2.39: First Trial Wave Function

The first trial wavefunction is based on the orbital concept - electrons have wavefunctions that are independent of the coordinates of other electrons. Since it does not provide for electron correlation it will serve as the benchmark in the subsequent series of calculations. The remaining trail wavefunctions will include electron correlation to an increasing degree.

$$\Psi(1,\ 2) = \frac{\alpha^3}{\pi} \exp\left(-\alpha r_1\right) \exp\left(-\alpha r_2\right)$$

When this wavefunction is used in a variational calculation for the ground state energy for two-electron atoms or ions the expression shown below for the energy, E(α), is obtained. This equation is then minimized with respect to the adjustable parameter, α. The calculation for He is shown below.

Nuclear charge: Z = 2

Seed value for scale factor: $\alpha = 2$

Contributions to total energy:

$$T(\alpha) = \alpha^2 \quad V_{ne}(\alpha) = -2Z\alpha \quad V_{ee}(\alpha) = \tfrac{5}{8}\alpha$$

Minimization of the total energy with respect to the variational parameter:

$$E(\alpha) = T(\alpha) + V_{ne}(\alpha) + V_{ee}(\alpha) \quad \alpha = \text{Minimize}(E,\ \alpha) \quad \alpha = 1.6875 \quad E(\alpha) = -2.8477$$

Calculate the orbital energy:

$$\varepsilon = \tfrac{\alpha^2}{2} - Z\alpha + \tfrac{5}{8}\alpha \quad \varepsilon = -0.8965$$

Compare the results of this calculation to experiment in two ways. [1] Minus the sum of the ionization energies is equal to the experimental ground state energy (you should show this). [2] The orbital energy is a good approximation to the first ionization energy. Repeat this exercise for H⁻ , Li⁺ and Be²⁺. Present your results and the comparison with experimental results in tabular form.

$H\Psi = E\Psi$	H	He	Li	Be
α	0.6875	1.6875	2.6875	3.6875
ε	−0.0215	−0.8965	2.7715	−5.6465
$-\text{IP}_1$	−0.0277	−0.904	−2.781	−5.658
%Error	22.4	0.83	0.34	0.20
E_{atom}	−0.4727	−2.8477	−7.2227	−13.5977
$-\left(\text{IP}_1 + \text{IP}_2\right)$	−0.5277	−2.9037	−7.2838	−13.6640
%Error	10.4	1.94	0.80	0.40

- Demonstrate that the virial theorem is satisfied for each calculation: <E> = <V>/2 = -<T>

$$E(\alpha) = -2.8477 \quad \frac{-2Z\alpha + \tfrac{5}{8}\alpha}{2} = -2.8477 \quad -\alpha^2 = -2.8477$$

- Complete the table below which breaks down the various contributions to the total energy.

Element	%T	%V_{ne}	%V_{ee}
H	20.8	60.4	18.9
He	26.7	63.4	9.9
Li	28.9	64.4	6.7
Be	29.9	65.0	5.1

Absolute value of energy:

$$E_{abs} = \alpha^2 + 2Z\alpha + \frac{5}{8}\alpha$$

Percent kinetic energy contribution to total energy:

$$\frac{T(\alpha)}{E_{abs}(\alpha)} = 26.7\%$$

Percent electron-nuclear potential energy contribution to total energy:

$$\frac{|V_{ne}(\alpha)|}{E_{abs}(\alpha)} = 63.4\%$$

Percent electron-electron potential energy contribution to total energy:

- Demonstrate that this wave function does not predict a stable hydride ion.
  - The hydride anion has a higher energy (-0.4727 E_h) than the hydrogen atom (-0.5000 E_h).
- Identify a deficiency in the wave function that might explain why it does not predict a stable hydride ion.
  - The wave function does not allow adequately for electron-electron correlation in a case where the nuclear charge is only +1.
- Explain the improved agreement between theory and experiment as the nuclear charge increases.
  - Nuclear-electron potential energy becomes increasingly important overwhelming electron-electron potential energy. The inadequacies of the wave function are becoming less important.
- Complete the summary table below. You will be asked to do this for each trial wave function we use in this exercise and subsequently compare the results.

$$E(\alpha) = -2.8477 \quad T(\alpha) = 2.8477 \quad V_{ne}(\alpha) = -6.7500 \quad V_{ee}(\alpha) = 1.0547$$

$$\begin{pmatrix} \text{WF1} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{H} & -0.4727 & 0.4727 & -1.375 & 0.4297 \\ \text{He} & -2.8477 & 2.8477 & -6.7500 & 1.0547 \\ \text{Li} & -7.2227 & 7.2227 & -16.1250 & 1.6797 \\ \text{Be} & -13.5977 & 13.5977 & -29.5000 & 2.3047 \end{pmatrix}$$

This table shows that Vee increases in magnitude from H⁻ to Be²⁺. Earlier, however, we saw that its percentage contribution to the total energy decreases in this series.

- You should also fill in the following tables for each of the elements and carry them forward to the next Mathcad document.

$$\begin{pmatrix} \text{H} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -0.4727 & 0.4727 & -1.375 & 0.4297 \\ \text{WF2} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF3} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF4} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF5} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix} \quad \begin{pmatrix} \text{He} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -2.8477 & 2.8477 & -6.7500 & 1.05447 \\ \text{WF2} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF3} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF4} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF5} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

$$\begin{pmatrix} \text{Li} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -7.2227 & 7.2227 & -16.1250 & 1.6797 \\ \text{WF2} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF3} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF4} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF5} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix} \quad \begin{pmatrix} \text{H} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -13.5977 & 13.5977 & -29.5000 & 2.3047 \\ \text{WF2} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF3} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF4} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{WF5} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$