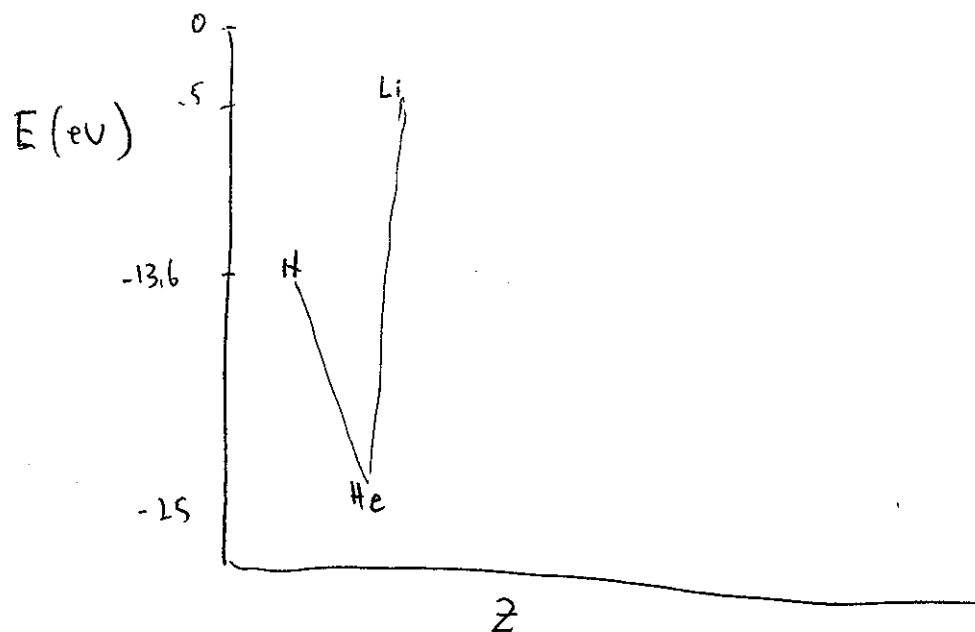


## Ionization Energy

- amount of energy needed to remove one electron



filled shells, subshells shield nuclear potential

## Spin-Spin coupling

$$s = \frac{1}{2}$$

for two electron

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$S = \sqrt{s(s+1)} \hbar$$

$$s = 0, 1$$

electrons with same spin are 'pushed' apart by Pauli-exclusion principle - lowering energy.

## Orbital-Orbital Coupling

$$\vec{L} = \vec{L}_1 + \vec{L}_2$$

$$l = |l_1 - l_2| \dots l_1 + l_2$$

$$L = \sqrt{l(l+1)} \hbar$$

larger  $l$  values correspond to states where electrons are further apart. This gives lower energy for larger  $l$ .

## Spin-Orbit Coupling

$$\vec{J} = \vec{L} + \vec{S}$$

$$j = |l - s|, \dots l + s$$

Small compared to spin-spin, orbital-orbital

consider 2 electrons ~~state~~ in 2 p state

wave function must be anti-symmetric

from Pauli exclusion principle

write  $\psi_{\text{total}} = \psi_{\text{space}} \psi_{\text{spin}}$

$$\psi_A = (\psi_{\text{space}})_A (\psi_{\text{spin}})_S$$

or  $\psi_A = (\psi_{\text{space}})_S (\psi_{\text{spin}})_A$

$S = 1$  - symmetric

$S = 0$  - anti-symmetric

States with  $l$  odd - anti-symmetric  
 $l$  even - symmetric

$$\chi_{\text{total}} = (-1)^{l+s+1} \chi(\text{total})$$

only  $l+s+1$  - odd are allowed

is  $s=1, l=1$

$$j = 0, 1, 2$$

is  $s=0$

$$l=0, 2$$

$$\Downarrow \quad \Downarrow$$

$$j=0, 2$$

no further splitting of levels  
beyond orbital-orbital.

## JJ Coupling

when  $Z$  is large, spin-orbit dominates  
over spin-spin, orbital-orbital coupling

treat each electron independently

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1$$

$$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$$

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

Singlet, triplet states

Consider the helium atom

total spin quantum number,  $s = 0, 1$

$s = 0$      $m_s = 0$     - singlet - para helium

$s = 1$      $m_s = \begin{matrix} -1 \\ 0 \\ 1 \end{matrix}$     ] triplet - orthohelium

ground state -  $1s^2$ ,  $s = 0$

$1s'2p'$  and  $1s'2s'$  can both  
have singlet, triplet states

triplet states,  $s = 1$ , can not  
decay to ground state because

$\Delta s$  would be 1

Selection rules

$$\Delta s = 0$$

$$\Delta l = \pm 1$$

Atoms in external Magnetic fields

Weak field

$$\Delta E = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B}$$

can't just use  $\vec{L}$  and  $\vec{S}$  since they  
are coupled through spin-orbit.

must use  $\vec{J} = \vec{L} + \vec{S}$

$$\Delta E = \frac{e}{2m} \left[ \frac{(\vec{L} + 2\vec{S}) \cdot (\vec{J})}{J} \right] \left( \frac{\vec{J} \cdot \vec{B}}{J} \right)$$

assume  $\vec{B}$  is in z direction

$$\Delta E = \frac{e}{2m} \left[ \frac{(\vec{L} + 2\vec{S}) \cdot (\vec{L} + \vec{S}) J_z B}{J^2} \right]$$

$$J_z = m_j \hbar$$

$$\Delta E = g_L m_j \mu_B B$$

$$g_L = \frac{3J^2 - L^2 + S^2}{2J^2}$$

Strong field

Breaks spin-orbit coupling

$$\Delta E = (m_L + 2m_S) B \mu_B$$