PH 585
AMO

Lecture #17

Many-electron atoms

Need at least this: $H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \vec{\nabla}_{r_i}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{i<j=1}^{N} \frac{e^2}{(4\pi\varepsilon_0) r_{ij}}$

$r_{ij} = |\vec{r}_i - \vec{r}_j|$

(in principle, need $\vec{L}_i \cdot \vec{S}_i$, $\vec{S}_i \cdot \vec{S}_j$, radiative corrections, interactions with nuclei, ...)

(ith, jth electron)

$H \Psi(q_1, q_2, \ldots q_N) = E \Psi(q_1, q_2, \ldots q_N)$ ← include spatial $\vec{r}_i$ and spin variables

Generally, $\sum_{i<j=1}^{N} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$ cannot be treated as a perturbation

neutral atoms: $Z = N$

$C_N^2 = \frac{N!}{(N-2)!\,2!} = \frac{N(N-1)}{2}$ terms $\sim \frac{e^2}{r_{ij}}$

vs N terms with $\frac{Ze^2}{r_i}$

$\frac{e\text{-}e}{e\text{-}n} \sim \frac{\frac{Z(Z-1)}{2}}{Z^2} \sim \frac{Z^2 - Z}{2Z^2} = \frac{1}{2} - \frac{1}{2Z} = \frac{1}{4}$ for (He), $\frac{1}{2}$ for $Z \to \infty$

e-e interaction is not much smaller

need other than perturbation theory approach!

Central field approximation ← Hartree Fock Slater

⇓

independent particles moving in an effective potential

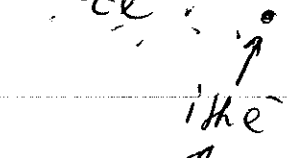
So, $H = H_c + H_1$

H_c: central; H_1: perturbation

$$\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\vec{\nabla}_{\vec{r}_i}^2 + V(r_i)\right) = \sum_{i<j=1}^{N}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_i\left(\frac{Ze^2}{4\pi\varepsilon_0 r_i} + V(r_i)\right)$$

$V(r_i)$: effective potential

↑ say, much closer to nucleus than other



further from nucleus than others ⇓ $r_i \approx r_{ij}$ sees "screened" nucleus $Z-(N-1)$

⇓ $(N-1)$ electrons

$r_{ij} \approx r_i \Rightarrow$

$$V(r_i) \approx -\frac{Ze^2}{4\pi\varepsilon_0 r_i} + \left\langle \sum_{j=1}^{N-1}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right\rangle \to$$

$\to -\frac{Ze^2}{4\pi\varepsilon_0 r_i}$ ← $r_i \to 0$

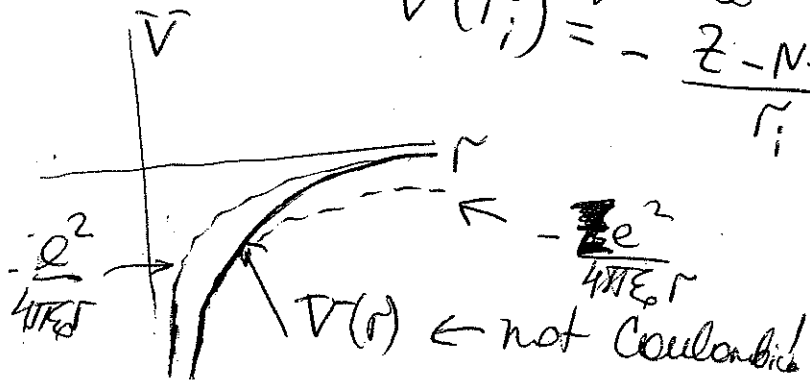
$\to$ average over distances from all other electrons to nucleus

$r_{ij} \approx r_j$

screen ⇐ each other

$$\Rightarrow V(r_i) \underset{r\to\infty}{=} -\frac{Z-N+1}{r_i}\frac{e^2}{4\pi\varepsilon_0} = -\frac{1}{r_i}\frac{e^2}{4\pi\varepsilon_0}$$

neutral atom $Z=N$



So, need to solve $H_c \Psi_c = E_c \Psi_c$

$H_c = \sum_i H_i$ ← unperturbed functions

and then $\langle \Psi_c | H_1 | \Psi_c \rangle$ ← hopefully small (with a good choice of $V(r)$)

$\Psi_c = u_{a_1}(\vec{r}_1)\, u_{a_2}(\vec{r}_2) \ldots u_{a_N}(\vec{r}_N)$

1-electron functions

$H_i\, u_{a_i}(\vec{r}_i) = E\, u_{a_i}(\vec{r}_i) \Rightarrow E_c = \sum_i E_{n_i \ell_i}$

spatial orbitals $(n\ell m_\ell)_i$

$E_{n\ell}$ ← recall: for central, but not Coulomb, potential won't have "accidental" degeneracy in ℓ

$2(2\ell+1)$-deg.

