = \sum_i (m_\ell)_i$, it follows that $L = 0$. 
Coupling between spin momenta is known as **ss coupling**. The coupling of \( s \) vectors is treated the same way as \( \ell \ell \) coupling. However, since \( s = \frac{1}{2} \), the vector for each electron always has a magnitude of \( 3^{1/2} \hat{\mathbf{s}} \). Two \( s \) vectors take up orientations w.r.t. one another such that

\[
[S(S + 1)]^{1/2} \hat{\mathbf{s}} = S^* \hat{\mathbf{s}}
\]

where \( S \) is the total spin quantum number, restricted to:

\[
S = s_1 + s_2, \ s_1 + s_2 - 1, \ldots, |s_1 - s_2|
\]

For two electrons, \( S = 0 \) or \( S = 1 \) (**Figure b**), with magnitudes 0 and \( 2^{1/2} \hat{\mathbf{s}} \).

The labels for the terms indicate the value of \( S \) by having a \( 2S + 1 \) pre-superscript on the \( S, P, D, F, \ldots \) labels. This value of \( 2S + 1 \) is called the **multiplicity**, and is the number of values that \( M_S \) can take:

\[
M_S = S, \ S - 1, \ldots, -S
\]

For two electrons, \( S = 0 \) or 1, and the multiplicity is 1 or 3, giving terms called **singlet** or **triplet**, respectively. For a filled orbital, just like \( L = 0, S = 0 \) for the same reasons.

For C and Si excited configurations:

- **C** \( 1s^22s^22p^13d^1 \)
- **Si** \( 1s^22s^22p^63s^23p^13d^1 \)

both possess \( P, D \) and \( F \) terms and considering multiplicity both possess \( ^1P, ^3P, ^1D, ^3D, ^1F \) and \( ^3F \) terms. Noble gases, which have all occupied orbitals filled, have only \( ^1S \) terms in their ground state configurations.
Total Angular Momentum

Some terms arising from configurations of non-equivalent and equivalent electrons are shown below:

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Terms</th>
<th>Configuration</th>
<th>Terms†</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s,s^1$</td>
<td>$^1S$</td>
<td>$p^2$</td>
<td>$^1S,^3P,^1D$</td>
</tr>
<tr>
<td>$s,p^1$</td>
<td>$^1S,^3P$</td>
<td>$p^3$</td>
<td>$^4S,^2P,^2D$</td>
</tr>
<tr>
<td>$s,d^1$</td>
<td>$^1S,^3P,^1D$</td>
<td>$d^2$</td>
<td>$^1S,^3P,^1D,^3F,^1G$</td>
</tr>
<tr>
<td>$s,f^1$</td>
<td>$^1D,^3F$</td>
<td>$d^3$</td>
<td>$^2P,^4P,^2D(2),^2F,$</td>
</tr>
<tr>
<td>$p,p^1$</td>
<td>$^1S,^3P,^1D,^3F$</td>
<td>$d^4$</td>
<td>$^1S(2),^3P(2),^1D(2),^3D,^3P,^3F(2),$</td>
</tr>
<tr>
<td>$p,d^1$</td>
<td>$^1D,^3F,^1G$</td>
<td>$d^5$</td>
<td>$^1G(2),^3G,^3H,^1I,$</td>
</tr>
<tr>
<td>$p,f^1$</td>
<td>$^1D,^3F,^1G$</td>
<td></td>
<td>$^2S,^6S,^2P,^4P,^2D(3),$</td>
</tr>
<tr>
<td>$d,d^1$</td>
<td>$^1D,^3F,^1G$</td>
<td></td>
<td>$^4D,^2F(2),^4F,^2G(2),$</td>
</tr>
<tr>
<td>$d,f^1$</td>
<td>$^1D,^3F,^1G$</td>
<td></td>
<td>$^4G,^2H,^2I$</td>
</tr>
<tr>
<td>$f,f^1$</td>
<td>$^1D,^3F,^1G$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† The numbers in brackets indicate that a particular term occurs more than once.

Coupling between resultant orbital angular and spin momenta is known as **LS coupling** (spin-orbit interaction). This interaction results from the positive Ze charge on the nucleus and is proportional to $Z^4$.

