Lecture 19 — 11/13

Announce:

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

Program:

- Many-electron atoms
- Symmetry

8) Many-electron atoms

a) Helium

$$H = \underbrace{\sum_{i=1}^{2}\left(\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2\tilde{e}}{r_i}\right)}_{H_i} + \underbrace{\frac{\tilde{e}}{r_{12}}}_{V}$$

- Ground state

• unperturbed (no V):

$$(H_1 + H_2)\,|\psi\rangle = E^{(0)}\,|\psi\rangle$$

$$\Rightarrow |\psi\rangle_{1s^2} = |\psi_1\rangle \otimes |\psi_2\rangle \qquad (Z=2)$$

$$E^{(0)} = 2E_1(Z=2) \approx -109\ eV$$

• V as perturbation: $\psi_{1s^2}^{(0)} = \frac{1}{4\pi} R_{1s}(r_1) R_{1s}(r_2)$

$$\langle V\rangle = \langle \psi_{1s^2} | V | \psi_{1s^2}\rangle \approx 34\ eV$$

$$\Rightarrow E^{(1)}(1s^2) \approx -75\ eV$$

ionization energy:

$$He^+ \longrightarrow He^{++} : \sim 54.5\ eV$$

$$He \longrightarrow He^+ : \sim 21\ eV$$

(Not very good approx: $34 \not\ll 75$ ⇒ use variational ansatz: $\langle V\rangle \approx 25\,eV \Rightarrow E(1s^2) \approx -79\ eV$

- Excited states

unperturbed (no V): $\psi_{1s}(1) = \frac{1}{\sqrt{4\pi}} R_{1s}(r_1)$

$$\psi_{nl}(2) = Y_{lm}(\vartheta_2, \varphi_2) R_{nl}(r_2)$$

$$\Rightarrow \psi = \left\{ \begin{matrix} \psi_{1s}(1)\,\psi_{nl}(2) \\ \psi_{nl}(1)\,\psi_{1s}(2) \end{matrix} \right\} \text{ or } \quad \text{"exchange degeneracy"}$$

Define: $\hat{P}_{12} f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1) = \pm f(\vec{r}_1, \vec{r}_2)$

$[H, \hat{P}_{12}] = 0$

$\Rightarrow \frac{1}{\sqrt{2}} \left(f(\vec{r}_1, \vec{r}_2) \pm f(\vec{r}_2, \vec{r}_1) \right)$: eigenfcts of $\hat{P}_{12}$

$\psi^{\pm} = \frac{1}{\sqrt{2}} \left(\psi_{1s}(1) \psi_{nl}(2) \pm \psi_{nl}(1) \psi_{1s}(2) \right)$

perturbed (V):

$\langle V \rangle^{\pm} = J \pm K$, where

$J = \langle (1,2) | V | (1,2) \rangle = \langle (2,1) | V | (2,1) \rangle$

$K = \langle (1,2) | V | (2,1) \rangle = \langle (2,1) | V | (1,2) \rangle$

e.g. $J_{1s,2p} \approx 2.8 \cdot 10^{-2}\,eV$ } much smaller

$K_{1s,2p} \approx 0.25\,eV$ } than $1s^2$-case!

- <u>spin eigenfunctions</u>

Remember: e^- are fermions $\Rightarrow$ total wavefunction has to be antisymmetric!

- ground state: $\psi^{(space)}_{1s^2}$ symmetric

$\psi^{(spin)}_{g.s.} \stackrel{!}{=}$ antisymmetric

- excited state: ψ^{space} : symm. <u>or</u> antisymm.

ψ^{spin} : antisymm. symm.

$\psi^{total} = \psi^{space} \cdot \psi^{spin} =$

$\psi^{space}_{S} \cdot \psi^{spin}_{A}$ <u>or</u> $\psi^{space}_{A} \cdot \psi^{spin}_{S}$

$\uparrow\uparrow$ $\uparrow\downarrow$ $\downarrow\uparrow$ $\downarrow\downarrow$

b) Many-e^- systems (with nucleus) (basically same idea)

$$H_{N,Z} = \frac{p_{nucl}^2}{2m_{nucl}} + \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i} - \frac{\tilde{e}^2 Z}{|\vec{r}_i - \vec{r}_{nucl}|}\right) + \frac{1}{2}\sum_{i\neq j}\frac{\tilde{e}^2}{|\vec{r}_i - \vec{r}_j|}$$