$u_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta, \varphi)$

not hydrogenic functions! But depend on $V(r)$

spherical harmonics ← no matter what $V(r)$ is

So far: haven't taken into account Pauli exclusion

need spin-orbitals $\Rightarrow u_{n\ell m_\ell m_s}(q) = u_{n\ell m_\ell}(\vec{r})\, \chi_{s m_s}$ ($m_s = \pm 1/2$)

build N-electron (A) function $\Rightarrow$ Slater determinant ($N \times N$) $\Rightarrow$

$$\Psi_c(q_1, q_2, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \dots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \dots & u_\nu(q_2) \\ \vdots & & & \\ u_\alpha(q_N) & u_\beta(q_N) & \dots & u_\nu(q_N) \end{vmatrix}$$

$N!$ ← # permutations

α, β, ν ← state

q_N ← coord. of Nth electron

$(n l m_l m_s)_N$

if two electrons are ~~in the same~~ in same spin/spin state, $q_1 = q_2$, or, say, $\alpha = \beta$ $\Rightarrow$ $\det = 0$ (if columns or rows are same)

any two

$\Downarrow$

at least one quantum number must be different

Example $(1s)^2$ of (He) $\Rightarrow$ ^1S (ground state)

$u_{\underset{n l m_l m_s}{100, 1/2}} = u_{100}(\vec{r})\,\alpha$; $u_{100,-1/2} = u_{100}(r)\,\beta$

α ↑ , β ↓

$\Downarrow$

$$\Psi_c(q_1, q_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} u_{100}(r_1)\alpha(1) & u_{100}(r_1)\beta(1) \\ u_{100}(r_2)\alpha(2) & u_{100}(r_2)\beta(2) \end{vmatrix} =$$

$$= \underbrace{u_{100}(r_1)\, u_{100}(r_2)}_{(S)} \underbrace{\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)}_{(A) \Leftarrow S = 0 \text{ (singlet)}}$$

Electron states

Electron configuration $\Rightarrow$ distribution of electrons with respect to n s l

e.g. $1s^2 2p^6 3d$ $\Leftarrow$

Electrons with same n & l $\Rightarrow$ belong to the same sub-shell $\Rightarrow$ e.g. $n=2$, $l=1$ $\Rightarrow$ $2p$

$2(2l+1)$ → 6 electrons in 2p-subshell

$m_l = 0, \pm 1$

$m_s = \pm \frac{1}{2}$

Max number of equivalent electrons:

$l=0 \Rightarrow 2(2l+1) = 2$	(s-electrons)	↑ equivalent electrons
1	6	(p-electrons)
2	10	(d-electrons)
3	14	(f)
4	18	(g)
⋮	⋮	

$2p^6$ ← closed (or filled) sub-shell

↑ max number of electrons

Electrons with same n $\Rightarrow$ shell

$n = 1\ 2\ 3\ 4$

K L M N

Max number of electrons in a shell $\Rightarrow 2n^2$

Let's say we have a $2p^2$ configuration ← closed shell

What is the degeneracy of this configuration (i.e. # of possibilities for different m_l & m_s combinations)?

6 configurations to choose from ⇐ need to choose 2 $\Rightarrow$

and in such a way that

e^- #1 in $|2p m_{\ell_1} m_{s_1}\rangle$.
e^- #2 in $|2p m_{\ell_2} m_{s_2}\rangle$

and

e^- #1 in $|2p m_{\ell_2} m_{s_2}\rangle$
e^- #2 in $|2p m_{\ell_1} m_{s_1}\rangle$

configuration counts as one (due to equivalency or indistinguishability of electrons)

use combinatorics

$$C_6^2 = \frac{6!}{4!\,2!} = 15$$ ← degeneracy of $2p^2$

In general ⇒

$$d_i = \frac{\delta_i!}{\nu_i!\,(\delta_i - \nu_i)!} \cdot 2(2\ell_i + 1)$$

d_i: degeneracy; $\delta_i!$: how many electrons have to be chosen; $2(2\ell_i+1)$: # choices

Note: $2p^6$ ← only 1 choice (since all possibilities are used)

$$\frac{6!}{6!\,0!} = 1$$

This is the case for any closed subshell ($1s^2, 3d^{10}, \ldots$)

Also: If there is a configuration like

carbon atom (C) → $1s^2\,2s^2\,2p^2$ ← only unfilled sub-shells contribute to degeneracy

$d=1$ $d=1$ $d=15$ → total $d=15$