Hydrogen Atom
non-relativistic Schrödinger's
Equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

In a Coulomb potential, this PDF is separable in spherical coordinates and the solutions are of the form

$$\Psi(r,\theta,\phi) \sim \frac{1}{r}R_{n\ell}(r)\,Y_\ell^m(\theta,\phi)$$

Laguerre Polynomials   Spherical Harmonics

The states are quantified by 4 quantum numbers:

$n =$ 1, 2, 3, ...   Principal quantum number

$\ell =$ 0, 1, 2, ...   Orbital angular momentum

$m_\ell = -\ell, -\ell+1, ..., +\ell$ $(2\ell+1)$ different projections of ℓ on a space axis "z".

$S = \pm\frac{1}{2}$ electron spin

The energy eigenvalues are given by

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2} \simeq \frac{-13.5984\ eV}{n^2}$$ ← Ionization potential of H

$$\mu = \frac{m_{nuc}\cdot m_{e^-}}{m_{nuc}+m_{e^-}}$$ nuclear charge $e=1$ for hydrogen

The allowed transitions are given by the selection rules for Electric Dipole transitions

$$\vec{\mu}_e = -e\vec{r}$$

by finding the matrix elements

$$\langle \Psi_{n'\ell'm'}(\vec{r}) | \hat{\mu}_e | \Psi_{n\ell m}(\vec{r}) \rangle \neq 0$$

where

$$\langle \Psi_{n'\ell'm'}(\vec{r}) | \hat{\mu}_e | \Psi_{n\ell m}(\vec{r}) \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi \Psi^*_{n'\ell'm'}(\vec{r}) \cdot (-e\vec{r}) \cdot \Psi_{n\ell m}(\vec{r}) \sin\theta \, d\theta \, d\phi$$
$$\times r^2 dr$$

USING the properties of orthoganality of spherical harmonics leads to the selection rules:

$$\boxed{\begin{array}{l} \Delta \ell = \pm 1 \\[2mm] \Delta m = 0, \pm 1 \end{array}}$$

Multi-electron atoms obey Pauli's Exclusion Principle:

○ ONLY $2 \cdot (2\ell+1)$ e^- are allowed in a given subshell with quantum numbers $n\ell$

i.e. $\ell = 0 \Rightarrow$ $\overset{s}{\text{shell}}$ $\Rightarrow 2 \cdot (2 \cdot 0 + 1) = 2$ e^- allowed

$\ell = 1 \Rightarrow$ $\overset{P}{\text{shell}}$ $\Rightarrow 2 \cdot (2 \cdot 1 + 1) = 6$ e^- allowed

$\ell = 2 \Rightarrow$ $\overset{d}{\text{shell}}$ $\Rightarrow 2 \cdot (2 \cdot 2 + 1) = 10$ e^- allowed

Due to electrostatic and magnetic interactions, the multiple
○ e^- orbital angular momenta and spins couple. We must use the rules of vector addition of quantized angular momenta. For elements in ~ first half of the Periodic Table, the individual angular momenta (ℓ_i) and spins (s_i) of all valence e^- couple as:

$$\vec{L} = \sum_i \vec{\ell}_i \qquad M_L = \sum_i m_{\ell_i}$$

$$\vec{S} = \sum_i \vec{s}_i \qquad M_S = \sum_i m_{s_i}$$

$$\vec{J} \equiv \vec{L} + \vec{S} \qquad \text{L-S coupling OR}$$
"Russell- Saunders" Coupling

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

Proof of Clebsch-Gordon Series

Consider two angular momenta $\vec{\ell_1}$ and $\vec{\ell_2}$

The quantum numbers m_{ℓ_1} and m_{ℓ_2} vary from:

$$-\ell_1 \leq m_{\ell_1} \leq +\ell_1, \quad AND \quad -\ell_2 \leq m_{\ell_2} \leq +\ell_2$$

