Second Trial Wavefunction

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

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: $\alpha := Z$ $\beta := Z + 1$

Variational energy expression:

$$E(\alpha,\beta) := \left[\frac{\frac{\alpha^2+\beta^2}{2} - Z\cdot(\alpha+\beta) - \frac{8\cdot\alpha^{1.5}\cdot\beta^{1.5}}{(\alpha+\beta)^2}\cdot\left(Z - \frac{\alpha\cdot\beta}{\alpha+\beta}\right)}{1 + \frac{8\cdot\alpha^{1.5}\cdot\beta^{1.5}}{(\alpha+\beta)^3}}\right] \ldots$$

$$+ \frac{\frac{5}{8}\cdot(\alpha+\beta) + \frac{2\cdot\alpha\cdot\beta\cdot\left(\alpha^2+3\cdot\alpha\cdot\beta+\beta^2\right)}{(\alpha+\beta)^3} + 4\cdot\left[\frac{8\cdot\alpha^{2.5}\cdot\beta^{1.5}\cdot\left(11\cdot\alpha^2+8\cdot\alpha\cdot\beta+\beta^2\right)}{(\alpha+\beta)^2\cdot(3\cdot\alpha+\beta)^3} \ldots + \frac{8\cdot\alpha^{1.5}\cdot\beta^{2.5}\cdot\left(11\cdot\beta^2+8\cdot\alpha\cdot\beta+\alpha^2\right)}{(\alpha+\beta)^2\cdot(3\cdot\beta+\alpha)^3} \ldots + \frac{20\cdot\alpha^3\cdot\beta^3}{(\alpha+\beta)^5}\right]}{4\cdot\left[1 + \frac{8\cdot\alpha^{1.5}\cdot\beta^{1.5}}{(\alpha+\beta)^3}\right]^2}$$

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

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

Calculate error in calculation: $\text{Error} := \left|\frac{E_{exp} - E(\alpha,\beta)}{E_{exp}}\right|$ $\text{Error} = 1.4931\,\%$

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.

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

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

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

WF2	E	T	V_{ne}	V_{ee}
H	−0.4870	0.4870	−1.3705	0.3965
He	−2.8603	2.8603	−6.7488	1.0281
Li	−7.2350	7.2350	−16.1243	1.6544
Be	−13.6098	13.6098	−29.4995	2.2799

Demonstrate that the virial theorem is satisfied.

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

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

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

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

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

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

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