Section 2
Atomic Spectra
(Lectures 2-3 ish)

Previously:

Atomic Structure:
IC yr 1

Quantum theory of atoms / molecules

H-Atom:
- Wavefunctions, quantum numbers and energy levels
- Spectral transitions: Rydberg series and selection rules
- Spin and spin-orbit coupling

Alkali Metal Atoms (e.g., Na):
- Penetration and shielding, quantum defects
- Larger spin-orbit coupling

He Atom
- Singlets and triplets
- Electron correlation

General
- Russell-Saunders and $j$-$j$ coupling
- Atoms in external fields
Lecture 2: Atomic Spectroscopy

2.1 Revision: The H-atom (& other 1e⁻ atoms)

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi = E\Psi
\]

\[
V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}
\]

Solutions: \( \Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\phi, \theta) \)

Quantum numbers:
- **Principal quantum number**, \( n \)
- **Orbital angular momentum quantum number**, \( l \)
- **Orbital angular momentum projection quantum number**, \( m_l \)
  (or “magnetic”)

Permitted values:
- \( n = 1, 2, 3, \ldots \)
- \( l = 0, 1, 2, 3, 4, \ldots n-1 \)
- \( m_l = -l, -l + 1, \ldots +l \)

\( e.g., \) \( n = 3: l = 0: m_l = 0 \)
\( l = 1: m_l = 0, \pm 1 \)
\( l = 2: m_l = 0, \pm 1, \pm 2 \)

\( \nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2 \)

\( \Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \)

Spherical harmonics (complex)

Laguerre functions

Solve in spherical polar coordinates
2.1.1 Atomic Quantum Numbers

The principal quantum number, \( n \):

determines the energies of orbitals:

\[
\text{n.b., } E_{ns} = E_{np} = E_{nd} \ldots
\]

\[
\frac{E}{hc} = \frac{-Z^2 R_y}{n^2}
\]

where \( R_y / \text{cm}^{-1} = \frac{\mu e^4}{8\hbar^3 \bar{c} \varepsilon_0^2} \) (= 109677 cm\(^{-1}\) for H)

and the mean radius

\[
\langle r \rangle = \frac{3n^2}{2Z} a_0 \quad \text{where the Bohr radius, } a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^4} = 0.5292 \text{ Å}
\]

Leads to radial wavefunctions / distribution functions:

\( \psi(r) \) has \( n - l - 1 \) nodes
2.1.1 Atomic Quantum Numbers

Orbital angular momentum quantum number, \( l \) & orb. ang. mom. projection (or magnetic) quantum number, \( m_l \)

The magnitude of the angular momentum come from \( l \):

\[
|l| = \hbar \sqrt{l(l+1)}^{1/2}
\]

and the projection of \( l \) on the z-axis is provided by \( m_l \):

\[
l_z = m_l \hbar
\]

Lead to the angular wavefunctions and shapes of orbitals (1e\(^{-}\) wavefunctions):

(n.b. Real linear combinations plotted)
2.2 H-Atom *Spectrum: Grotrian Diagrams*

**Selection Rules:**

- $\Delta n$ unrestricted
- $\Delta l = \pm 1$ (Laporte)
- $\Delta m_l = 0, \pm 1$

$\rightarrow$ Transitions observed at wavenumbers:

$$\nu = \frac{\Delta E}{hc} = Z^2 R_y \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$\rightarrow$ Multiple series of lines (different $n_1$)

$\rightarrow$ Graph of $\nu$ vs $1/n^2$ is straight with intercept = ionization energy
2. 3 Origin of selection rules

A physical picture: **Conservation of momentum**

The photon has intrinsic angular momentum of \( |l_{\text{ph}}| = \sqrt{2}\hbar \)

Total angular momentum must be conserved in the absorption/emission process

\[
\text{vectorially: } \quad L_F = L_I + \sqrt{2}\hbar
\]

**But** \( |L_F| \) is also quantised, 

\[
|L_F| = \sqrt{l_F (l_F + 1)}\hbar
\]

→ only specific relative orientations are permitted

It is easily shown that the maximum and minimum \( l_F \) are given by

\[
\begin{align*}
L_{F \text{ max}} &= l_I + 1 \quad \text{i.e., } \Delta l = +1 \\
L_{F \text{ min}} &= l_I - 1 \quad \text{i.e., } \Delta l = -1
\end{align*}
\]