The total angular momentum implies orbital plus electron spin, and has the symbol $J = L + S$ (if nuclear spin is included, it has the symbol $F = L+S+I$). The magnitude is

$$ [J(J + 1)]^{1/2} \hbar = J^* \hbar $$

and $J$ is restricted to

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

If $L > S$, then $J$ has $2S + 1$ values. If $L < S$, $J$ has $2L + 1$ values.
Term Symbols

Figure c illustrates 3 ways of coupling \( L \) and \( S \), e.g., in a \( ^3D \) term with \( L = 2, S = 1 \) and \( J = 3, 2 \) or \( 1 \). The value of \( J \) is attached as a **post-script**, so that the three **components** of \( ^3D \) are \( ^3D_3, ^3D_2 \) and \( ^3D_1 \).

For the previously discussed excited configurations of C and Si, we now have:

\[
1P_1, \quad 3P_0, \quad 3P_1, \quad 3P_2, \quad 1D_2, \quad 3D_1, \quad 3D_2, \quad 3D_3, \quad 1F_3, \quad 3F_2, \quad 3F_3, \quad 3F_4
\]

So the **term symbol** has the following structure:

- multiplicity, \( 2S + 1 \)
- total angular momentum, \( J = L + S, ..., |L - S| \)
- orbital angular momentum
  - \( L = 0, 1, 2, 3, ... \rightarrow S, P, D, F, ... \)

**Configuration**: gross approximation on filling orbitals. All configurations give rise to at least one **term** or **state**: So, the configuration \( 1s^12s^1 \) of He has two states \( ^1S_0 \) and \( ^3S_0 \)

**Term** is used to describe what arises from an approximate treatment of electron configuration, and **state** is used to describe something experimentally. For instance, the \( 1s^22s^22p^13d^1 \) configuration of C has a \( ^3P \) term, which when spin-orbit coupling is taken into account splits into \( ^3P_1, ^3P_2 \) and \( ^3P_3 \) states. Since spin-orbit coupling is excluded in theory, there is no real experimental observation of the \( ^3P \) term: confusing - since term and state are often mixed up!!

***Nuclear spins can further split states (so bad name in the first place) often called **components** of states***
Term Symbols, 2

An easy way to remember how term symbols work is shown in the flow chart below.

1. The letter $S, P, D, F, G, H, I, \ldots$ indicates the total orbital angular momentum quantum number $L = 0, 1, 2, 3, 4, 5, 6, \ldots$

2. The left superscript gives the multiplicity of the term $(2S+1)$

3. The right superscript on the term symbol is the value of the total angular momentum quantum number $J$

Configurations can be written to indicate the absence of an electron: e.g., F, $[\text{He}]2p^5 \equiv [\text{Ne}]2p^{-1}$

To derive a term symbol:
1. Write the configurations, ignore closed inner shells.
2. Couple the orbital angular momenta to find $L$.
3. Couple the spin angular momenta to find $S$.
4. Couple $L$ and $S$ to find $J$.
5. Express the term as $2S+1\{L\}_J$, where $\{L\}$ is the appropriate letter.

Spin-Orbit Coupling

So again considering the picture of spin-orbit coupling, which is the interaction between spin and orbital magnetic moments:

(a) When the magnetic moments are parallel, they are aligned unfavourably, and this is the high $j$ or high energy arrangement:
\[ j = \ell + s \]

(b) When the magnetic moments are antiparallel, they are aligned favourably, and this is the low $j$ or low energy arrangement:
\[ j = \ell - s \]

The dependence of the spin orbit coupling on $j$ is expressed in terms of the spin-orbit coupling constant, $A$ (usually a wavenumber), and energies of levels with quantum numbers of $s$, $\ell$ and $j$ are adjusted by
\[
E_{\ell,s,j} = \frac{1}{2} \hbar c A [j(j + 1) - \ell(\ell + 1) - s(s + 1)]
\]

Spin orbit coupling splitting the $^{2}P$ term of the $2p^1$ configuration/
If $A$ is +ve, the component with smallest value of $J$ is lowest in energy and the multiplet is normal. If $A$ is -ve, the multiplet is inverted.
Spin-Orbit Coupling, 2

Atoms with ground configurations having orbitals which are half filled always have an $S$ ground state (e.g., N($2p^3$), Mn($3d^5$), Eu($4f^7$))

For excited states, there are no general rules for normal or inverted multiplets.