- center-of-mass coords:

$$M = m_{nucl} + \sum_i m_i$$
$$\vec{R} = \frac{1}{M}\left(m_e \sum_i \vec{r}_{i,e} + m_{nucl}\vec{r}_{nucl}\right) \Big\} \text{ COM}$$

$$\vec{r}_i \leftarrow \vec{r}_{i,e} - \vec{r}_{com}$$

$$\vec{P} \Rightarrow \frac{\hbar}{i}\vec{\nabla}_R \quad , \quad \vec{p}_i = \frac{\hbar}{i}\vec{\nabla}_i$$

$$\vec{P}_{nucl} = \frac{m_{nucl}}{M}\vec{P} - \sum_i \vec{p}_i$$

$$\vec{p}_{i,e} = \frac{m_e}{M}\vec{P} + \vec{p}_i$$

$$\frac{\vec{P}_{nucl}^2}{2m_{nucl}} + \sum_i \frac{\vec{p}_{i,e}^2}{2m_{i,e}} = \frac{\vec{P}^2}{2M} + \sum_i \frac{\vec{p}_i^2}{2\mu} + \frac{1}{m_{nucl}}\sum_{i<j}\vec{p}_i\cdot\vec{p}_j$$

$$\mu = \frac{m_e m_{nucl}}{m_e + m_{nucl}}, \quad M = m_{nucl} + \sum_i m_i$$

"mass polarizable" (neglect)

$$\Rightarrow \boxed{H = \sum_i \frac{\vec{p}_i^2}{2\mu} + \sum_i V_i + \sum_{i<j} W_{ij}}$$ internal dof

$$V_i = -\frac{\tilde{e}^2 Z}{r_i} \quad , \quad W_{ij} = \frac{\tilde{e}^2}{r_{ij}}$$

my generic Hamiltonian: Kin.E + single Pot + 2-part. Pot

- Pauli principle & Slater determinant

Wave functions of N electrons depend on

- spatial coords $\vec{r}_i$
- spin coords m_{s_i}

$$\{\vec{r}_i, m_{s_i}\} \rightarrow x_i$$

① electrons indistinguishable $\Rightarrow [H, P] = 0$

where P is "permutation operator"

$$P\psi(x_1, \ldots, x_N) = \psi(x_{P(1)}, x_{P(2)}, \ldots, x_{P(N)})$$

Any perm. op. $\hat{P}$ can be built from swaps:

$\hat{P}_{ij}$ exchanges coords of i, j

$$\hat{P}_{ij}\,\psi(x_1 \dots x_i \dots x_j \dots x_N) = \psi(x_1 \dots x_j \dots x_i \dots x_N) = \pm\psi(x_1 \dots x_i \dots x_j \dots)$$

"+": bosons, ψ symmetric

"−": fermions: ψ antisymm.

② Permutations $\hat{P}$ consist of even or odd number of swaps $\Rightarrow$ $\hat{P}$ is "even" or "odd"

$$\hat{P}\psi \to (-1)^{\hat{P}}\psi, \quad (-1)^{\hat{P}} = \begin{cases} +1 & \text{if } \hat{P} \text{ even} \\ -1 & \text{if } \hat{P} \text{ odd} \end{cases}$$

fermions: $\hat{P}\psi = (-1)^{\hat{P}}\psi$, bosons: $\hat{P}\psi = \psi$

→ "antisymmetric wavefct":

use "antisymmetrization operator":

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{\hat{P}} (-1)^{\hat{P}} \hat{P} \qquad \text{(for } N! \text{ permutations)}$$

$\Rightarrow \hat{A}\,\psi(x_1 \dots x_N)$ is antisymm!

(proof: $\hat{P}\hat{A}\psi = \frac{1}{\sqrt{N!}} \sum_{\hat{Q}} (-1)^{\hat{Q}} \hat{P}\hat{Q}\psi = (\hat{P}\hat{Q} \equiv \hat{R})$

$(-1)^{\hat{Q}} = (-1)^{\hat{P}} \cdot (-1)^{\hat{P}\hat{Q}}$

$\sum_{\hat{P}\hat{Q}}$ (just sum over all permutations)

$$= (-1)^{\hat{P}} \frac{1}{\sqrt{N!}} \sum_{\hat{R}} (-1)^{\hat{R}} \hat{R}\psi$$

$\frac{1}{\sqrt{N!}} \sum_{\hat{R}} (-1)^{\hat{R}} \hat{R}\psi = \hat{A}$

$\Rightarrow$ for $\Psi_0(x_1 \dots x_N) = \prod_i \psi_i(x_i)$

H-like single-particle wavefcts ψ_i: $\left(\frac{p^2}{2m} + V\right)$

$\Rightarrow \Psi^{\text{fermion}} = \hat{A}\Psi_0 = \frac{1}{\sqrt{N!}} \det a_{ij}$

with $a_{ij} = \psi_i(x_j)$

"Slater determinant"

- Properties:

① any two ψ_i equal $\Rightarrow \Psi^{\text{fermion}} = 0$

$\Rightarrow$ **Pauli principle: no two fermions can occupy the same single-particle state.**

more general:
$\Psi^{\text{fermion}} = 0$ if single-part. states are linearly dependent.

