MANY-ELECTRON ATOMS

Central Field Approx & Vee

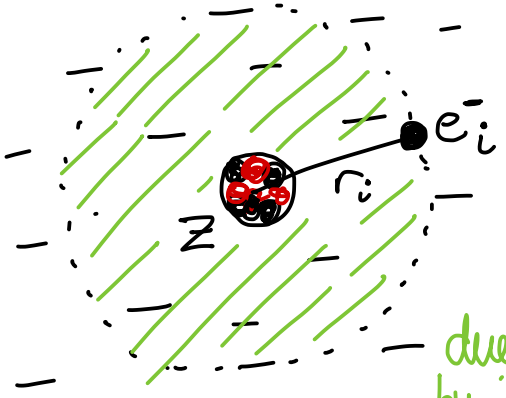
$$\mathcal{H} = \underbrace{\sum_{i=1}^{N_e} \frac{\hat{p}_i^2}{2m} - \sum_{i=1}^{N_e} \frac{Ze^2}{4\pi\varepsilon_0 r_i}}_{\mathcal{H}_{BohR}} + \underbrace{\sum_{i=1}^{N_e}\sum_{j>i} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}}_{V_{ee}} + \underbrace{\sum_{i=1}^{N_e} \xi \vec{s}_i \cdot \vec{l}_i}_{V_{s\text{-}o}}$$

for multi e⁻ atoms

V_{ee}: REPULSION betw e⁻ pairs

$V_{s\text{-}o}$ + $V_{relativ}$ + $V_{Lamb\ shift}$ + $V_{hyperfine}$

V_{ee}: SCREENING effect



sees Q_{enc} @ r_i < FULL $+Z|e|$

due to "screening" by OTHER e⁻

effective "$Z_{enclosed}$" < $Z_{nucleus}$

left-over $V_{ee}^{residual} \ll V_{ee}$ ⇐

∴ more tractable

Approximate:

$$\mathcal{H} = T - \sum_{i=1}^{N_e} \frac{Z^{SCR} e^2}{4\pi\varepsilon_0 r_i} + V_{ee}^{residual}$$

(SCREENED)

where $Z^{SCR} < Z$

screened single-electron potential = central field approx

a.k.a. mean-field approx

② screening explains FILLING ORDER of shells:

In multi-e^- atoms, shells filled by order of increasing $(n+\ell)$

$E_n^{\text{Bohr}} \sim -\frac{1}{n^2}$ ONLY ... $E_n \uparrow$ with n (less negative) $\therefore$ $n=1$ filled first, $n=2$ " next, etc...

... add screening effect: $\langle r \rangle$ of an e^- in state $|n\ell\rangle$ grows with $\ell\uparrow$ (centrifugal effect)

$\therefore$ amount of screening grows with $\ell\uparrow$

$\therefore$ higher E = weaker binding with $\ell\uparrow$

$\Rightarrow$ rule of thumb: $\boxed{E_{n\ell}\uparrow \text{ with } \sim(n+\ell)}$

③ Closed shells = all states occupied

For each shell $\equiv$ a given (n,ℓ) $\exists$ a finite # of states (m_ℓ, m_s)

e.g. s-shells: $m_s = \pm\frac{1}{2}$, $m_\ell = 0 \rightarrow$ 2 STATES

p-shells: $m_s = \pm\frac{1}{2}$, $m_\ell = -1,0,+1 \rightarrow$ 6 STATES

Filled shells are built from PAIRS with SAME m_ℓ & diff. m_s

e.g. $1s^2$ FILLED: $|gs\rangle = |1\,0\rangle_{m_{\ell_1}, m_{\ell_2}} |\uparrow\downarrow\rangle_{m_{s_1}, m_{s_2}} = |0^\uparrow\, 0^\downarrow\rangle_{1,2}$

anti-symmetrize: swap every pair of ptcle indices & subtract: $-|1\,0\rangle|\downarrow\uparrow\rangle$

$$|gs\rangle = A\left[|1\,0\,0\rangle|\uparrow\downarrow\rangle - |1\,0\,0\rangle|\downarrow\uparrow\rangle\right]$$

antisymmetrized for full 1s shell

$$= \underbrace{\frac{1}{\sqrt{2}}}_{\text{norm. factor}} \underbrace{|1\,0\,0\rangle}_{\text{spatial SYMMETRIC}} \times \underbrace{\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]}_{\text{spin ANTI-SYMMETRIC}}$$

What is term symbol $^{2S+1}L_J$? ... what is total S? → the $S=0$ singlet

In general, every pair of electrons with the same spatial q.nos will have $S_{pair}=0$