One further addition to symbolism is that sometimes a superscript “o” is used. For example, the ground state of B:

\[ ^2P_{1/2}^o \]

This symbol means that the arithmetic sum \( \sum_i \ell_i \) for all electrons in the atom is an odd number (1 in this case). If there is no subscript, the total sum is even.

The fine structure resulting from spin-orbit coupling in electronically excited Na results from two separate transitions: one from a \( j = 3/2 \) level and one from a \( j = 1/2 \) level. The yellow line from a sodium discharge lamp, at 589 nm, is actually a doublet with two lines at 589.76 and 589.16 nm (spin orbit coupling effects the energies of the split \(^3P\) states by about 17 cm\(^{-1}\))

*** Try example 13.5, Atkins p. 399
### Equivalent Electrons

The Russell-Saunders approximation for two (or more) equivalent electrons is a bit more lengthy to apply. The electrons have the same values of \( n \) and \( \ell \), for example, in the ground configuration for carbon:

\[
C \quad 1s^22s^22p^2
\]

For filled orbitals, \( L = 0, S = 0 \). For the \( 2p \) electrons, \( n = 2 \) and \( l = 1 \). In order not to violate the **Pauli-exclusion principle**, 2 electrons must always have different \( m_\ell \) and \( m_s \)

Label one of the \( p \) electrons \( 1, \ell_1 = 1, (m_\ell)_1 = +1, 0, -1 \) and \( s_1 = \frac{1}{2} \) and \( (m_s)_1 = +\frac{1}{2}, -\frac{1}{2} \). Same for electron 2.

\( (m_\ell)_1 \) and \( (m_s)_1 \) cannot simultaneously have the same values as for \( (m_\ell)_2 \) and \( (m_s)_2 \) due to Pauli exclusion principle.

There are 15 possible combinations summarized below:

<table>
<thead>
<tr>
<th>Quantum No.</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>((m_\ell)_1)</td>
<td>1 1 1 1 1 1 1 1 0 0 0 0 0 -1</td>
</tr>
<tr>
<td>((m_\ell)_2)</td>
<td>1 0 0 0 0 -1 -1 -1 -1 -1 -1 -1</td>
</tr>
<tr>
<td>((m_s)_1)</td>
<td>(\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (-\frac{1}{2})</td>
</tr>
<tr>
<td>((m_s)_2)</td>
<td>(-\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (\frac{1}{2}) (-\frac{1}{2}) (-\frac{1}{2})</td>
</tr>
<tr>
<td>(M_L = \sum_i (m_\ell)_i)</td>
<td>2 1 1 1 1 0 0 0 0 0 -1 -1 -1 -1 -2</td>
</tr>
<tr>
<td>(M_S = \sum_i (m_s)_i)</td>
<td>0 1 0 0 -1 1 0 0 -1 0 1 0 0 -1 0</td>
</tr>
</tbody>
</table>

Rearrange pairs of values of \( M_L \) and \( M_S \)

| \(M_L\) | 2 1 0 -1 -2 1 0 -1 1 0 -1 1 0 -1 0 |
| \(M_S\) | 0 0 0 0 0 1 1 1 0 0 0 -1 -1 -1 0 |

\[ {}^1D \quad {}^3P \quad {}^1S \]
Equivalent Electrons, 2

- Highest value of $M_L = 2$, highest value of $L$ as well, and there is a $D$ term
- $M_L = 2$ has only $M_S = 0$, so $^1D$ term - accounts for 5 of the combinations listed in the table.
- The next highest value of $M_L = 1$, with $M_S = +1, 0, -1$, so it is a $^3P$ term, associated with 9 combinations.
- This leaves $M_L = 0$ and $M_S = 0$, comprising a $^1S$ term.

Of the $^1S, ^3S, ^1P, ^3P, ^1D, ^3D$ terms which arise for 2 equivalent $p$ electrons, only the $^1S, ^3P$ and $^1D$ are allowed (Pauli-exclusion forbids the others).

For 3 equivalent electrons, similar treatment can be applied (somewhat more lengthy).