② Ψ^{fermion} invariant under elementary replacement of rows: $\psi_i \to \psi_i + \sum_{j \neq i} c_j \psi_j$

Slater determinant Ψ^{fermion} is not determined by particular set of ψ_i, but by the subspace they span

- Scalar products & expectation values

$- \langle \vec{x} \mid \Psi \rangle \equiv \Psi(\vec{x}) = \Psi(x_1, \dots, x_N)$

$- \langle \Phi \mid \Psi \rangle = \det \langle \phi_j \mid \psi_i \rangle$

Proof: $\langle \Phi \mid \Psi \rangle = \int d^N x \, \frac{1}{N!} \sum_{P,Q} (-1)^{PQ} \phi_i^*(x_{P(i)}) \, \psi_j(x_{Q(j)}) =$

$= \frac{1}{N!} \sum_{P,Q} (-1)^{PQ} \sum_k \langle \phi_{P'(k)} \mid \psi_{Q'(k)} \rangle = \det \langle \phi_j \mid \psi_i \rangle$

- similarly:

$$\langle \Phi \mid \sum_{i=1}^N V_i \mid \Psi \rangle = \langle \Phi \mid \Psi \rangle \sum_{i,j} \langle \phi_i \mid \sum_k V_k \mid \psi_j \rangle \, B_{ji}$$

$$\text{with } (B^{-1})_{ij} = \langle \phi_i \mid \psi_j \rangle$$

- $\langle \Phi | \sum_{i<j} w_{ij} | \Psi \rangle =$

$= \frac{1}{2} \langle \Phi | \Psi \rangle \sum_{ijkl} \langle \phi_i \phi_j | \Sigma w | \psi_k \psi_l \rangle \left(B_{ki} B_{lj} - B_{kj} B_{li} \right)$

Properties:

- $\langle \Psi | \Psi \rangle = 1$ (if ψ_i orthonormal)
- $\langle \Phi | \Psi \rangle \neq 0$ only if same single-particle states are occupied!
- ($\{\psi_i\}\{\phi_i\}$ orthonormal:)

$\langle \Psi | \Sigma V | \Psi \rangle = \sum_i \langle \psi_i | V | \psi_i \rangle$

$\langle \Phi | \Sigma V | \Psi \rangle \neq 0$ only if at most one $\psi_i =$ "ψ_{hole}" is replaced in Φ by some $\phi_j =$ "$\psi_{particle}$" which is occupied in ψ_i.

Φ in this case is called a "one particle - one hole" excitation $\Psi_{p.h.}$ of Ψ.

$\Rightarrow \langle \Psi_{p.h.} | \Sigma V | \Psi \rangle = \langle \psi_p | V | \psi_h \rangle$

- similar for W:

$\Rightarrow$ two particle - two hole excitations

$\langle \Phi | \Sigma W | \Psi \rangle \overset{!}{=} \langle \Psi_{p_1 p_2; h_1 h_2} | \Sigma W | \Psi \rangle =$

$= \langle \psi_{p_1} \psi_{p_2} | \Sigma W | \psi_{h_1} \psi_{h_2} \rangle - \langle \psi_{p_1} \psi_{p_2} | \Sigma W | \psi_{h_2} \psi_{h_1} \rangle$

"two-particle - two-hole" excitations

c) Hund's rules

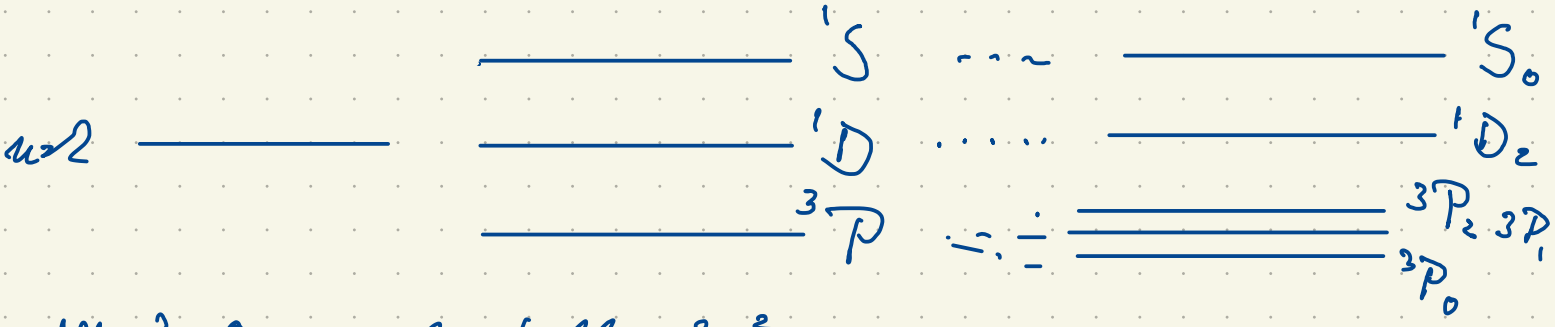
① In any given subshell (same n, same L), state with largest S is energetically lowest.

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

Reason in both cases: get 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: $2p^2$

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

$0 \leq L \leq 2$

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

$0 \leq S \leq 1$

$\Rightarrow$ 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!

1st Hund's rule: ^3P lowest

2nd " : S highest Term D

How to sort different J:

in principle: case-by-case

in practice:

"regular" (Energy ~ J) – for up to half-filled subshells (↑)

"inverted" ordering: otherwise

Note: "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) ⇐ more effective screening

②: higher L ⟺ larger distance between e^-

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

$\zeta > 0$ ("regular") for subshell filled by e^-

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

in general: (p^1 and p^5) or (p^2 and p^4)

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

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