2.40: Second Trial Wavefunction

$$\Psi = \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2)$$

When the wavefunction shown above is used in a variational method calculation for the ground state energy for two-electron atoms or ions the two-parameter equation shown below for the energy is obtained. This equation is then minimized simultaneously with respect to the adjustable parameters, α and β.

Nuclear charge: Z = 2

Seed values for scale factors: $\alpha = 2 \quad \beta = Z + 1$

Variational energy expression:

$$E(\alpha,\ \beta) = \frac{\left[\dfrac{\frac{\alpha^2+\beta^2}{2} - Z(\alpha+\beta) - \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^2}\left(Z - \frac{\alpha\beta}{\alpha+\beta}\right)}{1 + \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^3}}\right] \ldots \\ \frac{5}{8}(\alpha+\beta) + \dfrac{2\alpha\beta(\alpha^2+3\alpha\beta+\beta^2)}{(\alpha+\beta)^3} + 4\left[\begin{array}{c} \frac{8\alpha^{2.5}\beta^{1.5}(11\alpha^2+8\alpha\beta+\beta^2)}{(\alpha+\beta)^2(3\alpha+\beta)^3} \ldots \\ + \frac{8\alpha^{1.5}\beta^{2.5}(11\beta^2+8\alpha\beta+\alpha^2)}{(\alpha+\beta)^2(3\beta+\alpha)^3} \ldots \\ \frac{20\alpha^3\beta^3}{(\alpha+\beta)^5} \end{array}\right]}{4\left[1 + \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^3}\right]^2}$$

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \text{Minimize}(E,\ \alpha,\ \beta) \quad \begin{pmatrix} \alpha \\ beta \end{pmatrix} = \begin{pmatrix} 1.2141 \\ 2.1603 \end{pmatrix} \quad E(\alpha,\ \beta) = -2.8603$$

Experimental ground state energy:

$$E_{exp} = -2.9037$$

Calculate error in calculation:

$$\text{Error} = \left| \frac{E_{exp} - E(\alpha,\ \beta)}{E_{exp}} \right| \quad \text{Error} = 1.4931\%$$

Fill in the table and answer the questions below:

Ψ	H	He	Li	Be
α	0.3703	1.2141	2.0969	2.9993
β	1.0001	2.1603	3.2778	4.3756
E_{atom}	−0.487	−2.8603	−7.235	−13.6098
E_{atom}(exp)	−0.5277	−2.9037	−7.2838	−13.6640
%Error	7.72	1.49	0.670	0.397

Fill in the table below and explain why this trial wave function gives better results than the first trial wave function.

$$T(\alpha,\ \beta) = \left[\dfrac{\frac{\alpha^2+\beta^2}{2} + \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^2}\left(\frac{\alpha\beta}{\alpha+\beta}\right)}{1 + \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^2}}\right] \quad V_{ne}(\alpha,\ \beta) = \left[\dfrac{-Z(\alpha+\beta) - \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^2}Z}{1 + \frac{8\alpha^{1.5}\beta^{1.5}}{(\alpha+\beta)^3}}\right]$$

$$T(\alpha,\ \beta) = 2.8603 \qquad V_{ne} = -6.7488$$

$$V_{ee}(\alpha,\ \beta) = E(\alpha,\ \beta) - T(\alpha,\ \beta) - V_{ne}(\alpha,\ \beta) \quad V_{ee}(\alpha,\ \beta) = 1.0281$$

$$\begin{pmatrix} \text{WF2} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{H} & -0.4870 & 0.4780 & -1.3705 & 0.3965 \\ \text{He} & -2.8603 & 2.8603 & -6.7488 & 1.0281 \\ \text{Li} & -7.2350 & 7.2350 & -16.1243 & 1.6544 \\ \text{Be} & -13.6098 & 13.6098 & -29.4995 & 2.2799 \end{pmatrix}$$

Demonstrate that the virial theorem is satisfied.

$$E(\alpha,\ \beta) = -2.8603 \quad -T(\alpha,\ \beta) = -2.8603 \quad \frac{V_{ne}(\alpha,\ \beta) + V_{ee}(\alpha,\ \beta)}{2} = -2.8603$$

Add the results for this wave function to your summary table for all wave functions.

$$\begin{pmatrix} \text{H} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -0.4727 & 0.4727 & -1.375 & 0.4297 \\ \text{WF2} & -0.4870 & 0.4870 & -1.3705 & 0.3965 \end{pmatrix} \quad \begin{pmatrix} \text{He} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -2.8477 & 2.8477 & -6.7500 & 1.0547 \\ \text{WF2} & -2.8603 & 2.8603 & -6.7488 & 1.0281 \end{pmatrix}$$

$$\begin{pmatrix} \text{Li} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -7.2227 & 7.2227 & -16.1250 & 1.6797 \\ \text{WF2} & -7.2350 & 7.2350 & -16.1243 & 1.6544 \end{pmatrix} \quad \begin{pmatrix} \text{Be} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -13.5977 & 13.5977 & -29.5000 & 2.3047 \\ \text{WF2} & -13.6098 & 13.6098 & -29.4995 & 2.2799 \end{pmatrix}$$

These tables show that the improved agreement with experimental results (the lower total energy), is due to a reduction in electron-electron repulsion.