For 4 equivalent electrons, there is a useful rule that says a vacancy in a sub-shell behaves like an electron. So for the ground configurations of C and O:

\[
\text{C: } 1s^22s^22p^2 \\
\text{O: } 1s^22s^22p^4
\]

both have the same terms: $^1S, ^3P$ and $^1D$

The excited configurations of C and Ne also have the same allowed terms:

\[
\text{C: } 1s^22s^22p^13d^1 \\
\text{Ne: } 1s^22s^22p^53d^1
\]

Terms: $^1,^3P, ^1,^3D, ^1,^3F$
Hund’s Rules

(1) Of the terms arising from equivalent electrons, those with the highest multiplicity lie lowest in energy.

(2) Of these, the lowest is that with the highest values of $L$.

For the ground configurations of both C and O:

C: $1s^22s^22p^2$
O: $1s^22s^22p^4$

the $^3P$ term is the lowest in energy.

The ground configuration of Ti is $KL3s^23p^63d^24s^2$, and of terms arising from the $d^2$ configuration, $^3F$ is lowest.

The splitting of a term by the spin-orbit interaction is proportional to $J$:

$$E_J - E_{J-1} = AJ$$

where $E_J$ is the smallest energy corresponding to $J$. In this case a multiplet results.

If $A$ is +ve, the component with the smallest value of $J$ is lowest in energy and the multiplet is said to be normal.

If $A$ is -ve, the multiplet is inverted.

(3) Normal multiplets arise from equivalent electrons when a partially filled orbital is less than half full.

(4) Inverted multiplets arise from equivalent electrons when a partially filled orbital is more than half full.

For Ti, $^3F$ is split by spin-orbit coupling into a normal multiplet, and the ground state is $^3F_2$. The lowest energy term of C, $^3P$, splits into a normal multiplet, the ground state is $^3P_2$; for O, there is an inverted multiplet with ground state $^3P_0$. 

**$jj$ Coupling**

Russell-Saunders coupling fails when spin-orbit coupling is large (happens for heavy atoms). The individual spin and orbital angular momenta are coupled into individual $j$ values, which are combined into a grand total, $J$: this is known as **$jj$ coupling**.

For example, $p^2$ configuration, $j$ are 3/2 and 1/2 for each electron. If $s$ and $\ell$ are coupled strongly, each electron is considered a particle with $j = 3/2$ or 1/2. Then:

$$
\begin{align*}
  j_1 &= \frac{3}{2} \quad \text{and} \quad j_2 = \frac{3}{2} \quad J = 3, 2, 1, 0 \\
  j_1 &= \frac{3}{2} \quad \text{and} \quad j_2 = \frac{1}{2} \quad J = 2, 1 \\
  j_1 &= \frac{1}{2} \quad \text{and} \quad j_2 = \frac{3}{2} \quad J = 2, 1 \\
  j_1 &= \frac{1}{2} \quad \text{and} \quad j_2 = \frac{1}{2} \quad J = 1, 0
\end{align*}
$$

For heavy atoms, it is best to use the quantum numbers above to discuss energies, but the terms derived from RS coupling can still be used as labels.

The **correlation diagram** on the left shows how energies of the atomic states change with increasing spin-orbit coupling. So for low spin-orbit coupling (RS-coupling) and high spin-orbit coupling ($jj$-coupling) schemes, the RS labels are used.
Key Concepts

1. **Electronic spectroscopy** is the study of absorption and emission transitions between electronic states in an atom or a molecule. **Atomic spectroscopy** is concerned with the electronic transitions in atoms.

2. The **Hartree-Fock SCF method** is used to approximate the potential energy resulting from the interaction of electrons in a multi-electron atom.

3. The **aufbau principle** and **Pauli exclusion principle** are used to construct the ground configuration for all atoms in the periodic table.

4. There are two sources of angular momentum within an atom **orbital angular momentum** and **spin angular momentum**. The total angular momentum is the sum of these other contributions.

5. The interaction of magnetic moments from spin and orbital angular momenta is known as **spin-orbit coupling**, and is responsible for the splitting of energy levels and fine structure in atomic spectra. This can be accurately described by the Russell-Saunders coupling approximation.

6. **Term symbols** are used to describe different electronic atomic states.

7. **Hund’s rules** are used to determine the relative energy levels of electronic atomic states.
Hydrogen & One Electron Ions

The hydrogen atom and one-electron ions are the easiest to treat, since there are no electron-electron repulsions. However, there are a series of degeneracies that are absent in all other polyelectronic atoms which feature prominently in the atomic spectra of hydrogen and one-electron ions.

