

# The variational theorem

The variation method allows us to obtain an approximation to the ground state energy of the system without solving the Schrödinger equation.

The variation method is based on the following theorem:

Given a system with hamiltonian operator  $H$ , then if  $\phi$  is any normalized well-behaved function that satisfies the boundary conditions it is true that

$$\int \phi^* H \phi d\tau \geq E_0$$

where  $E_0$  is the true value of the lowest energy eigenvalue of  $H$ . This important theorem allows us to calculate an upper bound for the ground state energy.

# Practical significance

The variation method serves as the basis for all methods that use combinations of hydrogen-like orbitals to solve for the eigenfunctions (wave functions) and eigenvalues (energies) of atoms and molecules.

The radial part of the hydrogen-like wave functions is modified by a variational parameter, which is minimized. The theorem allows us to set the derivative with respect to any parameter  $\alpha$  equal to zero to find the value of that parameter that minimizes the energy:

$$\frac{\partial}{\partial \alpha} \int \phi^* H \phi d\tau = 0$$

We can be sure that the energy calculated in this way will be greater than the true energy (an upper bound).

# The hamiltonian for H

The electronic hamiltonian for the hydrogen atom consists of a kinetic energy term for the electron and the Coulomb attraction of the electron and proton (nucleus).

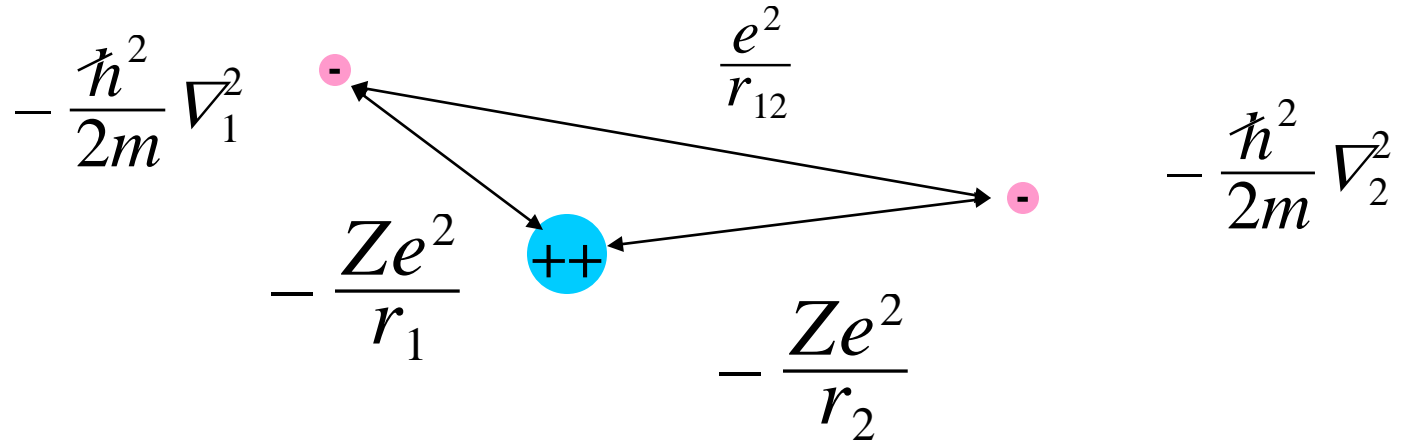
$$-\frac{\hbar^2}{2m} \nabla^2$$
$$-\frac{Ze^2}{r_1}$$

Of course, the nuclear charge of hydrogen is  $Z = 1$  so the  $Z$  is included for completeness. We know that the solutions of the Schrödinger equation ( $H\Psi = E\Psi$ ) gives energy levels:  
 $n$  is the principal quantum number.  
 $a_0$  is the Bohr radius.

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}$$

# The hamiltonian for He

For helium the same kinetic energy and Coulomb attraction terms are present, but there is also a Coulomb repulsion between the two electrons that must be included.



Because of the Coulomb repulsion there is no exact solution for He. To solve the problem we use two 1s orbitals from the solution for hydrogen and then apply the variational method.

