Fourth Trial Wavefunction

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

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: $\alpha := Z$ $\beta := .7$

Contributions to total energy:

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

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

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

Experimental ground state energy: $E_{exp} := -2.9037$

Calculate error in calculation: $\text{Error} := \left|\frac{E_{exp} - E(\alpha,\beta)}{E_{exp}}\right|$ $\text{Error} = 82.4782\,\%$

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}(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

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

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.

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

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

H	E	T	V_{ne}	V_{ee}
WF1	−0.4727	0.4727	−1.375	0.4297
WF2	−0.4870	0.4870	−1.3705	0.3965
WF3	−0.5133	0.5133	−1.3225	0.2958
WF4	−0.5088	0.5088	−1.3907	0.3731

He	E	T	V_{ne}	V_{ee}
WF1	−2.8477	2.8477	−6.7500	1.0547
WF2	−2.8603	2.8603	−6.7488	1.0281
WF3	−2.8757	2.8757	−6.7434	0.9921
WF4	−2.8911	2.8911	−6.7565	0.9743

Li	E	T	V_{ne}	V_{ee}
WF1	−7.2227	7.2227	−16.1250	1.6797
WF2	−7.2350	7.2350	−16.1243	1.6544
WF3	−7.2487	7.2487	−16.1217	1.6242
WF4	−7.2682	7.2682	−16.1288	1.5924

Be	E	T	V_{ne}	V_{ee}
WF1	−13.5977	13.5977	−29.5000	2.3047
WF2	−13.6098	13.6098	−29.4995	2.2799
WF3	−13.6230	13.6230	−29.4978	2.2519
WF4	−13.6441	13.6441	−29.5025	2.2144

Except for a hicup 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.