2.42: 129.4 Fourth Trial Wavefunction

$$\Psi(r) = \exp\left[-\alpha\left(r_1 + r_2\right)\right]\left(1 + \beta r_{12}\right)$$

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 b.

Nuclear charge: Z = 1

Seed values for scale factors: $\alpha = Z \quad \beta = .7$

Contributions to total energy:

$$T(\alpha,\ \beta) = \frac{\frac{1}{2} + \frac{25\beta}{16\alpha} + \frac{2\beta^2}{\alpha^2}}{\frac{1}{2\alpha^2} + \frac{35\beta}{16\alpha^3} + \frac{3\beta^2}{\alpha^4}} \quad V_{ne}(\alpha,\ \beta) = \frac{-\frac{Z}{\alpha} - \frac{15Z\beta}{4\alpha^2} - \frac{9Z\beta^2}{2\alpha^3}}{\frac{1}{2\alpha^2} + \frac{35\beta}{16\alpha^3} + \frac{3\beta^2}{\alpha^4}} \quad V_{ee}(\alpha,\ \beta) = \frac{-\frac{5}{16\alpha} - \frac{\beta}{\alpha^2} - \frac{35\beta^2}{32\alpha^3}}{\frac{1}{2\alpha^2} + \frac{35\beta}{16\alpha^3} + \frac{3\beta^2}{\alpha^4}}$$

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

$$E(\alpha,\ \beta) = T(\alpha,\ \beta) + V_{ne}(\alpha,\ \beta) + V_{ee}(\alpha,\ \beta) \quad \begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \text{Minimize}(E,\ \alpha,\ \beta) \quad \begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \begin{pmatrix}0.8257\\ 0.4934\end{pmatrix} \quad E(\alpha,\ \beta) = -0.5088$$

Experimental ground state energy:

$$E_{exp} = -2.9037$$

Calculate error in calculation:

$$\text{Error} = \left|\frac{E_{exp} - E(\alpha,\ \beta)}{E_{exp}}\right| \quad \text{Error} = 82.4782\%$$

Fill in the table and answer the questions below:

Ψ	H	He	Li	Be
α	0.8257	1.8497	2.8564	3.8592
β	0.4934	0.3658	0.3354	0.3213
E_{atom}	−0.5088	−2.8911	−7.2682	−13.6441
$E_{atom}(\text{exp})$	−0.5277	−2.9037	−7.2838	−13.6640
%Error	3.59	0.433	0.215	0.146

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

WF4	E	T	V_{ne}	V_{ee}
H	−0.5088	0.5088	−1.3907	0.3731
He	−2.8911	2.8911	−6.7565	0.9743
Li	−7.2682	7.2682	−16.1288	1.5924
Be	−13.6441	13.6441	−29.5025	2.2144

$$T(\alpha,\ \beta) = 0.5088 \quad V_{ne}(\alpha,\ \beta) = -1.3907 \quad V_{ee}(\alpha,\ \beta) = 0.3731$$

Explain the importance of the parameter β. Why does its magnitude decrease as the nuclear charge increases?

The parameter β adds weight to the r_{12} term which most directly represents electron correlation in the wavefunction. As the nuclear charge increases, as we have previously seen, V_{ee} becomes less important as a percentage of the total energy. Thus, the impact of the electron correlation term becomes less significant.

Demonstrate that the virial theorem is satisfied.

$$E(\alpha,\ \beta) = -0.5088 \quad -T(\alpha,\ \beta) = -0.5088 \quad \frac{V_{ne}(\alpha,\ \beta) + V_{ee}(\alpha,\ \beta)}{2} = -0.5088$$

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

$$\begin{pmatrix} \text{H} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -0.4727 & 0.4727 & -1.375 & 0.4297 \\ \text{WF2} & -0.4870 & 0.4870 & -1.3705 & 0.3965 \\ \text{WF3} & -0.5133 & 0.5133 & -1.3225 & 0.2958 \\ \text{WF4} & -0.5088 & 0.5088 & -1.3907 & 0.3731 \end{pmatrix} \quad \begin{pmatrix} \text{He} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -2.8477 & 2.8477 & -6.7500 & 1.0547 \\ \text{WF2} & -2.8603 & 2.8603 & -6.7488 & 1.0281 \\ \text{WF3} & -2.8757 & 2.8757 & -6.7434 & 0.9921 \\ \text{WF4} & -2.8911 & 2.8911 & -6.7565 & 0.9743 \end{pmatrix}$$

$$\begin{pmatrix} \text{Li} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -7.2227 & 7.2227 & -16.1250 & 1.6797 \\ \text{WF2} & -7.2350 & 7.2350 & -16.1243 & 1.6544 \\ \text{WF3} & -7.2487 & 7.2487 & -16.1217 & 1.6242 \\ \text{WF4} & -7.2682 & 7.2682 & -16.1288 & 1.5924 \end{pmatrix} \quad \begin{pmatrix} \text{Be} & \text{E} & \text{T} & \text{V}_{ne} & \text{V}_{ee} \\ \text{WF1} & -13.5977 & 13.5977 & -29.5000 & 2.3047 \\ \text{WF2} & -13.6098 & 13.6098 & -29.4995 & 2.2799 \\ \text{WF3} & -13.6230 & 13.6230 & -29.4978 & 2.2519 \\ \text{WF4} & -13.6441 & 13.6441 & -29.5025 & 2.2144 \end{pmatrix}$$

Except for a hiccup in the hydrogen anion results for WF4, these tables show that the improved agreement with experimental results (the lower total energy), is due to a reduction in electron-electron repulsion.