LECTURE 4

Note Title 9/12/2007

Last lecture:

Find eigenvalues and eigenvectors of Hydrogenic problem - 3D

n	ℓ
1	0
2	0 1
3	0 1 2
4	

n principal quantum number

$$\psi_{n\ell m} = Y_{\ell m}(\theta\,\phi)\,R_{n\ell}(r)$$

(2) Relativistic effects:

$\vec{S}_e \cdot \vec{\ell}$ spin orbit effect

Fine structure levels

$\vec{S}_e \cdot \vec{S}_N$ Hyperfine

Many-electron atoms   N electrons

$\vec{S} = \sum_i \vec{s}_i$ up to $\frac{N}{2}$ total spin

$\vec{L} = \sum_i \vec{l}_i$ total angular momentum

$\vec{J} = \vec{S} + \vec{L}$ $\vec{J}$ is a good quantum number for total hamiltonian with spin-orbit

α = spin orbit coupling

$$H_{so} = \sum_i \alpha_i \vec{l}_i \cdot \vec{s}_i \qquad [H_{so}, \vec{J}] = 0$$

Without spin orbit also L, S are good quantum numbers.

$$L = \overset{0}{\overset{\shortparallel}{S}}, \overset{1}{\overset{\shortparallel}{P}}, \overset{2}{\overset{\shortparallel}{D}}, F \ldots$$ capital

State of N electron atom:

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

Example: Ground state of He

2 e^- in a $\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$ singlet

$S = 0$ 2 e in s orbitals $L = 0$ ${}^1S_0$

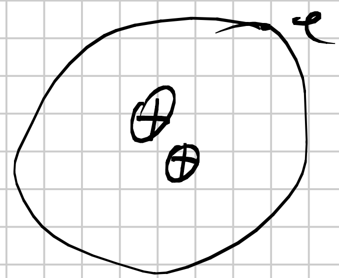
Shell Model

N e atom N protons

- last electron feels a self-consistent potential $V_{sc}(r)$ created by the N protons and $N-1$ electrons.

$V_{sc}(r)$ is isotropic $\Rightarrow$ still describe states of the "last" electron in terms of n l.

Example: $He \Rightarrow N = 2$



He^+

$(1s)$

Second e^- in He moves in potential created by He^+ $(1s)$ state too

$$(1s)(1s)\,{}^1S_0 \rightarrow \underbrace{(1s)^2}_{\text{electronic configuration}}\,{}^1S_0$$

Li $N = 3$ $(1s)^2(2s)$ $^2S_{1/2}$

$V_{sc}(r)$ not Coulomb includes many-body effects.

Even after $V_{sc}(r)$ solution of Schroedinger Eq for "last" electron is not exact. So we can use

VARIATIONAL PRINCIPLE

$V_{sc}(r) \rightarrow H$ We know that it exists

$\psi_n(r)$ $\hat{H}\,\psi_n(r) = E_n\,\psi_n(r)$ ψ_n complete set

$$\psi(r) = \sum_n c_n \psi_n(r)$$ for arbitrary $\psi(r)$

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

$$= \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2$$

ψ is normalized $\Rightarrow$ $\sum_n |c_n|^2 = 1$

$$\langle \psi | H | \psi \rangle \geq E_0$$

Variational method:

1) Make a guess on the possible form of $\psi(r)$ that depend on one or more parameters

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

2) $\langle \psi_\beta | H | \psi_\beta \rangle = E_\beta \geq E_0$

Calculate expectation value as a function of parameter(s)

3) Find minimum $\frac{dE_\beta}{d\beta} = 0 \Rightarrow \beta_{min}$

$\Downarrow$

$E_{\beta_{min}}$ upper bound for ground state energy

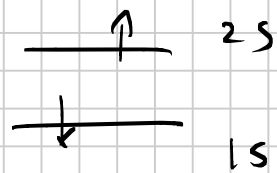
$\psi_\beta(n)$ good description of ground state.

$$\frac{\langle \psi_\beta | H | \psi_\beta \rangle}{\langle \psi_\beta | \psi_\beta \rangle} > E_0 \quad \text{if} \quad \langle \psi_\beta | \psi_\beta \rangle \neq 1$$

Shell model — Equivalent configuration

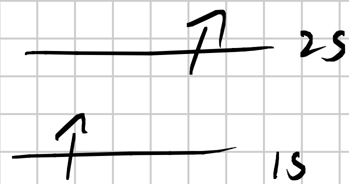
$(1s)^2\ {}^1S_0$ GROUND

$(1s)\ (2s)\ {}^1S_0$ → PARAHELIUM



total spin 0

$(1s)\ (2s)\ {}^3S_1$ → ORTHOHELIUM



total spin 1

Lowest energy

Intuition:

Parallel spin tend to avoid each other (Pauli principle) → reduce coulomb repulsion → lower energy.

1° of 3 HUND'S RULES

HUND'S RULES

(1) Largest S

(2) Largest L given (1)

(3) $J = |L - S|$ for shell less than half-filled

$J = L + S$ for shell more than half filled.

$(1s)^2(2s)$ $(1s)^2(2s)^2$
Li Be

$2p$ $2p^2$ $(2p)^3$ $(2p)^4$
B C N O
$\uparrow$

1 0 −1 (m)
$\boxed{\uparrow | \uparrow | \uparrow}$ $l = 1$ $m = -1, 0, 1$ (m is l_z)

$S = 3/2$
$L = 0$

$^4S_{3/2}$ N

For Carbon

$J = |L - S|$

1	0	-1
↑	↑	

$\rightarrow$ $\boxed{S = 1 \quad L = 1}$ $\rightarrow$ Highest L

2° Hund's rule

↑		↑

$\rightarrow$ $S = 1$, $L = 0$

$\boxed{{}^3P_0}$

For Oxygen

$S = 1$

$J = L + S$

$|l_+| = 1$

↑↓	↑	↑

$\boxed{L = 1}$ $\rightarrow$ $\boxed{{}^3P_2}$

↑	↑↓	↑

$L = 0$

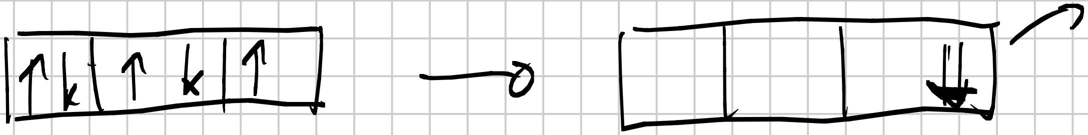
↑	↑	↓↑

$l_z = 1$

3° RULE related to spin orbit

$$\alpha\, \vec{s}\cdot\vec{\ell} = \alpha\, \frac{1}{2}\left(\vec{J}^2 - \vec{s}^2 - \vec{\ell}^2\right) \qquad \alpha > 0$$

Small $J \Rightarrow$ Smaller spin orbit



think about this as hole in a a completely filled shell

Spin-orbit changes sign