**Which is not quite our selection rule...**
2.3 Origin of selection rules II

All “dipole allowed” selection rules ultimately originate from the need for a non-zero transition dipole moment:

\[
\langle \psi_F | \hat{\mu} | \psi_I \rangle = \int \psi_F^* \hat{\mu} \psi_I d\tau \neq 0
\]

\[
\hat{\mu} = \sum_i q_i r_i
\]

To be non-zero the integrand must be totally symmetric under the symmetry operations of the group (the full rotation group, \(R_3\) for atoms).

Consider the operation \(i\):

- An atomic orbital with quantum number \(l\) has parity \((-1)^l\)

- Since \(i\) changes the parity, \(\psi_F\) and \(\psi_I\) must have opposite parity

- Hence \(\Delta l \neq 0\) for reasons of symmetry

- \(\Delta m_l = 0, \pm 1\) arises due to the helicity \((\sigma = \pm 1)\) of the photon
2.5 More than one electron

For any atom other than the H-atom, the Schrödinger equation becomes:

\[
\sum_i \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_i V_{iN} + \sum_{i \neq j} V_{ij} \right] \psi = E \psi
\]

The total energy, \( E \), is the energy of all electrons and all interactions.

The electron repulsion term, \( V_{ij} \), renders the Schrödinger equation insoluble.

\[
V_{iN} = \frac{-Ze^2}{4\pi\varepsilon_0 r_i}
\]

\[
V_{ij} = \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}
\]

The electron repulsion term, \( V_{ij} \), renders the Schrödinger equation insoluble.

The wavefunction, \( \psi \):

For one electron: \( \psi = \psi(x, y, z) \psi_{\text{spin}} = \psi(x, y, z, m_s) \)

For two electrons: \( \psi = \psi(x_1, y_1, z_1, (m_s)_1, x_2, y_2, z_2, (m_s)_2) \)

In general we need: 3\( N \) spatial and \( N \) spin coordinates.
2.6 The orbital approximation

In order to proceed, assume $\Psi_{\text{space}}$ is the product of $n$, one-electron wavefunctions (or orbitals)

$$\Psi_{\text{space}} = \varphi_a(r_1)\varphi_b(r_2)\varphi_c(r_3)\varphi_d(r_4)\ldots \varphi_z(r_n)$$

For each orbital

$$\left[ \frac{-\hbar^2}{2m_e} \nabla_i^2 + V_{iN} + \sum_{i \neq j} V_{ij} \right] \varphi(r_i) = E\varphi(r_i)$$

\[ e^- - e^- \text{ repulsion averaged over positions of all other electrons} \]

i.e., electron $i$ experiences the mean field of all other electrons

→ Solve using numerically by e.g., **Self Consistent Field approach** (Hartree) to yield orbital energies. Including exchange yields Hartree-Fock orbitals.

**Psst: a dirty secret**

This method is flawed because in order to satisfy the Pauli principle we must really write $\Psi_{\text{space}}$ as linear combinations of orbitals with defined symmetry with respect to electron permutation.

Oh, and it also neglects spin and correlation (see 2.18, 2.19). But apart from that.....
2.7 The spectra of alkali metal atoms

Ground state electron configurations [RG] $ns^1$ i.e., closed shell cores

We are only interested here in valence excitations (core excitations at higher energies). Within the orbital approximation only one electron can change orbital per photon.

Energy Levels: The effects of penetration and shielding

Consider the radial distribution functions of 3s, 3p

A 3s electron spends more of its time penetrating the core region and experiencing the full nuclear attraction (or equivalently, 3p is more shielded)

The Energy of a level now depends on $n$ and $l$ quantum numbers with $E_{ns} < E_{np} < E_{nd}$
2.8 The spectrum of the Na atom

We account for penetration, shielding with a quantum defect, $\delta_{nl}$ for each level:

$$E_{nl} = -\frac{Z^2 R_y \hbar c}{V_{nl}^2} = -\frac{Z^2 R_y \hbar c}{(n - \delta_{nl})^2} = \frac{Z^2 R_y \hbar c}{n^2}$$

For a given $l$, $\delta_{nl}$ is only weakly dependent on $n$

**Selection Rules:**

$\Delta n$ unrestricted

$\Delta l = \pm 1$

$\Delta m_l = 0, \pm 1$

$\Delta j = 0, \pm 1$

Absorption: $3s \rightarrow np$

Emission: $ns \rightarrow np$ “sharp”

$np \rightarrow ns$ “principal”

$nd \rightarrow np$ “diffuse”

$nf \rightarrow nd$ “fundamental”
2.9 Spin-Orbit Coupling

A minor effect for the H-atom SOC becomes increasingly important with atomic number.