The alkali metal ions are the next simplest case, as they all have a single electron in the outer $ns$ orbital, where $n = 2, 3, 4, 5, 6$ for Li, Na, K, Rb and Cs.

If the electrons in these systems only changed orbitals (i.e., values of $n$), the spectra would resemble the simple atomic spectra for hydrogen. Whereas the H atom only shows the Balmer series in the visible region of the spectrum, there are at least three different series for alkali metal atoms:

The series are shown above for Li: (i) principal series: observed via absorption through column of vapour; (ii) sharp & (iii) diffuse series: so-named because of their appearance; & (iv) fundamental series: sometimes observed
The **Grotrian diagram** is an energy level diagram used to describe atomic spectra. To the right is the Grotrian diagram for the ground configuration \((1s^22s^1)\) of Li.

The lowest energy level on the diagram, labelled \(2s\), corresponds to the ground configuration. Higher levels, e.g., \(4p\), correspond to excited configurations, e.g., \(1s^24p^1\).

There are large separations between energy levels with different values of \(\ell\) (e.g., \(3s, 3p, 3d\)) for all atoms except hydrogen. The selection rules for promotion of an electron to excited orbital (and return to lower energy orbital) are:

(a) \(\Delta n\) is unrestricted

(b) \(\Delta \ell = \pm 1\)

These rules lead to the **sharp**, **principal**, **diffuse** and **fundamental** series, in which the promoted electron is in an \(s, p, d\) and \(f\) orbital, respectively.
**Alkali Metal Atoms, 2**

Some excited configurations and states of Li (involving promotion of the valence electron only) are shown below:

<table>
<thead>
<tr>
<th>Configuration States</th>
<th>Configuration States</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^22s^1$</td>
<td>$1s^22s^1$</td>
</tr>
<tr>
<td>$2S_{1/2}$</td>
<td>$2S_{1/2}$</td>
</tr>
<tr>
<td>$1s^2ns^1$ ($n=3, 4, ...$)</td>
<td>$1s^2nd^1$ ($n=3, 4, ...$)</td>
</tr>
<tr>
<td>$2S_{1/2}$</td>
<td>$2D_{5/2}$</td>
</tr>
<tr>
<td>$1s^2np^1$ ($n=2, 3, ...$)</td>
<td>$1s^2nf^1$ ($n=4, 5, ...$)</td>
</tr>
<tr>
<td>$2P_{1/2}$, $2P_{3/2}$</td>
<td>$2F_{5/2}$, $2F_{7/2}$</td>
</tr>
</tbody>
</table>

Spin-orbit coupling splits apart the two components of the $^2P$, $^2D$, $^2F$, ... terms, and the splitting decreases with increasing $\ell$ and $n$, but increases with increasing atomic number (for Li, Grotrian diagram spectrum is not observed, but is easily observed for heavier alkali metal atoms).

$^2P_{1/2}$ and $^2P_{3/2}$ states result from the promotion of the $3s$ valence electron to any $np$ orbital with $n > 2$ (states are often labelled with $n$: $n^2P_{1/2}$ and $n^2P_{3/2}$)

The splitting of the $3^2P_{1/2}$ and $3^2P_{3/2}$ states of sodium is 17.2 cm$^{-1}$, which reduces to 5.6, 2.5, 1.3 cm$^{-1}$ for $n = 4, 5$ and 6, respectively.

The splitting of the $3^2D_{1/2}$ and $3^2D_{3/2}$ states of sodium is only 0.1 cm$^{-1}$, as increasing $\ell$ serves to decrease the splitting.

Pictured above is the “**simplified doublet**” of atomic sodium
Alkali Metal Atoms, 3

There is a fine structure selection rule:
\[ \Delta J = 0, \pm 1 \text{ except } J = 0 \oplus J = 0 \]

This means that the principal series will consist of pairs of \( ^2P_{1/2} - ^2S_{1/2} \) and \( ^2P_{3/2} - ^2S_{1/2} \) transitions (\( N-M \) notation, \( N \) higher state and \( M \) lower state, as for vibrational spectroscopy), which are known as simple doublets. All sharp series members show up as simple doublets.

