THIS WED 11:30 - 1:30 OFFICE HRS

SO FAR: HYDROGEN

\[ \Psi(l^2) = Y_{l}^{m}(\theta, \phi) R_{\text{me}}(r) \]

<table>
<thead>
<tr>
<th>m</th>
<th>l</th>
<th>l</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>-1 0 1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>2</td>
<td>-2 -1 0 1 2</td>
</tr>
</tbody>
</table>

RELATIVISTIC EFFECTS:

- SPIN ORBIT \( \propto \hat{s}_e \cdot \hat{r} \)
- HYPERFINE COUPLING \( \propto \hat{s}_e \cdot \hat{s}_p \)
Many-electron atoms \( N \) electrons

\[-\sum_{i=1}^{2N} \vec{s}_i = \frac{N}{2} \vec{S} \]

Max value is \( \frac{N}{2} \)

\[-\sum_{i=1}^{2N} \vec{l}_i \]

No limit

\[-\vec{j} = \sum_{i=1}^{2N} \vec{s}_i + \sum_{i=1}^{2N} \vec{l}_i \]

\[H_{\text{spin-orbit}} = \sum_{i=1}^{2N} \vec{a}_i \cdot \vec{s}_i \cdot \vec{l}_i \]

\[\vec{S}, \vec{L}, \vec{j} \]

Quantum \# for \( N-e \) atom

\[
\begin{bmatrix}
\hat{J}^z \\
\hat{H}_{\text{spin-orbit}}
\end{bmatrix} = 0 \Rightarrow \hat{J}^z \text{ remains a good quantum \# even including spin-orbit}
\]

\[
\begin{bmatrix}
\hat{J}_x \\
\hat{H}
\end{bmatrix} = 0
\]

\[
\begin{bmatrix}
\hat{J}_y \\
\hat{H}
\end{bmatrix} = 0
\]

\[
\left( \hat{J}_x, \hat{H} \right) = 0
\]

\[
\left( \hat{J}_y, \hat{H} \right) = 0
\]
**STANDARD NOTATION**

\[ L = S, P, D, F, G, \ldots \]

\[ S = 0 \quad \frac{1}{\sqrt{2}} |g^\uparrow - l^\uparrow \rangle \]

\[ L = 0 \quad J = 0 \]

**He (2 e\textsuperscript{-})**

**Quantum #s for all electrons**

**Electronic configuration:** Look at one by one to use SHELL-MODEL

**Last electron “feels” last electron a “self consistent” potential \( V_{Sc}(N) \) from \( N \) protons + \( N-1 \) electrons
$V_{sc}(n)$ has spherical symmetry, so $l$ is a good quantum number ~ similar to Coulomb.

So I can still label state of last electron as $(m_l m)$.

H

$N = 1$ EXACT

$\text{He}$ $N = 2$

$\text{He}^+$ EXACT

$\frac{e^2}{\hbar} \rightarrow 2 \cdot \frac{e^2}{\hbar}$

$\text{Hydrogenic ion}$

$\frac{e^2}{\hbar} \rightarrow 2 \cdot \frac{e^2}{\hbar}$

Second electron will move

$V_{sc}(n) \neq V_{\text{Coulomb}}$

$(1s)(1s) \, S_0 \rightarrow (1s)^2 \, S_0$
$N = 3$

$\begin{align*}
(1s)(1s)(2s) & \rightarrow (1s)^2(2s) \quad S_{\frac{1}{2}}^0 \\
\end{align*}$

$V(r)$ is an example of potential that does not give an S.E. analytically solvable.

We can use the

\textbf{Variational Principle}

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

We know that it exists $\psi_m(\mathbf{r})$ set such that $\mathbf{H} \psi_m(\mathbf{r}) = E_m \psi_m(\mathbf{r})$
Take $\psi(\vec{r}) = \sum_{n} c_n \psi_n(\vec{r})$ arbitrary

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

$$\langle H \rangle \psi = \sum_{n} |c_n|^2 E_n \geq (\sum_{n} |c_n|^2) \cdot E_0$$

$$\langle H \rangle \psi \geq E_0 \quad \text{This suggests the variational method to find $\psi_0$ and $E_0$.}$$

1. Make a "guess" for $\psi_{\beta}(\vec{r})$ that depends on a parameter "$\beta"$

$$\psi_{\beta}(\vec{r}) = e^{-\beta \vec{r}^2}$$
(2) \[
\frac{\langle H \rangle_{\psi_0}}{\langle \psi_0 | \psi_0 \rangle} = E_\beta > E_0
\]
\[\langle \psi_0 | \psi_0 \rangle \rightarrow \text{NORMALIZATION}\]

(3) \[\text{FIND MINIMUM}\]
\[
\left. \frac{dE_\beta}{d\beta} \right|_{\beta=\beta_{\text{min}}} = 0
\]

\[E_\beta_{\text{min}} \text{ IS AN UPPER BOUND FOR } E_0\]

\[\psi_{\beta_{\text{min}}} \text{ IS A GOOD APPROX FOR } \psi_0(x)\]
Shell Model: Equivalent Configurations

\[ (1s)^2 \frac{1}{2}S_0 \quad \text{ground state He} \]

\[ (1s)(2s) \quad ^1S_0 \quad \uparrow \quad \frac{1}{2} \quad 2s \quad \text{Para-He (Para-Helium)} \]

\[ (1s)(2s) \quad ^3S_1 \quad \uparrow \quad \text{Ortho-Helium} \]

Lowest energy \( S = 1 \) (Ortho-Helium)

Intuitive reason why parallel spins have lower energy:

\( \exists \) to be in the same "place" due to Pauli

\( \nabla \) Avoid each other

Don't like...
A electron-electron repulsion is small.

No Pauli exclusion = electrons as close as they want = 0 E-E repulsion can be big = 0 higher energy.

This is the first of 3 Hund's rules for electrons in equivalent configurations. The lowest energy state is the one that has

1. Largest $S$
LARGEST $I^0$ COMPATIBLE WITH $I$

$|L-S| < J < |L+S|$

$J = |L-S|$ FOR SHELLS LESS THAN
HAlF-FILLED

$J = L+S$ FOR SHELLS MORE THAN
HAlF-FILLED