Independent Electron Theory of Atoms

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2\mu}\sum_i \nabla_i^2 \;-\; \frac{e^2}{4\pi\varepsilon_0}\sum_i \frac{Z}{r_{i\mathrm{N}}} \;+\; \frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\sum_j \frac{1}{r_{ij}}$$

K.E. | electron-nucleus attraction | electron-electron repulsion

e.g. for Helium:

$$\hat{\mathrm{H}} = -\frac{\hbar^2}{2\mu}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{2}{r_{1\mathrm{N}}} + \frac{2}{r_{2\mathrm{N}}} - \frac{1}{r_{12}}\right]$$

$$\equiv \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2 + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}$$

H_1 = H atom-like Hamiltonian

$$E = \varepsilon_1 + \varepsilon_2 + \Delta\varepsilon$$

The Schrödinger Equation can not be solved exactly for this case.

But... if $\hat{\mathrm{H}} = \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2$ the problem is separable:

For $\Psi = \psi(r_1)\psi(r_2)$

$$\hat{\mathrm{H}}\Psi = \left\{\hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2\right\}\psi(r_1)\psi(r_2)$$

$$= \left\{\hat{\mathrm{H}}_1\psi(r_1)\right\}\psi(r_2) + \psi(r_1)\left\{\hat{\mathrm{H}}_2\psi(r_2)\right\}$$

$$= \left\{E_1\psi(r_1)\right\}\psi(r_2) + \psi(r_1)\left\{E_2\psi(r_2)\right\}$$

$$= (E_1 + E_2)\psi(r_1)\psi(r_2)$$

$$= E_{\mathrm{total}}\Psi$$

where $E_{\mathrm{total}} = E_1 + E_2$

Multi-Electron Atoms

Aufbau Principle

Periodic Table

- Treat the electrons as if they were independent of each other.
- Each electron is described by the same set of 4 quantum numbers that is used to describe H atom states.
- The relative arrangement of energy levels is approximately that of the H atom:

  $$1s < 2s < 2p < 3s < 3p < 3d \sim 4s < 4p$$

- Electrons are arranged in the lowest possible energy levels consistent with the Pauli Principle.

Pauli Principle (elementary version)

No two electrons may have the same set of four quantum numbers.

Objections

1. The orbital approximation implies non-interacting particles.

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \ldots \qquad E = \varepsilon_1 + \varepsilon_2 + \ldots \qquad \Psi = \prod \psi_i = \psi_1 \psi_2 \ldots$$

2. $\Psi \equiv 1s^2 2s^2 2p^6 3s^2 \ldots$ does not obey the general formulation of the Pauli Principle.

The Pauli Principle

Wave functions for half-integral spin particles (fermions) must be antisymmetric upon permutation of the coordinates of any two particles.

(symmetric for bosons)

Each independent electron wavefunction has a space and a spin part: $\psi_{1s} = \phi_{1s}(r)\alpha$ or $\phi_{1s}(r)\beta$

There are four simple product functions for He:

$$\left.\begin{aligned}
\Psi_1 &= \phi_{1s}(1)\phi_{1s}(2)\ \alpha(1)\alpha(2)\\
\Psi_2 &= \phi_{1s}(1)\phi_{1s}(2)\ \alpha(1)\beta(2)\\
\Psi_3 &= \phi_{1s}(1)\phi_{1s}(2)\ \beta(1)\alpha(2)\\
\Psi_4 &= \phi_{1s}(1)\phi_{1s}(2)\ \beta(1)\beta(2)
\end{aligned}\right\}$$

None of these obey Pauli.

An acceptable wavefunction is the antisymmetric combination:

$$\Psi_{-} = \frac{1}{\sqrt{2}}\phi_{1s}(1)\phi_{1s}(2)\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

$$= \phi_{1s}(1)\phi_{1s}(2)\cdot\frac{1}{\sqrt{2}}\cdot\begin{vmatrix}\alpha(1) & \alpha(2)\\ \beta(1) & \beta(2)\end{vmatrix}$$

Slater devised a general method of constructing acceptable wavefunctions from determinants.