The electron has spin quantum number \( s = \frac{1}{2} \)
and spin projection quantum number \( m_s = \pm \frac{1}{2} \).

Associated with any angular momentum of a charged particle is a magnetic moment via which orbital and spin angular momenta interact leading to spectral fine structure.

The orbital angular momentum \( l \) has (if \( l > 0 \)) an associated magnetic moment to which the spin angular momentum \( s \) can couple, yielding a total angular momentum, \( j \).

Vectorially: \[ j = l + s \]

The permitted range of quantum numbers, \( j \), are given by a Clebsch-Gordon series:

\[ j = l+s, l+s-1, l+s-2, \ldots \quad |l-s| \]

Hence, for a single electron, \( j = l \pm \frac{1}{2} \):
2.9.1 Spin-Orbit Coupling II: Quantitative

The spin-orbit Hamiltonian, \( \hat{H}_{so} \propto \mathbf{l}.\mathbf{s} \)

But \( j = l + s \) and so \( j^2 = (l + s)^2 = l^2 + s^2 + 2l.s \)

Hence: \( l.s = \frac{1}{2} \left( j^2 - l^2 - s^2 \right) \)

Substituting for eigenvalues: \( l.s = \frac{1}{2} \left( j(j + 1) - l(l + 1) - s(s + 1) \right) \)

The energy of a given \( |l, s, j> \) level is

\[
E_{l,s,j} = \frac{1}{2} \hbar c A \left( j(j + 1) - l(l + 1) - s(s + 1) \right)
\]

Where \( A \) is the spin-orbit coupling constant which, for one electron atoms is given by

\[
A = \frac{\alpha^2 R Z^4}{n^3 l \left( l + \frac{1}{2} \right) (l + 1)}
\]

n.b. spin-orbit coupling increases rapidly with atomic number

Spin-Orbit Coupling constants:
- \( \text{H}(2p) = 0.243 \text{ cm}^{-1} \)
- \( \text{H}(3p) = 0.072 \text{ cm}^{-1} \)
- \( \text{Li}(2p) = 0.3 \text{ cm}^{-1} \)
- \( \text{Na}(3p) = 17.2 \text{ cm}^{-1} \)
- \( \text{K}(4p) = 57.7 \text{ cm}^{-1} \)
- \( \text{Rb}(5p) = 237.6 \text{ cm}^{-1} \)
- \( \text{Cs}(6p) = 554.1 \text{ cm}^{-1} \)
2.10 Spectral Fine Structure

Spin-orbit coupling gives rise to splittings in spectra called fine structure.

\[ l = 1, s = \frac{1}{2} \]

\[ j = \frac{3}{2} \quad m_j = \pm \frac{1}{2}, \pm \frac{3}{2} \]

\[ j = \frac{1}{2} \quad m_j = \pm \frac{1}{2} \]

Selection Rule $\Delta j = 0, \pm 1$ (but not $0 \leftrightarrow 0$) arises from conservation of angular momentum.

\[ \text{e.g., Na} \]

\[ 3p \quad 2S_{1/2} \quad 2P_{1/2} \quad 2P_{3/2} \]

\[ 3s \quad \text{Na D-lines} \quad 17 \text{ cm}^{-1} \]

\[ \text{e.g., Na} \]

\[ 4d \quad 2D_{5/2} \quad 2D_{3/2} \]

\[ 3p \quad 2P_{3/2} \quad 2P_{1/2} \]

\[ \text{Na} \quad \text{X} \]
2.11 Atomic Term Symbols

Just a succinct notation for the angular momentum coupling in an atom. Term symbols contain 3 pieces of information:

