Fifth Trial Wavefunction

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

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 \( \alpha, \beta, \) 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:

\[
N(b, c, d) := \frac{\left[ -8 \cdot d^{10} + 40 \cdot d^8 + [ -80 \cdot d^6 + 88 \cdot d^4 + (-56 \cdot d^2 + 16 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots + \left[ -35 \cdot d^{10} + 175 \cdot d^8 + [ -349 \cdot d^6 + 335 \cdot d^4 + (-196 \cdot d^2 + 70 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots \right] \cdot b}{8 \cdot (c + d)^5 \cdot (c - d)^5 \cdot c^8}
\]

Define the electron kinetic energy:

\[
T(b, c, d) := \frac{\left[ 8 \cdot d^{12} + 48 \cdot d^{10} + 120 \cdot d^8 + [ -152 \cdot d^6 + 112 \cdot d^4 + (-56 \cdot d^2 + 16 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots + \left[ 35 \cdot d^{12} + 200 \cdot d^{10} + 474 \cdot d^8 + [ -598 \cdot d^6 + 353 \cdot d^4 + (-114 \cdot d^2 + 50 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots \right] \cdot b}{8 \cdot (c + d)^5 \cdot (c - d)^5 \cdot c^8 \cdot N(b, c, d)}
\]

Define electron-nucleus potential energy:

\[
VN(b, c, d) := \frac{-4 \cdot c \cdot Z \cdot \left[ -4 \cdot d^{10} + 20 \cdot d^8 + [ -40 \cdot d^6 + 44 \cdot d^4 + (-28 \cdot d^2 + 8 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots + \left[ -15 \cdot d^{10} + 75 \cdot d^8 + [ -149 \cdot d^6 + 139 \cdot d^4 + (-80 \cdot d^2 + 30 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots \right] \cdot b}{8 \cdot (c + d)^5 \cdot (c - d)^5 \cdot c^8 \cdot N(b, c, d)}
\]

Define electron-electron potential energy:

\[
VE(b, c, d) := \frac{\left[ 10 \cdot d^8 + [ -42 \cdot d^6 + 74 \cdot d^4 + (-62 \cdot d^2 + 20 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots + \left[ 32 \cdot d^8 + [ -128 \cdot d^6 + 192 \cdot d^4 + (-160 \cdot d^2 + 64 \cdot c^2) \cdot c^2 \right] \cdot c^2 \cdots \right] \cdot b}{16 \cdot (c + d)^4 \cdot (c - d)^4 \cdot c^2 \cdot N(b, c, d)}
\]

Define total energy:

\[
E(b, c, d) := T(b, c, d) + VN(b, c, d) + VE(b, c, d)
\]
Minimize total energy simultaneously with respect to the parameters, b,c,d:

\[
\begin{pmatrix}
  b \\
  c \\
  d
\end{pmatrix} = \text{Minimize}(E, b, c, d)
\]

\[
\begin{pmatrix}
  b \\
  c \\
  d
\end{pmatrix} = \begin{pmatrix}
  0.2934 \\
  1.8226 \\
  0.3862
\end{pmatrix}
\]

\[E(b, c, d) = -2.9014\]

**Experimental ground state energy:** \[E_{\text{exp}} := -2.9037\]

Calculate error in calculation:

\[
\text{Error} := \left| \frac{E_{\text{exp}} - E(b, c, d)}{E_{\text{exp}}} \right|
\]

\[\text{Error} = 0.0782\%\]

Calculate \(\alpha\) and \(\beta\) from the values of c and d:

Given \(c = \frac{\alpha + \beta}{2}\)

\[d = \frac{\alpha - \beta}{2}\]

Find \((\alpha, \beta) = \begin{pmatrix}
  1.4364 \\
  2.2088
\end{pmatrix}\]

Fill in the table and answer the questions below:

<table>
<thead>
<tr>
<th>(E_{\text{atom}})</th>
<th>(E_{\text{atom}}(\text{exp}))</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.5255</td>
<td>0.4090</td>
</tr>
<tr>
<td>He</td>
<td>-2.9014</td>
<td>0.0792</td>
</tr>
<tr>
<td>Li</td>
<td>-7.2772</td>
<td>0.0909</td>
</tr>
<tr>
<td>Be</td>
<td>-13.6525</td>
<td>0.0838</td>
</tr>
</tbody>
</table>

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, \(V_{\text{ee}}\) 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.

\[E(b, c, d) = -2.9014\]

\[T(b, c, d) = 2.9017\]

\[V_{\text{ne}}(b, c, d) = -6.7524\]

\[V_{\text{ee}}(b, c, d) = 0.9492\]
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.

### He

| 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 |

### Li

| 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 | -7.2772 | 7.2772 | -16.1265 | 1.5721 |

### Be

| 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 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.