2.43: Fifth Trial Wavefunction and Summary

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

When Chandrasakar's wavefunction is used in a variational calculation on a two-electron atom or ion the following expressions are obtained.

Enter the nuclear charge: Z = 2

Enter initial values for α. β, and b (use results from previous calculations):

$$\alpha = Z \quad \beta = Z + 1 \quad b = 0.3 \quad c = \frac{\alpha+\beta}{2} \quad d = \frac{|\alpha-\beta|}{2}$$

Define the normalization constant:

$$N(b,\ c,\ d) = \frac{\begin{bmatrix} -8d^{10} + \left[40d^8 + \left[-80d^6\left[88d^4 + \left(-56d^2 16c^2\right)c^2\right]c^2\right]c^2\right]c^2 \ldots \\ + \left[\left[-35d^{10} + \left[\begin{matrix} 175d^8 + \left[-349d^6 + \left[335d^4 + \left(-196d^2 + 70c^2\right)c^2\right]c^2\right]c^2 c^2 c \ldots \\ + \left[-48d^{10} + \left[240d^8 + \left[-480d^6\left[480d^4 + \left(-192d^2 + 96c^2\right)c^2\right]c^2\right]c^2\right]c^2\right]b \end{matrix}\right]b\right]\right] \end{bmatrix}}{8(c+d)^5(c-d)^5c^8}$$

Define the electron kinetic energy:

$$T(b,\ c,\ d) = \frac{\begin{bmatrix} 8d^{12} + \left[-48d^{10} + \left[120d^8 + \left[-152d^6 + \left[112d^4 + \left(-56d^2 + 16c^2\right)c^2\right]c^2\right]c^2\right]c^2\right]c^2 \ldots \\ + \left[\begin{matrix} \left[35d^{12} + \left[-200d^{10} + \left[474d^8 + \left[-598d^6 + \left[353d^4 + \left(-114d^2 + 50c^2\right)c^2\right]c^2\right]c^2\right]c^2\right]c^2\right]c \ldots \\ + \left[48d^{12} + \left[-272d^{10} + \left[640d^8 + \left[-800d^6 + \left[592d^4 + \left(\begin{matrix} -80d^2 \ldots \\ +64c^2 \end{matrix}\right)c^2\right]c^2\right]c^2\right]c^2\right]b \end{matrix}\right]b \end{bmatrix}}{\left[8(c+d)^5(c-d)^5c^8\right]N(b,\ c,\ d)}$$

Define electron-nucleus potential energy:

$$VN(b,\ c,\ d) = -4cZ\frac{\begin{bmatrix} arrayll\left[-4d^{10} + \left[20d^8 + \left[-40d^6 + \left[44d^4 + \left(-28d^2 + 8c^2\right)c^2\right]c^2\right]c^2\right]c^2 \ldots \\ + \left[\begin{matrix} \left[-15d^{10} + \left[75d^8 + \left[-149d^6 + \left[139d^4 + \left(-80d^2 + 30c^2\right)c^2\right]c^2\right]c^2\right]c^2\right]c \ldots \\ + \left[-18d^{10} + \left[90d^8 + \left[-180d^6 + \left[180d^4 + \left(-60d^2 + 36c^2\right)c^2\right]c^2\right]c^2\right]c^2\right]b \end{matrix}\right]b \end{bmatrix}}{\left[8(c+d)^5(c-d)^5c^8\right]N(b,\ c,\ d)}$$

Define electron-electron potential energy:

$$VE(b,\ c,\ d) = \frac{\begin{bmatrix} \left[10d^8 + \left[-42d^6 + \left[74d^4 + \left(-62d^2 + 20c^2\right)c^2\right]c^2\right]c^2\right]c^2 \ldots \\ + \left[\begin{matrix} \left[32d^8 + \left[-128d^6 + \left[192d^4 + \left(-160d^2 + 64c^2\right)c^2\right]c^2\right]c^2\right]c \ldots \\ + \left[35d^8 + \left[-140d^6 + \left[209d^4 + \left(-126d^2 + 70c^2\right)c^2\right]c^2\right]c^2\right]b \end{matrix}\right]b \end{bmatrix}}{\left[16(c+d)^4(c-d)^4c^7\right]N(b,\ c,\ d)}$$

Define total energy:

$$\mathrm{E(b,\ c,\ d)} = \mathrm{T(b,\ c,\ d)} + \mathrm{VN(b,\ c,\ d)} + \mathrm{VE(b,\ c,\ d)}$$

Minimize total energy simultaneously with respect to the parameters, b, c, d:

$$\begin{pmatrix} b \\ c \\ d \end{pmatrix} = \mathrm{Minimize(E,\ b,\ c,\ d)} \quad \begin{pmatrix} b \\ c \\ d \end{pmatrix} = \begin{pmatrix} 0.2934 \\ 1.8226 \\ 0.3862 \end{pmatrix} \quad \mathrm{E(b,\ c,\ d)} = \text{-}2.9014$$

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

Calculate error in calculation:

$$\mathrm{Error} = \left|\frac{E_{exp} - E(b,\ c,\ d)}{E_{exp}}\right| \quad \mathrm{Error} = 0.0782\%$$

Calculate α and β from the values of c and d:

$$\text{Given} \quad c = \frac{\alpha+\beta}{2} \quad d = \frac{|\alpha-\beta|}{2} \quad \text{Find(\alpha,~ \beta)} = \begin{pmatrix} 1.4364 \\ 2.2088 \end{pmatrix}$$

Fill in the table and answer the questions below:

Ψ	H	He	Li	Be
α	0.4925	1.4364	2.3616	3.2932
β	1.0744	2.2088	3.2996	4.3745
b	0.3326	0.2934	0.2769	0.2687
E_{atom}	−0.5255	2.9014	−7.227	−13.6525
$E_{atom}(\text{exp}) - 0.5277$	−2.9037	−7.2838	−13.6640	
%Error	0.4090	0.0792	.0909	0.0838

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

The parameter b 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.

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

$$E(b,\ c,\ d) = -2.9014 \quad T(b,\ c,\ d) = 2.9017 \quad VN(b,\ c,\ d) = -6.7524 \quad VE(b,\ c,\ d) = 0.9492$$

WF5	E	T	V_{ne}	V_{ee}
H	−0.5275	0.5275	−1.3738	0.3208
He	−2.9017	2.9017	−6.7524	0.9492
Li	−7.2772	7.2772	−16.1265	1.5721
Be	−13.6525	13.6525	−29.5011	2.1960

Demonstrate that the virial theorem is satisfied for the helium atom:

$$E(b,\ c,\ d) = -2.9014 \quad T(b,\ c,\ d) = 2.9017 \quad \frac{VN(b,\ c,\ d)+VE(b,\ c,\ d)}{2} = -2.9016$$

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
WF5	−0.5275	0.5275	−1.3738	0.3208

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	−6.7565	0.9743
WF4	−2.8911	2.8911	−6.7565	0.9743
WF5	−2.9017	2.9017	−6.7424	0.9492

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
WF5	−7.2227	7.2227	−16.1265	1.5721

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
WF5	−13.6526	13.6525	−29.5011	2.1960

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 through the use of trial wavefunctions that improve electron correlation.