“Spin multiplicity”

\[ = 2S + 1 \]

(Where \( S \) is the total spin quantum number for the atom)

Gives \( L \), the total orbital angular momentum quantum number for the atom:

- S: \( L = 0 \)
- P: \( L = 1 \)
- D: \( L = 2 \)
- F: \( L = 3, \text{ etc.} \)

\( J \), the total angular momentum quantum number for the atom. i.e., how \( L \) and \( S \) are coupled.
2.12 Atomic Term Symbols: one unpaired electron

For atoms with a single unpaired electron:

A. \( s = \frac{1}{2} \) and therefore \( S = \frac{1}{2} \)
   \( 2S+1 = 2 \) and all terms are “doublets”

B. \( l \) (and therefore \( L \)) is dependent on the orbital the electron is in:
   \( l = 0(s), 1(p), 2(d) \), give rise to \( S \), \( P \) and \( D \) terms, respectively

C. As we’ve seen, \( J \) depends on how \( L \) and \( S \) are coupled but the possible quantum numbers are given by the Clebsch-Gordan series:
   \[ J = L+S, L+S-1, L+S-2, \ldots \ |L-S| \]

\( e.g. \), So, the [Ne]3s\(^1\) ground state configuration of Na is \( ^2S_{1/2} \)

The excited [Ne]3p\(^1\) configuration yields \( ^2P_{3/2} \) and \( ^2P_{1/2} \) terms.

\( n.b., \) In the absence of external fields, each \( J \) level has \( (2J+1) \) degeneracy arising from \( m_J \) states:
2.13 Atomic Term Symbols: General Russell-Saunders Coupling

Term symbols really become useful when dealing with many-electron atoms. In Russell-Saunders Coupling:

A. The spins of all electrons, \( s_i \), couple to yield a total spin angular momentum \( S \). The possible values of the corresponding \( S \) quantum number arise from a Clebsch-Gordan Series.

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

for two electrons

B. The orbital angular momenta of all electrons, \( l_i \), couple similarly to yield a total orbital angular momentum \( L \). The possible values of the corresponding \( L \) quantum number arise from a Clebsch-Gordan Series.

\[
L = l_1 + l_2, \; l_1 + l_2 - 1, \ldots \; |l_1 - l_2|
\]

for two electrons

e.g., coupling of two electron spins to give \( S=0, 1 \)

e.g., coupling of orbital angular momenta \( l = 1,2 \)
C. \( L \) and \( S \) can then couple to yield the total angular momentum, \( J \).
The possible values of the corresponding \( J \) quantum number arise from a Clebsch-Gordan Series.

\[
J = L+S, \ L+S-1, \ldots \ |L-S|
\]

\( \text{e.g., } ^3D \text{ terms} \)

\( L = 2, \ S = 1 \)

\( ^3D_3 \)

\( ^3D_2 \)

\( ^3D_1 \)

\textit{n.b.}, the above coupling scheme is appropriate in the limit of weak spin-orbit coupling (small \( Z \)) and is known as \textbf{Russell-Saunders Coupling}
2.14 The spectrum of the He atom

The simplest example of a 2 valence electron atom:
The ground state is simple: configuration $1s^2$, electrons spin-paired, hence a $^1S_0$ term.

This satisfies the **Pauli Exclusion Principle** as formulated:

"No two electrons may have identical quantum numbers"

- Since $n$, $l$, $m_l$ and $s$ are the same for both electrons they must have different $m_s$. This lies at the heart of the aufbau principle of electronic configurations.

Singly excited configurations, $1s^1nl^1$ ($n \geq 2$) are more interesting:

- Now the electrons may be spin-paired (antiparallel) or spins-aligned (parallel)
- These differ in their overall spin angular momentum ($S = 0$ and $S = 1$, respectively) denoted singlet and triplet states.

