LECTURE # 4

Note Title — 9/8/2008

THIS WED 11:30 - 1:30 OFFICE HRS

SO FAR : HYDROGEN

n	l	m
1	0	0
2	0 1	-1 0 1
3	0 1 2	-2 -1 0 +1 +2
$\vdots$		$\vdots$

$$\Psi_{nlm}(\vec{r}) = Y_l^m(\theta, \phi)\, R_{nl}(r)$$

RELATIVISTIC EFFECTS :

→ SPIN ORBIT $\propto \vec{S}_e \cdot \vec{l}$

→ HYPERFINE COUPLING $\propto \vec{S}_e \cdot \vec{S}_{PROTON}$

MANY-ELECTRON ATOMS $\qquad$ N ELECTRONS

$\rightarrow \vec{S} = \sum_{i=1}^{N} \vec{s}_i$ $\qquad$ MAX VALUE IS $\frac{N}{2}$

$(\hat{S}_x, \hat{S}_y, \hat{S}_z) \rightarrow \vec{S}$

$\rightarrow \vec{L} = \sum_{i}^{N} \vec{l}_i$ $\qquad$ NO LIMIT

$\rightarrow \vec{J} = \vec{L} + \vec{S}$ $\qquad$ $H_{SPIN-ORBIT} = \sum_{i=1}^{N} \alpha_i \vec{s}_i \cdot \vec{l}_i$

$\vec{S}, \vec{L}, \vec{J}$ $\qquad$ QUANTUM # FOR $N-e$ ATOM

$[\vec{J}, \hat{H}_{SP-ORBIT}] = 0 \Rightarrow \vec{J}$ REMAINS A GOOD QUANTUM # EVEN INCLUDING SPIN-ORBIT

$[J_x \ H] = 0$

$[J_y \ H] = 0$

$[J_z \ H] = 0$

STANDARD NOTATION

$$\boxed{^{2S+1}L_J}$$

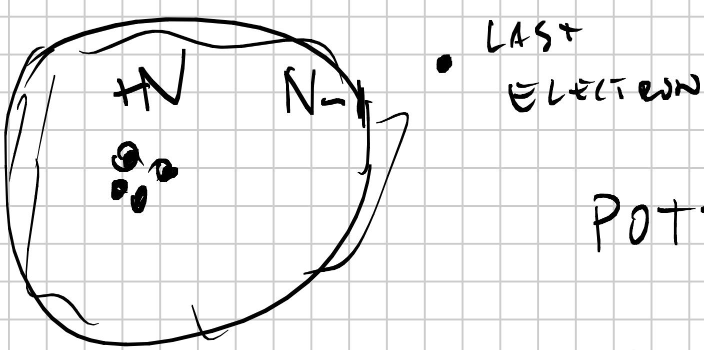
$$L = \overset{0}{S},\ \overset{1}{P},\ \overset{2}{D},\ \overset{3}{F},\ \overset{4}{G},\ \ldots$$

He (2 e)

QUANTUM #S FOR ALL ELECTRONS

$$\boxed{^1S_0} \rightarrow \begin{cases} S = 0 \\ L = 0 \\ J = 0 \end{cases} \qquad \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

ELECTRONIC CONFIGURATION : LOOK AT e ONE BY ONE $\Longrightarrow$ USE SHELL-MODEL



LAST ELECTRON "FEELS" A "SELF CONSISTENT" POTENTIAL $V_{sc}(r)$ FROM

N PROTONS + N-1 ELECTRONS

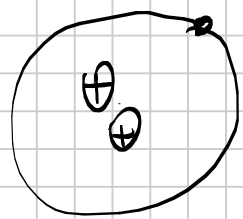
$V_{sc}(r)$ HAS SPHERICAL SYMMETRY $\Rightarrow$ ℓ IS A GOOD QUANTUM # ~ SIMILAR TO COULOMB

$\Rightarrow$ I CAN STILL LABEL STATE OF LAST ELECTRON AS $(n\ \ell\ m)$

H $\quad N=1 \quad$ EXACT

He^+ EXACT $\quad \dfrac{e^2}{r} \to 2\cdot\dfrac{e^2}{r}$

He $\quad N=2$



HYDROGENIC ION $\quad \dfrac{e^2}{r} \to \overset{\#\ \text{PROTONS}}{Z}\dfrac{e^2}{r}$