The \( 3^2P_{1/2} \) and \( 3^2P_{3/2} \) excited states involved in the sodium D line are the lowest excited energy states of the atom. Discharge in the vapour (where collisional deactivation of excited states readily occurs) results in many of the atoms being in these state before emission of radiation. The D line is prominent, given sodium lamps their characteristic yellow colouration.

In the diffuse series, compound doublets are often observed, but the splitting between the closely spaced \( ^2D_{3/2} \) and \( ^2D_{5/2} \) states may be too close to be resolved (why it is called a compound doublet instead of a triplet).
Atomic Hydrogen

Unique case for development of quantum mechanics:

1. Schrödinger equation is exactly soluble
2. Orbital energies (at this level of approximation) are independent of \( \ell \) since the electron moves in a coulombic field free from the effects of electron repulsions.

Dirac included the effect of relativity in quantum mechanical treatments, and predicted the splitting of the \( n = 2 \) level into two components 0.365 cm\(^{-1}\) apart (\( n = 2, \ell = 1 \) or 0). Since \( s = 1/2 \), \( j \) can be 3/2 or 1/2 for \( \ell = 1 \) and 1/2 for \( \ell = 0 \). One component of the \( n = 2 \) level has \( j = 3/2, \ell = 1 \), other is doubly degenerate with \( j = 1/2, \ell = 0, 1 \).

In 1947, Lamb & Rutherford observed the \( 2^2P_{3/2} \rightarrow 2^2S_{1/2} \) transition using microwave techniques (off by 0.0354 cm\(^{-1}\) of Dirac’s prediction). The shift of the \( 2^2P_{3/2} \) level is the Lamb shift (quantum electro-dynamics or QED is the modified Dirac theory). The \( 1^2S_{1/2} \) state is shifted but not split, nuclear spin (\( s = 1/2 \)) splits it into two components 0.0475 cm\(^{-1}\) apart.
Hydrogen and Astronomy

Interpreting spectra of atomic hydrogen is of paramount importance in the study of stars, which are largely composed of atomic hydrogen.

The interior temperature of a star is ca. $10^6$ K, whereas the exterior (photosphere) is ca. $10^3$ K. The observed absorption spectrum has the interior as a continuum source and the photosphere as the absorber. Thus, the absorption spectrum of a star shows the Lyman ($n = 1$) and Balmer ($n = 2$) series (the ratio of $n=2:n=1$ populations is only $2.9 \times 10^{-5}$ at $10^3$ K, but the high concentration of H atoms and long absorption path length through the photosphere makes it possible to observe these series quite easily.

In the first five series of the atomic H spectrum there are an infinite number of energy levels, and there are also an infinite number of series. As $n''$ increases, levels become closer so that series with high $n''$ values start showing up in the radiofrequency region.

Scanning of the interstellar medium with radiotelescopes has resulted in the observations of the $n'' = 90, 104, 109, 126, 156, 158, 159$ and $166$ series

The quantity of H atoms in stars is determine by measuring the $F = 1-0$ hyperfine transition
Helium and Alkaline Earth Metals

The emission spectrum of discharge in helium gas in the visible and UV regions appears like the spectrum of two alkali metals. There are two sets of lines which converge slowly to high energy which can be divided into one group of single lines & one group of double lines - no transitions are observed between the two sets of levels.

In 1925, when electron spin was taken into account, it became apparent that the two groups arise from singlet and triplet forms of helium.

For hydrogen and alkali metal atoms, there is only one electron with an unpaired spin (all states are doublet states)

If spin-orbit coupling is small (it is in He), the total electronic wavefunction $\psi_e$ can be factorized into an orbital part and a spin part:

$$\psi_e = \psi_e^o \psi_e^s$$

The spin part is derived by labelling electrons 1 and 2, and writing the four functions: $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$. The latter two are neither symmetric nor antisymmetric w.r.t. electron exchange, so we write the linear combinations:

1 antisymmetric function (**singlet**)  

$$2^{-1/2} \ [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

3 symmetric functions (**triplet**)  

$$\alpha(1)\alpha(2) \quad \beta(1)\beta(2)$$

$$2^{-1/2} \ [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$
Helium and Alkaline Earth Metals, 2

For the orbital part of the wavefunction, electrons in two different atomic orbitals, $\chi_a$ and $\chi_b$, are considered. There are two ways of placing the electrons into these orbitals, giving the wavefunctions $\chi_a(1)\chi_b(2)$ and $\chi_a(2)\chi_b(1)$ - but since these are not symmetric to exchange, we must use:

$$\psi_e^o = 2^{-1/2} [\chi_a(1)\chi_b(2) + \chi_a(2)\chi_b(1)]$$
$$\psi_e^o = 2^{-1/2} [\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)]$$

The most general statement of the Pauli exclusion principle for electrons is that the total wavefunction must be antisymmetric w.r.t. electron exchange.