Why singlet and triplet? We need to understand the Spin wavefunctions and to do that we must consider the more general form of the Pauli Principle:
2.15 The Pauli Principle

“Any acceptable wavefunction must be anti-symmetric with respect to the exchange of two identical fermions and totally symmetric with respect to the exchange of identical bosons”

Applies to the total wavefunction. We will see several manifestations of this throughout this course but for the exchange of two electrons (Fermions, \( s = \frac{1}{2} \)):

\[
\Psi(1,2) = -\Psi(2,1)
\]

\( \Psi_{\text{tot}} = \Psi_{\text{space}} \Psi_{\text{spin}} \). Consider \( \Psi_{\text{spin}} \) for He:

Each electron can have either \( m_s = \frac{1}{2} \) (spin up, or \( \alpha \) state) or \( m_s = -\frac{1}{2} \) (spin-down, \( \beta \))

Four combinations can arise: \( \alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \alpha(2)\beta(1) \)

The first two are clearly symmetric with respect to exchange but the latter two are neither symmetric, \( \alpha(1)\beta(2) \neq \alpha(2)\beta(1) \), nor anti-symmetric, \( \alpha(1)\beta(2) \neq -\alpha(2)\beta(1) \).
2.16 The Pauli Principle

The two electrons are, however, indistinguishable and we can take linear combinations of these to form eigenfunctions of the $S^2$ and $S_z$ operators:

$$\sigma_+ (1,2) = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right]$$

and

$$\sigma_- (1,2) = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right]$$

$\sigma_+ (1,2)$ is clearly symmetric with respect to exchange, $\sigma_- (1,2)$ anti-symmetric.

So our four spin wavefunctions are:

$$\begin{align*}
\alpha(1) \alpha(2) \\
\beta(1) \beta(2) \\
\sigma_+ (1,2) = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right] \\
\sigma_- (1,2) = \frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right]
\end{align*}$$

Of which the 1st three are symmetric wrt exchange and the final one anti-symmetric.

These need pairing with $\Psi_{\text{space}}$ to give anti-symmetric total wavefunctions $\Psi_{\text{tot}}$. 
2.17 Picturing spin states

**SINGLET** (spin paired): Complete cancellation of $s_1, s_2$ to give
$S = 0, S = 0, M_s = 0$ a single arrangement

**TRIPLET:** three arrangements with $S = 1 \quad [\mid S \mid = (2)^{1/2}\hbar]

$n.b., m_{s1}, m_{s2}$ are no longer well-defined
2.18 The Energy of Singlet and Triplet states: Electron Correlation

For states arising from the same configuration, the triplet state lies lower in energy than the singlet. To understand why, consider the space wavefunctions:

Consider the 1s\(^1\)2s\(^1\) configuration: \(\Psi_{\text{space}} = \varphi_{1s}(1) \varphi_{2s}(2)\) or \(\varphi_{1s}(2) \varphi_{2s}(1)\)

Which, again are neither symmetric nor anti-symmetric wrt exchange. Form linear combinations of these:

\[
\Psi_{\text{space}}^\pm (1,2) = \frac{1}{\sqrt{2}} \left\{ \varphi_{1s}(1) \varphi_{2s}(2) \pm \varphi_{1s}(2) \varphi_{2s}(1) \right\}
\]

Of which \(\Psi^+\) is symmetric under exchange and \(\Psi^-\) anti-symmetric.

As the spin wavefunctions for the triplet states are always symmetric wrt exchange these must be paired with \(\Psi^-\). Consider exchange for \(\Psi^-\):

\[
\Psi_{\text{space}}^- (1,2) = \frac{1}{\sqrt{2}} \left\{ \varphi_{1s}(1) \varphi_{2s}(2) - \varphi_{1s}(2) \varphi_{2s}(1) \right\} = -\Psi_{\text{space}}^- (2,1)
\]

When \(r_1 = r_2\) \(\Psi_{\text{space}}^- (1,1) = -\Psi_{\text{space}}^- (1,1)\) which can only be true if \(\Psi_{\text{space}}^- (1,1) = 0\).
2.19 The Energy of Singlet and Triplets: Fermi Heaps & Fermi Holes

There is zero probability of finding two electrons in the same region of space if they are described by $\Psi^-$ (and triplet states are). Conversely there is a slight maximum in the probability of finding two electrons described by $\Psi^+$ in exactly the same place.