} closed shells are composed of such pairs

∴ they have TOTAL $S=0$

... similarly, TOTAL $L=0$

LS Coupling scheme a.k.a. Russel-Saunders scheme

For all but heaviest atoms,
good q. nos for multi-e^- atoms are APPROXIMATELY

L = total OAM = $\left|\sum_{i=1}^{N_e} \vec{l}_i\right|$

S = total SPIN = $\left|\sum_{i=1}^{N_e} \vec{s}_i\right|$

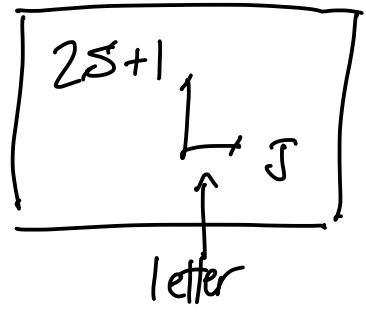
} when ↓ spin-orbit term $V_{s\text{-}o}$ ignorable, i.e. $\ll V_{coul} + V_{ee}$

and J = total AM = $|\vec{L} + \vec{S}|$ ← not approx!

- no $\vec{\tau}_{EXT}$ on atom?
- $\mathcal{L}$ / $\mathcal{H}$ spherically symmetric ≡ unchanged by global rotation

(FYI: when $V_{s\text{-}o} \not\ll V_{ee}$, use "jj coupling scheme")

In LS scheme, term symbol describing state of multi-e^- atom is



HUND RULES

Which $^{2S+1}L_J$ states have LOWEST ENERGY?

ie. finding ground state

Recall: $V_{ee} \gg V_{s\text{-}o}$ for all but heaviest atoms

① S maximized: ↑↑↑ aligned as much as poss.

symm. χ when ↑↑↑ aligned → ψ_A → REPULSIVE exchange force, keeps ee apart

② L maximed

max L: $\uparrow \ell_1$, $\uparrow \ell_2$ electrons meet less than $\uparrow \ell_1$, $\downarrow \ell_2$

both minimize V_{ee}

③ J minimized for shells that are $\leq \frac{1}{2}$ full
maximized " " " " $> \frac{1}{2}$ full

$V_{s\text{-}o} \sim \vec{\ell} \cdot \vec{s}$ smallest when $\ell^{\uparrow} s^{\downarrow}$ anti-aligned

→ minize $|\vec{J}| = \vec{L} + \vec{S}$

minimizes $V_{s\text{-}o}$

Apply sequentially: ① then ② then ③

e.g. Level diagram for $2p^2$ valence electrons of Carbon

↑ outside filled shells ∴ "active" electrons

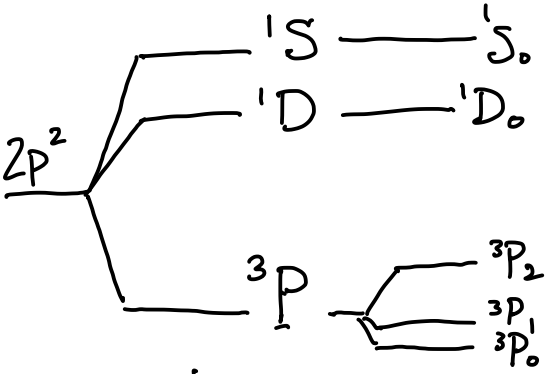
↑ Hund rules identify ground state ... what about excited states?

Possible states: $S: \frac{1}{2} \times \frac{1}{2} = 0, 1 \Rightarrow$ ^{1}singlet, ^{3}triplet
ANTI SYMM

$^{2S+1}L_J$ $\quad L: 1 \times 1 = 0, 1, 2 \Rightarrow S, P, D$

SYMM ANTI SYMM
*stretched state

Total state SPACE · SPIN = ANTI = $^1S_0, \ ^1D_2, \ ^3P_{0,1,2}$
(L) (S) ↑ ground state



E_{BOHR} $n=2$

Vee
Hund #1: max S
#2: max L
to minimize E

$V_{SO} \sim \vec{s} \cdot \vec{l}$
splits J degeneracy
Hund #3

1×1	D	D	P
	2 (+2)	2 (+1)	1 (+1)
+1 +1	1		
+1 0	1/2	1/2	
0 +1	1/2	−1/2	

	D	P	S
	2	1	0
	0	0	0
+1 −1	1/6	1/2	1/3
0 0	2/3	0	−1/3
−1 +1	1/6	−1/2	1/3

	D	P
	2	1
−1	−1	

	D
0 −1	2
−1 0	−2
−1 −1	1

m_{l_1} m_{l_2}