Review: atomic structure

hydrogen atom:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r}) = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\hat{r}}$$

solve $H\psi = E\psi$ to get eigenfunctions ψ_{nlm}
and energy eigenvalues E_n

We can write $\hat{p} \to -i\hbar\nabla$ in spherical coords
and solve.

We can also express $\hat{p}^2$ in terms of radial and
angular operators

e.g.

$$\frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{L}^2\right]\psi + V\psi = E\psi$$

this explicitly separates the angular $\hat{L}^2$ term

$$\hat{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi)$$

↳ spherical harmonics.

Then solve radial equation $\to R_{nl}(r)$

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2} = \frac{E_1}{n^2} \quad \left(\text{independent of } l, m!\right)$$

with $E_1 = -13.6\,eV$ = 1 Rydberg

Dirac notation: $\psi_{nlm}(r,\theta,\phi) \to |nlm\rangle$

Spin states + multielectron atoms

electron = fermion = spin $\frac{1}{2}$

When a system has more than 1 electron: Pauli exclusion

Specifically:

overall electron ψ must be antisymmetric on exchange of any 2 identical fermions.

If we could identify the spin state of each one of 2 electrons: $|+\rangle|+\rangle$, $|-\rangle|-\rangle$, $|+\rangle|-\rangle$, $|-\rangle|+\rangle$

But the particles are identical

$\therefore$ must have a superposition state with well-defined exchange symmetry

Also consider: what is total spin state $\vec{S} = \vec{S}_1 + \vec{S}_2$

- max $S = \frac{1}{2} + \frac{1}{2} = 1$ e.g. $|+\rangle|+\rangle \rightarrow |1,1\rangle$ $\rightarrow S_z = 1$

  min $S = 1$ $S_z = -1$ $|-\rangle|-\rangle \rightarrow |1,-1\rangle$

- we can also have $|1,0\rangle$ and $|0,0\rangle$ states.

  $|+\rangle|-\rangle$ is not allowed

$$\rightarrow |1,0\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle|-\rangle + |-\rangle|+\rangle\right) \text{ symmetric}$$

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle|-\rangle - |-\rangle|+\rangle\right) \text{ antisymm.}$$

So when we add the spin ang. mom states we get states of well-defined exchange symmetry

$|0,0\rangle$ = "singlet" state = antisymm.

$|1,1\rangle, |1,0\rangle, |1,-1\rangle$ = "triplet" state = symmetric.

→ general $\vec{J} = \vec{L_1} + \vec{L_2}$ next pg.

examples: ground state He atom

$1s^2$ $n=1$ $l=0$ 2 electrons in <u>same</u> spatial Ψ

∴ spin state must be antisymm. → singlet

notation $^1S_0$ $\quad$ $^{2S+1}L_J$ spectroscopic notation.

total $S=0$ → $2S+1=1$

total $J = L+S = 0$

ground state Li:

$1s^2 2s$ $\quad$ $^2S_{1/2}$

why 2s, not 2p? $\Psi_{200}(\,)$ is closer to nucleus

∴ less screening by $1s^2$

$^2S_{1/2}$ describes state of valence electron

2 → doublet total $S=\frac{1}{2}$ → $2S+1=2$

S total orbital ang. mom: $L=0$

1/2 total orb+spin $J = 0 + \frac{1}{2} = \frac{1}{2}$

general case:

$\vec{J} = \vec{L}_1 + \vec{L}_2$ $\qquad$ J = total

$\vec{L}_i$ = orbital or spin.

allowed ranges

$j = |l_1 - l_2| \cdots |l_1 + l_2|$ integer spacings.
always ≥ 0

$j_z = -j \to +j$ integer spacing.

examples:

$l_1 = 1$	$l_2 = 1/2$	$l_1 = 2$	$l_2 = 1$
j	j_z	j	j_z
$1/2$	$\pm\frac{1}{2}$	1	$0, \pm 1$
$3/2$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	2	$0, \pm 1, \pm 2$
		3	$0, \pm 1, \pm 2, \pm 3$

each one of these states is a combination of individual $|l_1, l_{1z}\rangle |l_2, l_{2z}\rangle$ states.

- coeff: Clebsch-Gordon coeff.

How does spin state affect energy?

- electrons have spatial $\psi(\vec{r})$
- symmetric combinations: e^- on avg closer $\to$ higher energy.

Ex He $1s^2$ ground state

each e^- in same spatial ψ: S

$\therefore$ spin state must be antisymmetric

$\to$ singlet $\to$ ^1S

Be: $(He)(2s)^2$ $\quad {}^1S_0$

B: $(He)(2s)^2(2p)$ $\quad {}^2P_{1/2}$ $\qquad$ P : $l=1$

2 : $S=\frac{1}{2}$ doublet

$1/2$: $J = L - S$

here $J = L + S = 3/2$ is also allowed

Hund's rules

1) highest total spin → lowest energy

ex: excited states of He

$1s2s \qquad S = s_1 + s_2 = 0$ or 1

$\qquad\qquad\qquad\qquad {}^1S_0 \qquad {}^3S_1$

$\qquad\qquad\qquad\qquad$ ↑ higher $\qquad$ ↑ lower

anti-sym spin → symm. spatial state → electrons are closer together → higher E

sym spin → anti sym spatial → lower energy

note that highest S must be symmetric spin - all aligned.

2) given the value of S, highest allowed L → lowest energy

note symmetrization must be obeyed.

e.g. C : $(1s)^2(2s)^2(2p)^2 \qquad L = 0, 1, 2$

for $S=1$ (triplet) need antisymm L state

highest L is symmetric.

3) subshell (n,l) $\quad < \frac{1}{2}$ full $\quad$ lowest $J = |L - S|$

$\qquad\qquad\qquad > \frac{1}{2}$ full $\quad$ highest $J = |L + S|$