$(1s)$

SECOND ELECTRON WILL MOVE

$V_{sc}(r) \neq V_{COULOMB}$

$$(1s)(1s)\,{}^1S_0 \to (1s)^2\,{}^1S_0$$

Li $N=3$

$$(1s)(1s)(2s) \rightarrow \overset{\downarrow\uparrow}{(1s)^2}\overset{\uparrow}{(2s)} \quad {}^2S_{\frac{1}{2}}$$

$V_{sc}(r)$ EXAMPLE OF POTENTIAL THAT DOES NOT GIVE A S.E ANALYTICALLY SOLVABLE

WE CAN USE THE

$\boxed{\text{VARIATIONAL PRINCIPLE}}$

$V(r)$ GIVEN $\rightarrow$ H

WE KNOW THAT IT EXISTS $\psi_n(\vec{r})$ SET SUCH THAT

$$H\,\psi_n(\vec{r}) = E_n\,\psi_n(\vec{r})$$

TAKE $\psi(\vec{r}) = \sum_n c_n \psi_n(\vec{r})$ ARBITRARY

$$\langle \psi | H | \psi \rangle = \langle H \rangle_\psi = \int \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) \, d^3r$$

$$\langle H \rangle_\psi = \sum_n |c_n|^2 E_n \geq \Big(\underbrace{\sum_n |c_n|^2}_{=1} \Big) \cdot E_0$$

$\langle H \rangle_\psi \geq E_0$ | THIS SUGGESTS THE

VARIATIONAL METHOD TO FIND ψ_0 AND E_0

(1) MAKE A "GUESS" FOR $\psi_\beta(r)$

THAT DEPENDS ON A PARAMETER "β"

$$\psi_\beta(\vec{r}) = e^{-\beta r^2}$$

② $\dfrac{\langle H \rangle_{\psi_\beta}}{\langle \psi_\beta | \psi_\beta \rangle} = E_\beta > E_0$

$\langle \psi_\beta | \psi_\beta \rangle \rightarrow$ NORMALIZATION

③ FIND MINIMUM

$$\left. \frac{d E_\beta}{d \beta} \right|_{\beta = \beta_{MIN}} = 0$$

$\Downarrow$

Ⓐ $E_{\beta_{MIN}}$ IS AN UPPER BOUND FOR E_0

Ⓑ $\psi_{\beta_{MIN}}(\vec{r})$ IS A GOOD APPROX FOR $\psi_0(\vec{r})$

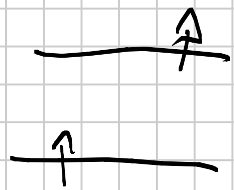
SHELL MODEL: EQUIVALENT CONFIGURATIONS

$(1s)^2\ {}^1S_0$ GRND He

$(1s)(2s)$ ${}^1S_0$

PARAHELIUM

$(1s)(2s)$ ${}^3S_1$



ORTHOHELIUM

LOWEST ENERGY $S=1$ (ORTHOHELIUM)

INTUITIVE REASON WHY PARALLEL SPINS HAVE LOWER ENERGY:

DONT LIKE TO BE IN THE SAME "PLACE" DUE TO PAULI $\Rightarrow$ AVOID EACH OTHER

$\Rightarrow$ ELECTRON - ELECTRON REPULSION IS SMALL

NO PAULI EXCLUSION $\Rightarrow$ ELECTRONS AS CLOSE AS THEY WANT $\Rightarrow$ E-E REPULSION CAN BE BIG $\Rightarrow$ HIGHER ENERGY

THIS IS THE FIRST OF 3 HUND'S RULES FOR ELECTRONS IN EQUIVALEN CONFIGURATIONS

THE LOWEST ENERGY STATE IS THE ONE THAT HAS

(1) LARGEST $\vec{S}$

(2) LARGEST $\vec{L}$ COMPATIBLE WITH (1)

$|\bar{L}-\bar{S}| < \bar{J} < |L+S|$

(3) $J = |L-S|$ FOR SHELLS LESS THAN HALF-FILLED

$J = L+S$ FOR SHELLS MORE THAN HALF FILLE