The electrons are *correlated* – the location of each depends intimately on the other.

\[ |\Psi^-|^2 \quad |\Psi^+|^2 \]

$r_1 = r_2$ is maximum electron repulsion (*i.e.*, high energy) : Lower energy

The degeneracy of singlet and triplet is lifted by the electron repulsion. A more detailed treatment (*e.g.*, MQM) shows the energy difference to be $\Delta E = 2K$ where $K$ is the *exchange integral*:

\[
K = \frac{e^2}{4\pi \varepsilon_0} \left\langle \phi_{1s}(1) \phi_{2s}(2) \right| \frac{1}{r_{12}} \left| \phi_{1s}(2) \phi_{2s}(1) \right\rangle
\]
2.20 The Grotrian diagram of the He atom (finally)

Singlet

\( ^1S \)

\( 1s2s \)

\( 1s2s \)

\( 1s3s \)

\( 1s3s \)

\( 1s3p \)

\( 1s3p \)

\( 1s3d \)

\( 1s3d \)

\( ^1P \)

\( 1s3s \)

\( 1s3s \)

\( 1s3p \)

\( 1s3p \)

\( 1s3d \)

\( 1s3d \)

\( ^1D \)

\( 1s3s \)

\( 1s3s \)

\( 1s3p \)

\( 1s3p \)

\( 1s3d \)

\( 1s3d \)

For each configuration, every triplet state is lower in energy than the corresponding singlet

Selection Rules:
Single e\(^{-}\) changes
\( \Delta n \) unrestricted
\( \Delta l = \pm 1 \) (= \( \Delta L \))
\( \Delta S = 0 \)

NEW!
Singlet \( \leftrightarrow \) Triplet
forbidden

Absorption:
\( 1s^2 \ (^1S) \rightarrow 1s^1np \ (^1P) \)

Emission:
\( 1s^1ns \ (^1S) \rightarrow 1s^1np \ (^1P) \)
\( 1s^1ns \ (^3S) \rightarrow 1s^1np \ (^3P) \)
\( 1s^1np \ (^1P) \rightarrow 1s^1ns \ (^1S) \)
\( 1s^1np \ (^3P) \rightarrow 1s^1ns \ (^3S) \)
\( 1s^1np \ (^1P) \rightarrow 1s^1nd \ (^1D) \)
\( 1s^1np \ (^3P) \rightarrow 1s^1nd \ (^3D) \)
etc.,
A given electron configuration may give rise, within Russell-Saunders coupling, to several Terms (different \( L, S \) combinations). These in turn are split by spin-orbit coupling into Levels (unique \( J \)) which comprise \( 2J+1 \) degenerate quantum states (\( m_j \)).

For example:

\[
\begin{align*}
\text{ns np} & \quad \text{configuration} \quad \text{terms} \quad \text{levels} \quad \text{states} \quad (12 \text{ in total}) \\
1P & \quad 1P_1 & \quad \text{levels} & \quad 3 \\
3P & \quad 3P_1 & \quad 3P_0 & \quad 1 \\
3P_2 & \quad \text{levels} & \quad 5 \\
\end{align*}
\]

Electrostatic / Spin correlation magnetic

\( J_z = m_j \hbar \)

2\( J+1 \) components (degenerate in zero field)
2.22 But beware the Pauli principle......

Consider the C atom ground state, 1s²2s²2p² and which terms arise.

Naively: \( s_1 = \frac{1}{2}, s_2 = \frac{1}{2} \) and thus \( S = 0, 1 \) \( \text{(i.e., singlet and triplet terms)} \)

\[ l_1 = 1, l_2 = 1 \text{ and thus } L = 0, 1, 2 \text{ \( \text{(i.e., } S, P \text{ and } D \text{ terms)} \)} \]

\( i.e., \text{ we expect } {^1}S, {^3}S, {^1}P, {^3}P, {^1}D, {^3}D \)

But think carefully about the \(^3D\) term:

\( L = 2 \) hence it must have \( M_L = 2 \) component which must mean \( m_{l1} = 1 \) and \( m_{l2} = 1 \)

\( S = 1 \) hence it must have \( M_S = 1 \) component which must mean \( m_{s1} = \frac{1}{2} \) and \( m_{s2} = \frac{1}{2} \)

But \( l_1 = l_2 = 1 \) \text{ and } \( n_1 = n_2 = 2 \)

These two electrons would have to have identical quantum numbers which would violate the \textbf{Pauli Exclusion Principle}.

