

2.41: Third Trial Wavefunction

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

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

Variational energy expression:

$$E(\alpha, \beta) = \frac{64\alpha^3\beta^3[\alpha\beta - Z(\alpha + \beta)] \frac{\alpha\beta}{\alpha + \beta} + \frac{\alpha^2\beta^2}{(\alpha + \beta)^3} + \frac{20\alpha^3\beta^3}{(\alpha + \beta)^5}}{1 + \frac{64\alpha^3\beta^3}{(\alpha + \beta)^6}}$$

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \text{Minimize}(E, \alpha, \beta) \quad \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 1.1885 \\ 2.1832 \end{pmatrix} \quad E(\alpha, \beta) = -2.8757$$

Experimental ground state energy:

$$E_{exp} = -2.9037$$

Calculate error in calculation:

$$\text{Error} = \left| \frac{E_{exp} - E(\alpha, \beta)}{E_{exp}} \right| \quad \text{Error} = 0.9656\%$$

Summarize the calculations in the following table.

Ψ	H	He	Li	Be
α	0.28322	1.18853	2.07898	2.98472
β	1.023923	2.18317	3.29491	4.38972
E_{atom}	-0.5133	-2.8757	-7.2488	-13.6230
$E_{atom}(\text{exp})$	-5.277	-2.9037	-7.2838	-13.6640
%Error	2.73	0.964	0.481	0.300

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

$$T(\alpha, \beta) = \frac{\frac{\alpha^2 + \beta^2}{2} + \frac{64\alpha^3\beta^3(\alpha\beta)}{(\alpha + \beta)^6}}{1 + \frac{64\alpha^3\beta^3}{(\alpha + \beta)^6}} \quad V_{ne}(\alpha, \beta) = \frac{-Z(\alpha + \beta) + \frac{64\alpha^3\beta^3(\alpha\beta)}{(\alpha + \beta)^6}}{1 + \frac{64\alpha^3\beta^3[-Z(\alpha + \beta)]}{(\alpha + \beta)^6}}$$

$$V_{ee}(\alpha, \beta) = \frac{\frac{\alpha\beta}{\alpha + \beta} + \frac{\alpha^2\beta^2}{(\alpha + \beta)^3} + \frac{20\alpha^3\beta^3}{(\alpha + \beta)^5}}{1 + \frac{64\alpha^3\beta^3}{(\alpha + \beta)^6}} \quad \begin{aligned} T(\alpha, \beta) &= 2.8757 \\ V_{ne}(\alpha, \beta) &= -6.7434 \\ V_{ee}(\alpha, \beta) &= 0.9921 \end{aligned}$$

WF3	E	T	V_{ne}	V_{ee}
H	-0.5133	0.5133	-1.3225	0.2958
He	-2.8757	2.8757	-6.7434	0.9921
Li	-7.2487	7.2487	-16.1217	1.6242
Be	-13.6230	13.620	-29.4978	2.2519

Demonstrate that the virial theorem is satisfied.

$$E(\alpha, \beta) = -2.8757 \quad -T(\alpha, \beta) = -2.8757 \quad \frac{V_{ne}(\alpha, \beta) + V_{ee}(\alpha, \beta)}{2} = -2.8757$$

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	

	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	

	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	

	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	

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

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