

Exploring the Variational Method

Purpose: The purpose of this lab is to explore the variational principle as it is applied in quantum chemistry to compute the energies of multi-electron atoms. Specifically we explore the helium-like atoms (e.g. H^- , He , Li^+ , Be^{+2} , etc.) containing 2 electrons. These 2-electron systems cannot be solved analytically, and must be approximated using other means.

1 Background

The variational principle states that any approximate energy corresponding to a trial wavefunction E_{trial} will always be greater than or equal to the true ground state energy E_{exact} .

$$E_{\text{trial}} \geq E_{\text{exact}} \quad (1)$$

Specifically it will only be exact for the true ground state wave function. The derivation of this principle was discussed in class and can be found in standard quantum chemistry textbooks.

Using the variational principle, it can be shown that adding additional parameters to a selected wavefunction increases the flexibility and results in a better trial function and consequently a lower energy.

The energy of any trial wavefunction can be computed as

$$E_{\text{trial}} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2)$$

where the denominator accounts for the fact that the wavefunction may not be normalized. For a helium-like atom the electronic Hamiltonian, in atomic units, is given by

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_1 - r_2|} \quad (3)$$

where r_1 and r_2 are vectors describing the position of electron 1 and 2 respectively and Z is the nuclear charge. The first two terms describe the kinetic energy of each electron, the two the potential energy of attraction between the electrons and the nucleus and the last one describes the electron-electron repulsion. The trial wavefunction can take on various forms and a few of these will be explored in this assignment. Generally any function that satisfies the requirements of a wave equation will be suitable (i.e. not 0 everywhere, fulfills boundary conditions, etc.).

Minimizing the energy by setting the partial derivatives with respect to each of the variational parameters equal to 0 provides a method to solve for the optimal wavefunction of the selected form.

2 Procedure

There are integrals for three types of wavefunctions provided in the accompanying MATLAB notebook. The indexing and mathematical expressions are shown in the table below. Note

| Type Index | Expression |
|------------|---|
| 1 | $e^{-ar_1} e^{-ar_2}$ |
| 2 | $e^{-ar_1} e^{-br_2} + e^{-br_1} e^{-ar_2}$ |
| 3 | $e^{-ar_1} e^{-ar_2} e^{b r_1-r_2 }$ |

that wavefunction 1 only had one variational parameter while the others have two. The normalization for a wavefunction is given by

$$N = \langle \Psi | \Psi \rangle \quad (4)$$

and the unnormalized energy as

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle \quad (5)$$

2.1 One-variational parameter

In the sample MATLAB notebook you will find a nearly completed code for computing the energy of each of the trial wavefunctions. We will first begin looking at the one parameter function. This form of the wavefunction is essentially two H-atom wavefunctions multiplied together, with a single adjustable parameter a . Note that the wavefunction does not include any direct interaction between the two electrons. In the MATLAB notebook you will need to do the following

1. Select the helium atom by setting the nuclear charge $Z = 2$
2. Choose a value for the variational parameter a . Note that you can use a range for a in the form $a_{min} : step : a_{max}$, which can be used to determine the value of the parameter that gives the lowest energy
3. Insert an expression for the trial energy, E in terms of N , T , and V which are defined in the notebook
4. Determine the optimal variational parameter graphically to three decimal places
5. Label the axes and save a plot of the energy and variational parameter
6. Once the optimal variational parameter is obtained compute the percent error relative to the very accurate value for helium given in the notebook
7. Repeat these steps for a minimum of two other isoelectronic atoms ($Z = 1 - 10$)

2.2 Two variational parameters

Now consider the second and third trial wavefunctions. In the second case the two electrons are essentially allowed to be in their own orbitals (equivalent to unrestricting the wavefunction), and in the third case an explicit dependence on the distance between the two electrons is used.

1. For helium only, determine the optimal parameters a and b as for Ψ_2
2. Once the optimal variational parameters are obtained compute the percent error relative to the very accurate value for helium given in the notebook
3. Repeat these steps wavefunction Ψ_3

3 Questions

Summarize your results in a table including the optimal values of the variational parameters and the percent error. Then answer the following questions.

1. How does the percent error change as the nuclear charge increases when using Ψ_1 ? Should this trend hold for any trial function?
2. Compare the best energy obtained for helium with each wavefunction. Which wavefunction performs the best? How do you know this one is the best?
3. Instead of solving graphically for the minimum energy as a function of the variational parameters one can evaluate the partial derivatives of the energy and set them to be 0. Explain why this would be preferable for a function consisting of multiple variational parameters. For Ψ_1 evaluate the derivative of your energy expression with respect to a to solve for the minimum. Does this value agree with your MATLAB results?