It is possible to invoke group theory to tell if a given term is allowed (MQM p238) or we can consider all possible combinations of \( M_L \) and \( M_S \).
2.23 Microstate tables

\[ l_1 = l_2 = 1 \quad m_l = -1, 0, 1 \quad s_1 = s_2 = \frac{1}{2} \quad m_s = -\frac{1}{2}, \frac{1}{2} \]

Draw up a table of every possible combination of \( m_s \) and \( m_l \) permitted by Pauli:

<table>
<thead>
<tr>
<th>( m_l )</th>
<th>( m_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \uparrow )</td>
</tr>
<tr>
<td>0</td>
<td>( \uparrow )</td>
</tr>
<tr>
<td>-1</td>
<td>( \uparrow )</td>
</tr>
<tr>
<td>( \Sigma m_l )</td>
<td>2</td>
</tr>
<tr>
<td>( \Sigma m_s )</td>
<td>0</td>
</tr>
</tbody>
</table>

The largest value of \( \Sigma m_l = 2 \) which must correspond to a D term. This only occurs with \( \Sigma m_s = 0 \). Hence a \(^1\)D term with all it’s 5 \( M_L \) states (\( M_L = \pm 2, \pm 1, 0 \)) must exist.

Strike 5 such states from the table:
### 2.23 Microstate tables

<table>
<thead>
<tr>
<th>$m_l$</th>
<th>$\Sigma m_l$</th>
<th>$\Sigma m_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 1</td>
<td>0 0</td>
</tr>
<tr>
<td>0</td>
<td>0 -1 1 0</td>
<td>0 0 1 1 1</td>
</tr>
<tr>
<td>-1</td>
<td>-1 1 0 1</td>
<td>1 -1 -1 -1</td>
</tr>
</tbody>
</table>

The largest remaining $\Sigma m_l = 1$ which must correspond to a P term. This occurs with $\Sigma m_s = 0, \pm 1$, i.e., triplet terms. Hence a $^3P$ term with all it’s 9 states must exist.

<table>
<thead>
<tr>
<th>$m_l$</th>
<th>$\Sigma m_l$</th>
<th>$\Sigma m_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 -1 1 0</td>
<td>1 -1 -1 -1</td>
</tr>
<tr>
<td>0</td>
<td>0 0 1 1 1</td>
<td>1 1 1 -1 -1</td>
</tr>
<tr>
<td>-1</td>
<td>-1 1 0 1</td>
<td>-1 -1 -1 -1</td>
</tr>
</tbody>
</table>

Leaving only a $^1S$ term remaining. Hence a $p^2$ configuration gives rise to $^1D$, $^3P$ and $^1S$. Interestingly, a $p^4$ configuration gives the same terms.
Within Russell-Saunders (LS) Coupling, for a given configuration:

1. The term with largest $S$ is lowest in Energy
2. For a given $S$ the term with largest $L$ is lowest in Energy
3. For a term with several levels:
   - if the sub-shell is less than half full the lowest $J$ level is lowest in Energy
   - if the sub-shell is more than half full the highest $J$ level is lowest in Energy

Assumes spin-correlation $\gg$ orbital angular mom$^m$ coupling $\gg$ spin-orbit coupling

Strictly applies only to finding ground states of atoms.

As we’ve seen, the C atom ground state $p^2$ configuration yields $^1D$, $^3P$, $^1S$ terms.
2.25 LS (Russell-Saunders) versus \( \vec{J} \)-\( \vec{J} \) coupling

Russell-Saunders (LS) Coupling:

\[
l_1 + l_2 + l_3 \ldots \rightarrow L
\]

\[
s_1 + s_2 + s_3 \ldots \rightarrow S
\]

\[
\downarrow
\]

\[
J
\]

Good quantum numbers: \( L, S, J \)

Selection Rules:

- \( \Delta n \) unrestricted
- \( \Delta l = \pm 1 \)
- \( \Delta L = 0, \pm 1 \)
- \( \Delta J = 0, \pm 1 \) (not \( 0 \leftrightarrow 0 \))
- \( \Delta S = 0 \)
2.25 *LS (Russell-Saunders) versus j-j coupling*