Spin Orbit Coupling:
Fine Structure in Atomic Spectra

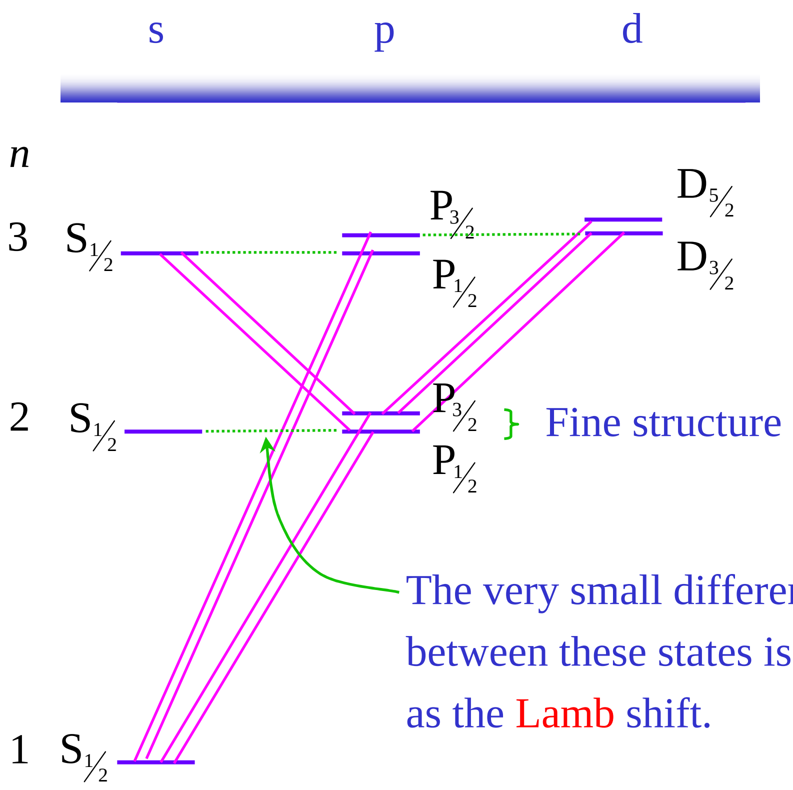
Electrons in atoms have both:

orbital angular momentum	spin angular momentum
$l = 0, 1, 2, \ldots$	$s = ½$
$m\ (l_z) = 0, \pm 1, \pm 2, \ldots \pm l$	$m_s\ (s_z) = \pm ½$

which interact by spin-orbit coupling $\vec{j} = \vec{l} + \vec{s}$ vectors

$j = l \pm ½$

Selection rules: Δn = any integer, $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$



Fine structure splitting

The very small difference between these states is known as the Lamb shift.

Quantum Numbers of Many-Electron Atoms

single electrons:	n	l	m	s	m_s
many-e atoms:		L	M_L	S	M_S

$$\hat{L}^2\,\Psi_{\text{tot}} = L(L+1)\hbar^2\Psi_{\text{tot}}$$

$$\hat{S}^2\,\Psi_{\text{tot}} = S(S+1)\hbar^2\Psi_{\text{tot}}$$

$$\hat{L}_z\Psi_{\text{tot}} = M_L\,\hbar\,\Psi_{\text{tot}} \qquad M_L = L, L-1, \ldots -(L-1), -L$$

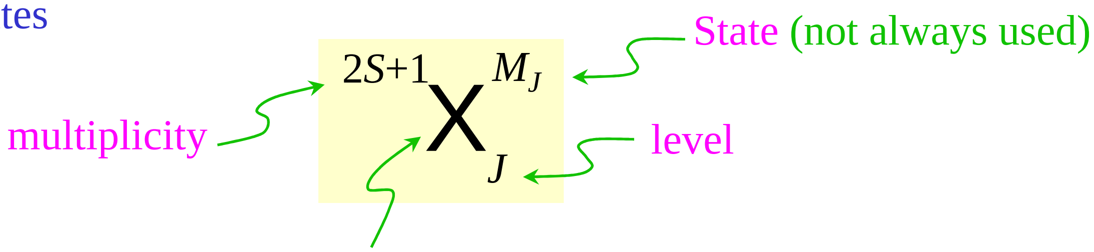
$$\hat{S}_z\Psi_{\text{tot}} = M_S\,\hbar\,\Psi_{\text{tot}} \qquad M_S = S, S-1, \ldots -(S-1), -S$$