# The He wave function

The hydrogen 1s wave functions for electrons 1 and 2 are:

$$f_1 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr_1/a}, f_2 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr_2/a}$$

The aufbau approach for atoms assumes that the total wave function for a many-electron atom is just a product of one electron wave functions. In the present case:

$$\phi = f_1 f_2$$

Note that the hydrogen wave functions are normalized so:

$$\int f_1^* f_1 d\tau = \int f_2^* f_2 d\tau = 1$$

# Variational approach for the He atom

The He wave function used for the variation method is a product of two hydrogen 1s orbitals. However, instead of the nuclear charge  $Z$  we use a variational parameter  $\zeta$ .

$$\phi = \frac{1}{\pi} \left( \frac{\zeta}{a} \right)^3 e^{-\zeta r_1/a} e^{-\zeta r_2/a}$$

$\zeta$  has a physical interpretation. Since one electron tends to screen the other from the nucleus, each electron is subject to a nuclear charge that is less than  $Z$ .

The hamiltonian is:

$$H = \left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\zeta e^2}{r_2} \right) + (\zeta - Z) \frac{e^2}{r_1} + (\zeta - Z) \frac{e^2}{r_2} + \frac{e^2}{r_{12}}$$

# Evaluation of the integrals

If we consider only the part of the hamiltonian in parentheses  
We have the solution to a hydrogen atom with two electrons  
in the 1s orbital.

$$\left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\zeta e^2}{r_2} \right) \phi = -\frac{\zeta^2 e^2}{a} \phi$$

where the right hand side is twice the energy of a 1s electron.  
The energy can be calculated:

$$: \int \phi^* H \phi d\tau = -\frac{\zeta^2 e^2}{a} \int \phi^* \phi d\tau$$

$$+ e^2 (\zeta - Z) \left( \int \frac{\phi^* \phi}{r_1} d\tau + \int \frac{\phi^* \phi}{r_2} d\tau \right) + e^2 \int \frac{\phi^* \phi}{r_{12}} d\tau$$

# Evaluation of the integrals

We can evaluate each of the integrals as follows:

$$\int \frac{\phi^* \phi}{r_1} d\tau = \int \frac{\phi^* \phi}{r_2} d\tau = \frac{\zeta}{a}$$

$$\int \frac{\phi^* \phi}{r_{12}} d\tau = \frac{5\zeta e^2}{8a}$$



# Evaluation of the variational parameter $\zeta$

We have:

$$\int \phi^* H \phi d\tau = \left( \zeta^2 - 2\zeta Z + \frac{5\zeta}{8} \right) \frac{e^2}{a}$$

We now vary  $\zeta$  to minimize the variational integral:

$$\frac{\partial}{\partial \zeta} \int \phi^* H \phi d\tau = \frac{\partial}{\partial \zeta} \left( \zeta^2 - 2\zeta Z + \frac{5\zeta}{8} \right) \frac{e^2}{a} = 0$$

$$\frac{\partial}{\partial \zeta} \left( \zeta^2 - 2\zeta Z + \frac{5\zeta}{8} \right) = 0$$

$$2\zeta - 2Z + \frac{5}{8} = 0$$

$$\zeta = Z - \frac{5}{16}$$

# The variational energy: comparison with experiment

The variational energy is

$$\int \phi^* H \phi d\tau = \left( -Z^2 + \frac{5}{8}Z - \frac{25}{256} \right) \frac{e^2}{a} = - \left( Z - \frac{5}{16} \right)^2 \frac{e^2}{a}$$

Our first guess would be to calculate the energy of the 1s Electron in He using the hydrogen energy level with a nuclear charge  $Z = 2$ ,  $E = -Ze^2/a_0$  which gives  $-2(13.6) \text{ eV} = -27.2 \text{ eV}$ . Using the value obtained by the variational method we have,  $E = -(27/16)e^2/a_0 = -(27/16)(13.6) \text{ eV} = -22.95 \text{ eV}$ .

The experimental value is  $-24.5 \text{ eV}$ . The variational energy is much closer to the true value and in accord with the variational theorem, the true ground state energy is less than that given by variational method.

# Summary for the variational principle

The hydrogen atom is the only atom with an exact solution.

Hydrogen wave functions are used as the approximation for atomic wave functions in multielectron atoms.

The variational principle states that any wave function we choose that satisfies the Schrödinger equation will give an energy greater than the true energy of the system.

The variation method provides a general prescription for improving on any wave function with a parameter by minimizing that function with respect to the parameter.