Many $e^-$ Atoms

Big Idea
Approximation is needed because of $e^-$-$e^-$ repulsion

Skills
- Apply the variation method
- Construct Slater-Type Orbitals
Futility: Many $e^-$ atoms

He atom

\[ V = \frac{1}{4\pi\varepsilon_0} \left( \frac{e^2}{r_{12}} - \frac{2e^2}{r_1} + \frac{2e^2}{r_2} \right) \]

The Schrödinger eq cannot be solved for this potential.

We must resort to approximate methods.
The Variation Theorem

The ground-state energy of a made-up wavefunction will always be higher than the ground-state energy of the true wavefunction.

\[ \langle E_{\text{trial}} \rangle = \frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\int \psi_0^* \psi_0 \, d\tau} \geq E_{\text{real}} \quad \text{for ground state only!} \]

the better our trial wavefunction, the closer this is to an equality.
Variation principle

Trial wave function for 1-D PIB: \( \psi = x(x-l) \)

\[ \hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \]

\[ \langle E \rangle = \frac{\int \psi^* \hat{H} \psi \, dx}{\int \psi^* \psi \, dx} \]

<Maple> (see handout)

\[ \langle E \rangle = \frac{5 \frac{\hbar^2}{m \ell^2}}{\text{for trial wave function}} \]

\[ E_1 = \frac{i^2 \hbar^2}{8m \ell^2} = \frac{\hbar^2 4\pi^2}{8m \ell^2} = \frac{\pi^2 \frac{\hbar^2}{2m \ell^2}}{\text{for free } \psi} \]

\[ \frac{\pi^2}{2} = 4.93 \]

\( E = \frac{4.93 \frac{\hbar^2}{m \ell^2}}{\text{true}} \quad \frac{5 \frac{\hbar^2}{m \ell^2}}{\text{trial}} \)

Note \( E_{\text{trial}} > E_{\text{true}} \)
The Variation Method

1) Pick a trial wavefunction w/ at least 1 adjustable parameter

2) Calculate an expression for $\langle E_{\text{trial}} \rangle$ using the wave function

3) take the derivative of this expr. w/ respect to the adjustable parameter.

4) Minimize E by setting $\frac{dE}{d(\text{parameter})} = 0$

5) Solve for the value of the parameter.

But how do we construct a trial wavefunction?

Strategy: Product of adapted hydrogen orbitals
\[ E \times 7 \]

Let's apply variation principle to He.

\[ \psi_0 = \phi_1 \phi_1' \]

\[ \phi_1 = \frac{1}{\sqrt{\pi}} \left( \frac{2}{a_0} \right)^{3/2} e^{-2r/a_0} \quad \text{for } le - \text{atoms is } \text{nuc charge} \]

\[ \phi_1' = \frac{1}{\sqrt{\pi}} \left( \frac{2}{a_0} \right)^{3/2} e^{-2r/a_0} \quad \text{make } z' \quad \text{the parameter} \]

so

\[ \psi_0 = \phi_1 \phi_1' = \frac{1}{\pi} \left( \frac{2}{a_0} \right)^3 e^{-\frac{2r_1}{a_0}} e^{-\frac{2r_2}{a_0}} \]

- find \( <E_0> = \int \psi_0^* H \psi_0 \ dx \)
- take \( \frac{\partial E_0}{\partial z'} \leftarrow \leftarrow \)
- set \( \frac{2E_0}{\partial z'} = 0 \rightarrow \rightarrow \)

\[ z' = z - \frac{5}{16} \]

\[ z' = 2 - \frac{5}{16} \]

\[ z' = \frac{27}{16} = 1.69 \quad \text{effective nuclear charge} \]
Slater-type orbitals

STOs are the adopted H orbitals we use.

key: We treat e^-e^- repulsion by means of effective nuclear charge. (Screening)

\[ \phi = r^{n^* - 1} e^{-\frac{Z_{e\text{ff}}}{a_0 n^*}} \cdot \mathbb{H} \cdot \mathbb{H} \]

<table>
<thead>
<tr>
<th>n</th>
<th>n^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>3.7</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Z</th>
<th>Z_{e\text{ff}}</th>
<th>2s</th>
<th>2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.69</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.68</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.68</td>
<td>2.58</td>
<td>2.42</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total: 10.1