

Five Trial Wavefunctions for two-electron Atoms and Ions

The purpose of this exercise is to examine five trial wavefunctions for the helium atom and several two-electron ions. The calculations begin with an uncorrelated wavefunction in which both electrons are placed in a hydrogenic orbital with scale factor α . The next four trial functions use several methods to increase the amount of electron correlation in the wave function. As the summary of results that is appended shows this gives increasingly more favorable agreement with the experimentally determined value for the ground state energy of the species under study. The detailed calculations show that the reason for this improved agreement with experiment is due to a reduction in electron-electron repulsion.

Because of the electron-electron interaction Schrodinger's equation cannot be solved exactly for the helium atom or more complicated atomic or ionic species. However, the ground state energy of the helium atom can be calculated using approximate methods. One of these is the variation method which requires the evaluation of the following variational integral.

$$E = \frac{\int_0^{\infty} \Psi_{\text{trial}} \cdot H \cdot \Psi_{\text{trial}} d\tau}{\int_0^{\infty} \Psi_{\text{trial}}^2 d\tau}$$

First Trial Wavefunction

The variation method is discussed in all of the standard physical chemistry textbooks. As is clear from the expression above this method requires that a trial wavefunction with one or more adjustable parameters be chosen. A logical first choice for such a function would be to assume that the electrons in the helium atom occupy scaled hydrogen 1s orbitals.

$$\Psi(1,2) = \Phi(1)\Phi(2) = \exp[-\alpha (r_1 + r_2)]$$

He1ans.mcd illustrates how the ground state energy and the optimum value for the scale factor, α , can be found using Mathcad. The value of -2.8477 hartrees is within 2% of the known ground state energy of the helium atom. The error in the calculation is attributed to the fact that the wavefunction is based on the orbital approximation and, therefore, does not adequately take electron correlation into account. In other words, this wavefunction gives the electrons too much independence, given that they have like charges and tend to avoid one another.

Second Trial Wavefunction

Some electron correlation can be built into the wavefunction by assuming that each electron is in an orbital which is a linear combination of two scaled hydrogen 1s orbital.

$$\Phi = \exp(-\alpha r) + \exp(-\beta r)$$

Under the orbital approximation this assumption gives a trial wavefunction of the form

$$\Psi(1,2) = \Phi(1)\Phi(2) = \exp(-\alpha r_1)\exp(-\alpha r_2) + \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2) + \exp(-\beta r_1)\exp(-\beta r_2)$$

Inspection of this wavefunction indicates that 50% of the time the electrons are in different orbitals, while for the first trial wavefunction the electrons were in the same orbital 100% of the time. He2ans.mcd illustrates how this calculation would be executed. Notice the enormous increase in the complexity of the variational expression for the energy. However, also notice that the calculation is very similar to that using the previous trial wavefunction. The differences are that in this case the expression for the energy is more complex and that it is being minimized simultaneously with respect to two parameters rather than just one. It is also clear that introducing some electron correlation into the trial wavefunction has improved the agreement between theory and experiment.

Third Trial Wavefunction

The extent of electron correlation can be increased further by eliminating the first and last term in the second wavefunction. This yields a wavefunction of the form,

$$\Psi(1,2) = \exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)$$

This trial wavefunction places the electrons in different scaled hydrogen 1s orbitals 100% of the time and He3ans.mcd shows that further improvement in the agreement with the literature value of the ground state energy is obtained. This result is within 1% of the actual ground state energy of the helium atom.

Fourth Trial Wavefunction

The third trial wavefunction, however, still rests on the orbital approximation and, therefore, doesn't treat electron correlation adequately. Hylleraas took the calculation a step further by introducing electron correlation directly into the wavefunction by adding a term, r_{12} , involving the inter-electron separation.

$$\Psi(1,2) = \exp[-\alpha (r_1 + r_2)][1 + \beta r_{12}]$$

In the trial wavefunction shown above, if the electrons are far apart r_{12} is large and the magnitude of the wave function increases favoring that configuration. He4ans.mcd shows that this modification of the trial wavefunction has further improved the agreement between theory and experiment to within 0.5%.

Fifth Trial Wavefunction

Chandrasakar brought about further improvement by adding Hylleraas's r_{12} term to the third trial wavefunction as shown here.

$$\Psi(1,2) = [\exp(-\alpha r_1)\exp(-\beta r_2) + \exp(-\beta r_1)\exp(-\alpha r_2)][1 + br_{12}]$$

As can be seen in He5ans.mcd Chandrasakar's three parameter wavefunction gives rise to a fairly complicated variational expression for ground state energy. However it also gives a result for helium that is within .07% of the experimental value for the ground state energy. The experimental value for the ground state energy of the helium atom is $2.90372 E_h$.

The calculations that have been outlined here for the helium atom can be repeated for H^- , Li^+ , Be^{++} , etc. The hydride anion is a particularly interesting case because the first two trial wavefunctions do not predict a stable ion. This indicates that electron correlation is an especially important issue for atoms and ions with small nuclear charge.

Summary of the Results for the Helium Atom

$$\Psi = \frac{\alpha^3}{\pi} \cdot \exp(-\alpha \cdot r_1) \cdot \exp(-\alpha \cdot r_2)$$

$$E := -2.84766$$

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

$$E := -2.86035$$

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

$$E := -2.87566$$

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

$$E := -2.89112$$

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

$$E := -2.90143$$

Experimentally Determined Ground State Energy

$$E_{\text{exp}} := -2.90372$$