

## Review: atomic structure

hydrogen atom:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r) = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

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

We can write  $\hat{p} \rightarrow -i\hbar\nabla$  in spherical coordinates  
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  $\rightarrow R_{nl}(r)$

$$E_n = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} = \frac{E_1}{n^2} \quad (\text{independent of } l, m)$$

$$\text{with } E_1 = -13.6 \text{ eV} = 1 \text{ Rydberg}$$

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

## Spin states + multi-electron atoms

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

When a system has more than 1 electron: Pauli exclusion  
Specifically:

overall electron  $\Psi$  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!

i. must have a superposition state with well-defined  
exchange symmetry

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

$$\begin{aligned} \text{max } S &= \frac{1}{2} + \frac{1}{2} & \text{e.g. } |+\rangle|+\rangle &\rightarrow |1,1\rangle \\ &= 1 & &\rightarrow S_z = 1 \end{aligned}$$

$$\text{min } S = 1 \quad S_z = -1 \quad |-\rangle|-\rangle \rightarrow |1,-1\rangle$$

\* we can also have  $|1,0\rangle$  and  $|0,0\rangle$  states.  
 $|+\rangle|-\rangle$  is not allowed

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

$$|0,0\rangle = \frac{1}{\sqrt{2}} (|+\rangle|-\rangle - |-\rangle|+\rangle) \text{ antisymmetric}$$

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.

examples: ground state He atom

$1S^2$   $n=1$   $\ell=0$  2 electrons in same spatial  $\Psi$   
i.e. spin state must be antisymm.  $\rightarrow$  singlet

notation 'S<sub>0</sub>

$2S+1$   $L_J$  spectroscopic notation,  
total  $S=0 \rightarrow 2S+1=1$

ground state Li:

$1S^2 2S$   $^2S_{1/2}$

total  $J=L+S=0$

why  $2S$ , not  $2P$ ?  $\Psi_{200}(\vec{r})$  is closer to nucleus  
 $\therefore$  less screening by  $1S^2$

$^2S_{1/2}$

describes state of valence electron

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

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

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

general case:

$$\vec{J} = \vec{l}_1 + \vec{l}_2$$

$\vec{J}$  = total

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

allowed ranges

$$j = |l_1 - l_2| \dots |l_1 + l_2| \text{ integer spacing.}$$

always  $> 0$

$$j_z = -j \rightarrow +j \text{ integer spacing.}$$

examples:

$$l_1 = 1 \quad l_2 = l_2$$

$$\begin{array}{c} j \\ \hline l_2 \\ \pm \frac{1}{2} \\ \pm \frac{3}{2}, \pm \frac{1}{2} \end{array}$$

$$l_1 = 2 \quad l_2 = 1$$

$$\begin{array}{c} j \\ \hline l_2 \\ 0, \pm 1 \\ 0, \pm 1, \pm 2 \\ 0, \pm 1, \pm 2, \pm 3 \end{array}$$

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

\* coeff: Clebsch-Gordan coeff.

How does spin state affect energy?

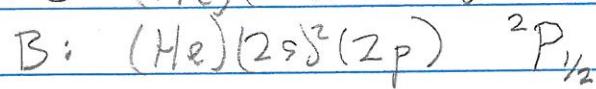
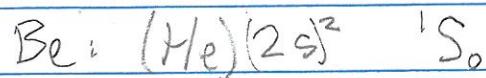
- electrons have spatial  $\Psi(\vec{r})$

- symmetric combination:  $e^-$  on  $a\beta$  closer  $\rightarrow$  higher energy.

Ex He  $1s^2$  ground state

each  $e^-$  in same spatial  $\Psi$ : S

i. spin state must be antisymmetric  
 $\rightarrow$  singlet  $\rightarrow ^1S$



P:  $\ell=1$

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

$\frac{1}{2}$ :  $J=L-S$

here  $J=L+S=\frac{3}{2}$  is also allowed

### Hund's rules

1) highest total spin  $\rightarrow$  lowest energy

ex: excited states of He

$$1s\ 2s \quad S = S_1 + S_2 = 0 \text{ or } 1$$
$$^1S_0 \quad ^3S_1$$

anti-sym spin  $\rightarrow$  symm. spatial state  $\rightarrow$  electrons are closer together  $\rightarrow$  higher E  
higher lower

sym spin  $\rightarrow$  anti-sym spatial  $\rightarrow$  lower energy

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

2) given the value of S, highest allowed L  $\rightarrow$  lowest energy

note symmetry must be obeyed.

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

for  $S=1$  (triplet) need antisymmetric L state  
highest L is symmetric.

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

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