Now let's couple (vectorially add) $\vec{\ell_1}$ and $\vec{\ell_2}$:

$$\vec{L} = \vec{\ell_1} + \vec{\ell_2}$$

Since $M_L = m_{\ell_1} + m_{\ell_2}$, the inequalities become:

$$-\ell_1 \leq M_L - m_{\ell_2} \leq +\ell_2 \qquad -\ell_2 \leq M_L - m_{\ell_1} \leq +\ell_2$$

Now let M_L, m_{ℓ_1}, and m_{ℓ_2} assume their maximal values:

$$M_L = +L \qquad m_{\ell_1} = +\ell_1 \qquad m_{\ell_2} = +\ell_2$$

then we have:

$$-\ell_1 \leq L - \ell_2 \leq \ell_1 \qquad\qquad -\ell_2 \leq L - \ell_1 \leq +\ell_2$$

$$ADDING + \ell_2: \qquad\qquad ADDING + \ell_1:$$

$$\ell_2 - \ell_1 \leq L \leq \ell_1 + \ell_2 \qquad \ell_1 - \ell_2 \leq L \leq \ell_1 + \ell_2$$

Since $L \geq \ell_2 - \ell_2$ AND $L \geq \ell_1 - \ell_2 \Rightarrow L \geq |\ell_1 - \ell_2|$

$$\Rightarrow \quad |\ell_1 - \ell_2| \leq L \leq \ell_1 + \ell_2$$

Finally, since L is an angular momentum, it can only change by intergral values

$$\Rightarrow \quad L = \ell_1 + \ell_2, \ \ell_1 + \ell_2 - 1, \ \ldots, \ |\ell_1 - \ell_2|$$

$$Q.E.D.$$

What is Parity?

Parity is the behavior of a wavefunction under the __inversion__ of the coordinate system

$$x \rightarrow -x$$
$$y \rightarrow -y \qquad \underline{OR} \qquad$$
$$z \rightarrow -z$$

$$r \rightarrow r$$
$$\theta \rightarrow \pi - \theta \qquad \underline{or} \quad \vec{r} \rightarrow -\vec{r}$$
$$\phi \rightarrow \phi + \pi$$

Why does parity go like $\prod_i (-1)^{\ell_i}$?

For single e^- wavefunctions $\quad \Psi \sim R_{n\ell}(r) Y_\ell^m(\theta, \phi)$

$R_{n\ell}(r)$ is unaffected by inversion because $r \rightarrow r$ and it is symmetric about the origin. The only component to Ψ that matters is $Y_\ell^m(\theta, \phi)$

$$Y_\ell^m(\pi - \theta, \phi + \pi) = (-1)^\ell Y_\ell^m(\theta, \phi)$$

$$\Downarrow$$

$$\hat{P} Y_\ell^m(\theta, \phi) = (-1)^\ell Y_\ell^m(\theta, \phi)$$

So the individual parities of the single wavefunctions simply multiply to get the final parity

$$\begin{cases} \hat{P}(\vec{\mu}_e) = \\ \hat{P}(e\vec{r}) = e(-\vec{r}) \\ \qquad = -e\vec{r} \\ \qquad = -\vec{\mu}_e \end{cases}$$

Electric Dipole $\longrightarrow$ Parity __changes__
Magnetic Dipole $\longrightarrow$ Parity same
Electric Quadrupole $\rightarrow$ Parity same

EXAMPLE :   Let's take a   2 valence e^- atom
in the ground state configuration $1s^2 2s^2 2p^2$ (CⅠ, NⅡ, etc.)

$$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2 \implies L = \ell_1 + \ell_2, \ \ell_1 + \ell_2 - 1, \ \dots, \ |\ell_1 - \ell_2|$$
$$= 1+1, \ 1+1-1, \ |1-1|$$
$$= 2, \quad 1, \quad 0$$

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \implies S = S_1 + S_2, \ \dots, \ |S_1 - S_2|$$
$$= \tfrac{1}{2} + \tfrac{1}{2}, \ |\tfrac{1}{2} - \tfrac{1}{2}|$$
$$= 1, \quad 0$$

Possible   terms   are

L	S	J	Term
0	0	0	$^1S_0$
1	0	1	$^1P_1$
2	0	2	$^1D_2$
0	1	1	$^3S_1$
1	1	2,1,0	$^3P_2, \ ^3P_1, \ ^3P_0$
2	1	3,2,1	$^3D_3, \ ^3D_2, \ ^3D_1$

However, we must   use   Pauli's exclusion principle to
determine   which   terms   are   allowed.