So for He, the singlet spin wavefunction can only combine with the symmetric orbital wavefunction

$$\psi_e = 2^{-1} [\chi_a(1)\chi_b(2) + \chi_a(2)\chi_b(1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

and for the triple spin wavefunctions:

$$\psi_e = 2^{-1} [\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)][\alpha(1)\alpha(2)]$$

or $$2^{-1/2} [\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)][\beta(1)\beta(2)]$$

or $$2^{-1/2} [\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

The ground configuration, $1s^2$, has an orbital wavefunction

$$\psi_e^o = \chi_a(1)\chi_b(2)$$

which is symmetric to electron exchange. This configuration has only a singlet term, whereas an excited configuration has singlet & triplet terms, where the latter is lower in energy.
The Grotrian diagram for He is shown below, which derives from the selection rules:

\[ \Delta \ell = \pm 1, \text{ for promoted electron, and } \Delta s = 0 \]

Atoms which get into the lowest triplet state, \( 2^3S_1 \), do not easily revert to the \( 1^1S_0 \) state: forbidden by both orbital and spin selection rules - so the lowest triplet state is metastable, and in a typical discharge has a lifetime on the order of 1 ms!

The first excited singlet state, \( 2^1S_0 \), is also metastable since the transition to ground state is forbidden by the \( \Delta \ell \) selection rule, but the transition is not spin forbidden so it is not as long lived as the \( 2^3S_1 \) state.
All triplet terms, except $^3S$, are split into three components (in the case of the $^3P$ term, for instance, $L = 1$ and $S = 1$, so $J$ can be 2, 1, 0 (Clebsch-Gordan series)).

The fine structure of a $^3P$-$^3S$ transition of an alkaline earth metal is shown below. The $\Delta J$ selection rule results in a simple triplet (small separation of $2^3P_1$ and $2^3P_2$ in helium accounts for early description of the low resolution spectrum of triplet helium consisting of “doublets”)

The $^3D$-$^3P$ transition, shown (b), has six components. In medium resolution, the 6 lines appear as a triplet (compound triplet), since the multiplet splitting decreases rapidly with increasing $L$. 
Spectra of Polyelectronic Atoms

The emission spectra of most other atoms are quite complex and no obvious series are observed. The Russell-Saunders coupling approximation (or $jj$ coupling, heavy atoms) can be used to derive the states which arise from any configuration:

1. $\Delta L = 0, \pm 1$ except $L = 0 \pm L = 0$
   This general rule applies to the promotion of any number of electrons and involves the total angular momentum quantum number, $L$

2. even $\pm$ even, odd $\pm$ odd, even $\leftrightarrow$ odd
   Even and odd refer to the arithmetic sum $\sum_i \ell_i$ over all electrons (called the Laporte rule). This rule forbids transitions between states arising from the same configuration. For instance, the $^1P - ^1D$ transition is forbidden for the $1s^22s^22p^13d^1$ configuration of carbon, though it is allowed by the $\Delta L$ and $\Delta S$ selection rules. Similarly, any transitions arising from the $1s^22s^22p^13d^1$ configuration, with $\sum_i \ell_i = 3$ and the $1s^22s^23d^13f^1$ configuration, with $\sum_i \ell_i = 5$, are also forbidden. This is also consistent with $\Delta \ell = \pm 1$, when only one electron is promoted from the ground configuration.

3. $\Delta J = 0, \pm 1$, except $J = 0 \pm J = 0$
   Same for all atoms.

4. $\Delta S = 0$
   Applies to atoms with small nuclear charge (see next page)
Spectra of Polyelectronic Atoms, 2

In atoms with large nuclear charge the factorization of $\psi_e$ no longer applies and states are no longer accurately described as singlet, doublet, triplet, etc.

