Lecture 20 — 11/17

Announce:

- Will do group theory/symm. for rest of class → who knows?
  I'll post pages from Dresselhaus book.

Program:

- Many-electron atoms
- Symmetry

c) Hund's rules

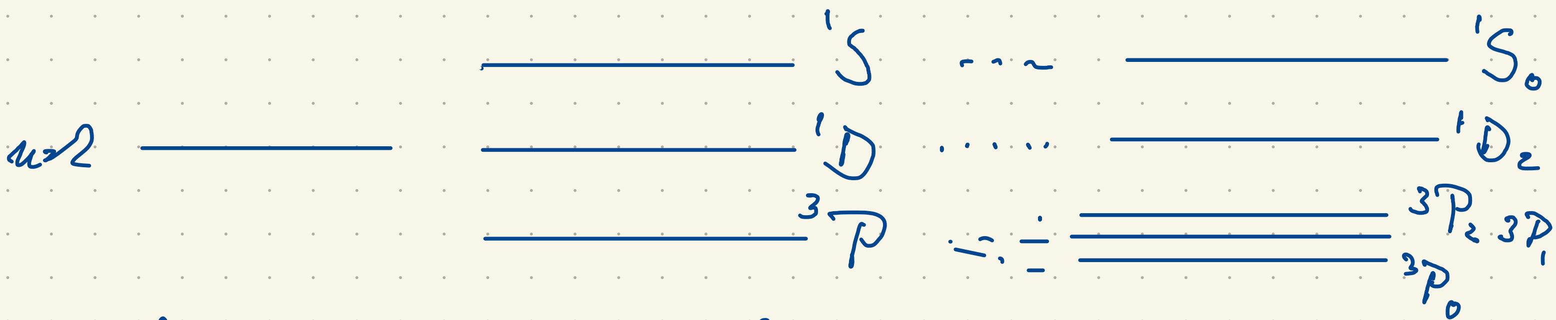
① In any given subshell (same n, same L), state with largest S is energetically lowest.

② For same shell (same n), same S state with highest L has lowest energy.

Reason in both cases: get $\bar{e}$'s as far apart as possible!

① gives bigger energy difference than ②.

Example: $1s^2\, 2s^2\, 2p^2$



Why? Open sub-shell: $2p^2$

$$|l_1 - l_2| \leq L \leq |l_1 + l_2| \qquad (l_1 = l_2 = 1)$$

$$0 \leq L \leq 2$$

$$|s_1 - s_2| \leq S \leq |s_1 + s_2| \qquad (s_1 = s_2 = \tfrac{1}{2})$$

$$0 \leq S \leq 1$$

$\Rightarrow$ in principle: $L = \{0, 1, 2\}$, $S = \{0, 1\}$

$^{2S+1}L_J \rightarrow {}^1S_0,\ {}^3S_1,\ {}^1P_1,\ {}^3P_{0,1,2},\ {}^1D_2,\ {}^3D_{1,2,3}$

which allowed?

Symmetry: S: $S = 0$ (odd) $\quad S = 1$ (even)

L: S, D (even) $\quad P$ (odd)

only $\Rightarrow$ $^1S_0,\ {}^1D_2,\ {}^3P_{0,1,2}$ allowed!

1^{st} Hund's rule : ^3P Correct

2^{nd} " : S higher than D

How to sort different J:

in principle : case-to-case

in practice :

"regular" (Energy $\sim J$) - for up to half-filled subshells (✓)

"inverted" ordering : otherwise

<u>Note</u>: "reason" for Hund's rules:

①: subshells (e.g., p_x, p_y, p_z) singly occupied before pairing (due to e^--repulsion), all same spin (if possible) $\Leftarrow$ more effective screening

②: higher $L \Longleftrightarrow$ larger distance between e^-

"③": $\langle H_{spin-orbit} \rangle = \xi \langle \vec{L} \cdot \vec{S} \rangle \Rightarrow E_{J+1} - E_J \Big|_{\text{equal } L, S} = \xi (J+1)$

$\xi > 0$ ("regular") for subshell ruled by e^-

$\xi < 0$ ("inverted") holes

<u>in general</u>: (p^1 and p^5) or (p^2 and p^4)

(d^1 and d^9) or (d^2 and d^8)...

have <u>same</u> configuration (i.e. e^- in empty subshells have same effect as holes in full subshells)!

9) Symmetry

a) Short review (selection rules)

So far:

parity: $\Delta l, \Delta j$ = odd

spherical symmetry: $\Delta l = \pm 1, \; \Delta j = \pm 1, 0$

$\Delta m_l, \Delta m_j = \pm 1, 0$

In general:

$$\boxed{\begin{gathered}\text{System is symmetric under operator } \hat{R}: \\ \Updownarrow \\ [H_0, \hat{R}] = 0\end{gathered}}$$

b) time reversal symmetry

$\hat{T}: \; t \rightarrow -t$

even: $\vec{r} \Rightarrow \ddot{\vec{r}}, \vec{F}, E, V(\propto r^\alpha), \vec{d}, \ldots$

odd: $\dot{\vec{r}} \Rightarrow \vec{L}, \vec{j}, \vec{B}, \ldots$

Simple case: (S.Eq.)

$$\hat{T}\,\psi(t) = \hat{T}\,\psi(0)\,e^{-\frac{i}{\hbar}Ht} = \psi(0)\,e^{+\frac{i}{\hbar}Ht} = \psi^*(t)$$

Properties

① $[\hat{T}, H] = 0$

② $\boxed{\hat{T}\,i = -i\,\hat{T}} \Rightarrow \hat{T}a = a^*\hat{T}$

"anti-linear"

③ $\hat{T}\,\psi(t) = \psi^*(t)\,\hat{T}$

④ no spin: $\hat{T}$ is just "c.c." operator $\hat{K}$

with spin: $\hat{T} = \hat{K}\,\sigma_y$

no spin : $\hat{T}^2 = 1$

with spin : $\hat{T}^2 = -1$

$\underbrace{\vec{d}\cdot\vec{B}}$

(more details: Diesselhaus script)

<u>Consequences:</u>

- $\hat{T}$ (and $\hat{K}$) is "anti-unitary"
- <u>Kramer's theorem</u> : for $\hat{T}^2 = -1$ has to have at least a 2D irred representation (two degenerate eigenfunctions)

  (Proof: time-reversed state <u>also</u> eigenstate, but cannot be the same.)
- Electric field cannot split states $\pm|m|$: $\vec{E}$ is even under $\hat{T}$, angular mom. is odd: energy has to be invariant under $\hat{T}$.

$\square$

- Electric dipole moment: EDM:

An intrinsic (i.e. not induced) EDM violates both T and P symmetries.

Proof: total angular mom (of particle, e.g. e^-) : $\vec{J}$

assume dipole moment $\vec{d}$:

$\vec{d}$ has to be parallel to $\vec{J}$ (all components $\perp$ to $\vec{J}$ average out, $\vec{J}$ <u>only</u> preferred direction!)

$\Rightarrow \vec{d} = \beta\,\vec{J} \quad (\beta \in \mathbb{C})$

$\vec{J}$ changes under $\hat{T}$, but not under $\hat{P}$.
$\vec{d}$ changes under P, but not under T

$\Rightarrow$ either (separately):

$$\vec{d} = \beta \vec{J} \quad \underset{P}{\overset{T}{\Longrightarrow}} \quad \vec{d} = -\beta \vec{J}$$

$$\Rightarrow \beta = 0 \quad \Rightarrow \quad \vec{d} \overset{!}{=} 0 \qquad \square$$