Russell-Saunders coupling of orbital and spin angular momenta

⇒ total angular momentum characterized by J

$$\vec{L} = \sum_i \vec{l}_i \qquad \vec{S} = \sum_i \vec{s}_i \qquad \vec{J} = \vec{L} + \vec{S}$$

Term Symbols are shorthand descriptions of multi-electron states



$${}^{2S+1}\mathrm{X}_J^{M_J}$$

State (not always used)

multiplicity

level

X = S P D F

for L = 0 1 2 3

Closed shells have L = 0 and S = 0 so the term symbol is always ^{1}S

Calculation of Term Symbols

In general, a given electron configuration can give rise to *several different terms* – the electrons can couple their orbital and spin angular momenta in different ways.

To find S

$$S = \sum_{i=1}^{N} s_i,\ \sum_{i=1}^{N} s_i - 1,\ \ \sum_{i=1}^{N} s_i - 2,\ \ldots \begin{cases} \tfrac{1}{2} & \text{for } N \text{ odd} \\ 0 & \text{for } N \text{ even} \end{cases}$$

To find L

$$L = \sum_{i=1}^{N} l_i,\ \sum_{i=1}^{N} l_i - 1,\ \ \sum_{i=1}^{N} l_i - 2,\ \ \ldots L_{\min}$$

where $\quad L_{\min} = l_{\max} - \sum_{i \neq \max} l_i$ or 0 if $\sum_{i \neq \max} l_i > l_{\max}$

Easier way to find L

Calculate $M_L = \sum_i (m_l)_i$ for all possible combinations of possible values of m_l. Then infer the allowed values of L from groups of M_L.

e.g. $l_1 = 1, l_2 = 1.$ Find L

	−1	0	+1		
−1	−2	−1	0	⇨	$L = 1$ P
0	−1	0	+1	⇨	$L = 0$ S
+1	0	+1	+2	⇨	$L = 2$ D

To find J $\quad J = L+S,\ L+S-1,\ L+S-2, \ldots |L-S|$

$2S+1$ values if $L \geqslant S$

$2L+1$ values if $L \leqslant S$

Calculation of Term Symbols – 2

Inequivalent electrons — different orbitals

Find L; find S; consider all combinations.

e.g. $(1s^2\ 2s^2)\ 2p\ 3p$ The closed shell is ignored since $S = L = 0$

$$\left.\begin{array}{r} L = 0, 1, 2 \\ S = 0, 1 \end{array}\right\} \quad \begin{array}{llll} {}^1S_0 & {}^3S_1 & & \\ {}^1P_1 & {}^3P_2 & {}^3P_1 & {}^3P_0 \\ {}^1D_2 & {}^3D_3 & {}^3D_2 & {}^3D_1 \end{array}$$

Equivalent electrons — same orbitals

Some combinations of L and S are restricted by the Pauli Principle,

e.g. If two electrons have the same n, l, and m_l ...

... then they can't have identical m_s.

e.g. ${}^3S \equiv$ $\boxed{}\boxed{\uparrow\uparrow}\boxed{}$ is not allowed

Thus, $(1s^2\ 2s^2)\ 2p^2$ gives only ${}^1D$, ${}^3P$, and ${}^1S$ terms.

Complementary configurations

Since for closed shells $M_L = \sum_n (m_l)_n = 0$

$$\sum_{i=1}^{k} (m_l)_i = -\sum_{i=k+1}^{n} (m_l)_i$$

i.e. work the problem for k electrons or n-k, whichever is easier – the terms are the same.

Relative Energies of Terms:

There is no simple way to predict the order of energies of multi-electron terms. However the ground state (lowest energy state) can be predicted by:

Hund's Rules

1. The ground state of the lowest electron configuration has the maximum spin multiplicity (largest S).
2. Of the terms with maximum multiplicity, the one with lowest energy has the largest L.
3. If the electron shell is...
   less than half-filled, the smallest J has the lowest energy
   more than half-filled, the largest J has the lowest energy.

What about half-filled shells?
This has L = 0, so J = S, i.e. only one state.