For example, Hg, $KLN5s^25p^65d^{10}6s^2$ ground configuration is similar to an alkaline earth metal. Promotion of an electron from the $6s$ to the $6p$ orbital results in $6^1P_1$, $6^3P_0$, $6^3P_1$ and $6^3P_2$ states, with three components of $6^3P$ widely split by spin-orbit coupling. This interaction also breaks down the spin selection rule so much that the $6^3P_1$-$6^3S_0$ transition at 253.652 nm is one of the strongest in the Hg emission spectrum.

**Worked Example:**

From the ground electron configuration of Zr derive the ground state (values of $L$, $S$ and $J$). Then derive the states arising from the configuration: $KLM4s^24p^64d^{15}5s^25f^1$

1. The ground electron configuration of Zr is:

   $KLM4s^24p^64d^{15}5s^2$

   - all filled orbitals contribute zero to all angular momenta
   - only the 2 equivalent $4d$ electrons need to be considered

   According to the table (tot. ang. mom, earlier), terms are:

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

2. Hund’s rule: $^3F$ is the lowest energy term, since it has the highest spin multiplicity ($2S+1=3$) and the highest value of $L$ (3 for an $F$ term). For the $F$ term:

   $J = L + S$, $L + S - 1$, $|L - S| = 4, 3, 2$

Thus giving states: $^3F_4$, $^3F_3$, $^3F_2$
Spectra of Polyelectronic Atoms, 3

Since the unfilled orbital, \(4d\), is less than half full, the \(^3F\) multiplet is normal and the component with the lowest value of \(J\) (i.e., \(^3F_2\)) is lowest in energy. Ground state is \(^3F_2\).

3. In the excited electron configuration there are two electrons in partially filled orbitals (\(4d\) and \(5f\), electrons \#1 and \#2).

For the coupling of orbital angular momenta, \(\ell_1 = 2, \ell_2 = 3\), and \(L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2| = 5, 4, 3, 2, 1\) giving \(H, G, F, D\) and \(P\) terms.

For the coupling of spin angular momenta, \(s_1 = \frac{1}{2}, s_2 = \frac{1}{2}\), and \(S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2| = 1, 0\) giving multiplicities \((2S + 1)\) of 3 and 1.

4. The total number of terms:
   \[1^H, 1^G, 1^F, 1^D, 1^P, 3^H, 3^G, 3^F, 3^D, 3^P\]

5. For each of the triplet terms, there are three states. For example, for the \(^3H\) term, \(L = 5\) and \(S = 1\), so
   \[J = L + S, L + S - 1, \ldots, |L - S| = 6, 5, 4\]
   So the total number of states is:
   \[1^H_5, 1^G_4, 1^F_3, 1^D_2, 1^P_1, 3^H_6, 3^H_5, 3^H_4, 3^G_5, 3^G_4, 3^G_3, 3^F_4, 3^F_3, 3^F_2, 3^D_3, 3^D_2, 3^D_1, 3^P_2, 3^P_1, 3^P_0\]

So it is no wonder the atomic spectra of polyelectronic atoms are so complex - remember that the Laporte rule forbids transitions between states arising from the same configuration!
**Key Concepts**

1. The atomic spectra of alkali metal ions are relatively simple to interpret, as they all have a single electron in the outer $ns$ orbital, where $n = 2, 3, 4, 5, 6$ for Li, Na, K, Rb and Cs. This gives rise to the (i) **principal** series: observed via absorption through column of vapour; (ii) **sharp** & (iii) **diffuse** series: so-called because of their appearance; & (iv) **fundamental** series: sometimes observed.

2. The atomic spectra of hydrogen exhibit fascinating fine structure due to effects of Einstein’s special relativity (included by Dirac) and quantum electrodynamics (measured by Lamb & Rutherford).

3. The atomic spectra of helium gas (or alkaline earth metals) in the visible and UV regions appears like the spectrum of two alkali metals. There are two sets of lines which converge slowly to high energy which can be divided into one group of single lines & one group of double lines - no transitions are observed between the two sets of levels. When electron spin is taken into account, it became apparent that the two groups arise from singlet and triplet forms of helium.

4. The emission spectra of most other atoms are quite complex and no obvious series are observed. The Russell-Saunders coupling approximation (or $jj$ coupling, heavy atoms) can be used to derive the states which arise from any configuration.