But if spin-orbit coupling is strong (large $Z$) then the spin, $s$, of an electron prefers to couple to its own orbital angular momentum, $l$, to give $j$:

**j-j Coupling:**

\[
\begin{array}{ccc}
  l_1 & l_2 & l_3 \\
  \uparrow & \uparrow & \uparrow \\
  s_1 & s_2 & s_3 \\
 \downarrow & \downarrow & \downarrow \\
  i_1 & + & i_2 + i_3 \ldots \rightarrow J
\end{array}
\]

Good quantum numbers:

\[
j_i = l_i \pm \frac{1}{2}
\]

\[
J = j_1 + j_2 + \ldots, j_1 + j_2 + \ldots -1, \text{ etc.}
\]

\[n.b. \; L, \; S \text{ undefined}\]

**Selection Rules:**

\[
\Delta n \; \text{unrestricted}
\]

\[
\Delta l = \pm 1, \; \Delta j = 0, \pm 1 \; \text{for one electron}
\]

\[
\Delta l = 0, \; \Delta j = 0 \; \text{for other electrons}
\]

\[
\Delta l = 0, \; \pm 1 \; (\text{not} \; 0 \leftrightarrow 0)
\]

e.g., down Group IV:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coupling:</td>
<td>LS</td>
<td>intermediate</td>
<td>j-j</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.26 Atoms in External Fields: lifting degeneracy

As we’ve seen $S$ and $L$ give rise to magnetic moments. These can interact with an externally applied $B$ field:

2.26.1 The Normal Zeeman Effect (when $S = 0$)

In the absence of external fields the 3 $M_L$ components of an $^1P$ term are degenerate.

But the magnetic moment associated with the orbital angular momentum can interact with any external $B$ field to lift this degeneracy.

Classically, the interaction energy:

$$E = -m_B B = -\gamma_e L_z B$$

[ $\gamma_e$ is the gyromagnetic (or magnetogyric) ratio]

Hence, quantum mechanically:

$$E = -\gamma_e M_L \hbar B = \mu_B M_L B$$

$$\gamma_e = \frac{-e}{2m_e}$$  and  $$\mu_B = -\gamma_e \hbar$$  = the Bohr magneton

→ lifts the field-free degeneracy resulting in splittings in the spectrum
Selection Rule: $\Delta M_L = 0, \pm 1$

The Normal Zeeman Effect (when $S = 0$) cont.

$B = 0$

$B > 0$

$E = \mu_B M_L B$

$\Delta M_L = -1, 0, 1$

$\nu \rightarrow$

$M_L = 0, \pm 1$

$m_B = 0$

$B > 0$
2.26.2 The Anomalous Zeeman Effect (when $S \neq 0$)

Of course the spin angular momentum also gives rise to a magnetic moment and when both $L$ and $S$ are non-zero the splittings are more complex.

Now, $E = -\gamma_e (L + 2S).B$

But we need consider only projections of $L$ and $S$ on $B$.

$$E = -\gamma_e g_J J . B = -\gamma_e g_J \hbar M_J B$$

Where the Landé $g$-factor,

$$g_J (L,S) = 1 + \frac{J( J + 1) + S(S + 1) - L(L + 1)}{2J( J + 1)}$$

e.g., $g_J = 1.5$ for a $^3P_2$ level

$= 2.00$ for $^3S_1$ level (normal spin $g$-factor)

n.b., when $S = 0$, $J = L$ and $g_J = 1 \rightarrow$ Normal Zeeman Effect
2.26.2 The Anomalous Zeeman Effect \textit{cont.}

So the levels are split into $2J + 1$ components but the splitting itself is dependent on $J$, $L$, and $S$.

Selection Rule: $\Delta M_J = 0, \pm 1$

\[
\begin{align*}
B = 0 & \quad B > 0 \\
2D_{3/2} & \quad M_J = -1, 0, 1 \quad \begin{array}{c}
3/2 \\
1/2 \\
-1/2 \\
-3/2
\end{array} \\
2P_{1/2} & \quad 1/2, -1/2
\end{align*}
\]

\[E = -\gamma_e g_J \hbar M_J B\]

\textit{i.e.}, splitting proportional to $\mu_B M_J$ and $B$

$\Delta M_J = -1, 0, 1$