For each e^-, $\ell=1 \implies m_\ell = -1, 0, +1$ and $m_s = \pm\tfrac{1}{2}$

$\implies$ there   are $3 \times 2 = 6$ possible   one e^- states

Therefore, there are $\binom{6}{2} = \dfrac{6!}{2!(6-2)!} = \dfrac{6 \cdot 5}{2} = 15$ unique two e^- states

m_e (-1)	m_e (0)	m_e (+1)	M_L	M_S	Number
↑↓			−2	0	1
	↑↓		0	0	2
		↑↓	+2	0	3
↑	↑		−1	+1	4
↑	↓		−1	0	5
↓	↑		−1	0	6
↓	↓		−1	−1	7
↑		↑	0	+1	8
↑		↓	0	0	9
↓		↑	0	0	10
↓		↓	0	−1	11
	↑	↑	+1	+1	12
	↑	↓	+1	0	13
	↓	↑	+1	0	14
	↓	↓	+1	−1	15

15 unique
15 ← two e⁻ states!

ADDING UP
M_L's and M_S's
we make the
   table:

M_L \ M_S	1	0	−1
+2	0	1	0
+1	1	2	1
0	1	3	1
−1	1	2	1
−2	0	1	0

Example
Still con't :   Now which terms can exist ?

● $L = 2$ $S = 1$ $\Rightarrow$ $M_L = 2$ $M_S = 1$ should appear
    ^3D term   in our table. It does _not_, so
                                ^3D term is disallowed by Pauli Exclusion.

$L = 2$ $S = 0$ $\Rightarrow$ $M_S = 0$
    ^1D term $M_L = -2, 1, 0, +1, +2$

    Let's subtract those 5 states from our table:

M_L \ M_S	+1	0	-1
+2	0	0	0
+1	1	1	1
0	1	2	1
-1	1	1	1
-2	0	0	0

●

$L = 1$ $S = 1$ $\Rightarrow$ $M_S = -1, 0, +1$ There are 9 combinations
    ^3P term $M_L = -1, 0, +1$ of M_L and M_S

    Subtracting these 9 states leaves:

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

Remaining state
has $M_L = 0$ $M_S = 0$
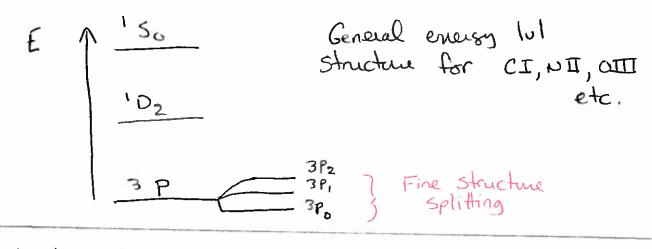$\Rightarrow$ this has to be
^1S term

● So the terms for $1s^2 2s^2 2p^2$ (CI, NII, etc.)
    are $^1D, ^3P,$ and ^1S

(^3D eliminated and ^3S eliminated)

Example
Con't: How do we order these states
by energy?

USE   HUND'S Rules

① Maximum multiplicity $2S+1$ ⇒ ^3P lowest energy

② Maximum L for same multiplicity is lower
in energy   ⇒ ^1D lower
                                      than ^1S

③ Since less than half the configuration is
filled, the state with lowest J is
lowest in energy   ⇒ $^3P_0$ lowest state

General energy lvl
Structure for $CI, NII, OIII$
                        etc.

$^1S_0$

$^1D_2$

^3P $^3P_2$
         $^3P_1$ } Fine structure
         $^3P_0$ }   splitting

FOR H, He, Li, Be
Alkali Metals

N, P, column V
       periodic table

etc.

Ground Electronic
State is

S ⇒

$L=0$ ⇒ Nothing
            to
          split

NO FINE
Structure
Splitting in
Ground State!