The Variation Method

The variational theorem
Application to LCAO-MO theory
The He atom
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:

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

We can be sure that the energy calculated in this way will be greater than the true energy (an upper bound).
Application of the Variational Method
The linear combination of atomic orbitals (LCAO)

Calculations of the energy and properties of molecules requires hydrogen-like wave functions on each of the nuclei. The Hartree-Fock method begins with assumption that molecular orbitals can be formed as a linear combination of atomic orbitals.

\[ \phi_i = \sum_{\mu=1}^{N} C_{\mu i} \chi_{\mu} \]

The basis functions \( \chi_{\mu} \) are hydrogen-like atomic orbitals that have been optimized by a variational procedure. The HF procedure is a variational procedure to minimize the coefficients \( C_{\mu i} \). Note that we use the index \( m \) for atomic orbitals and \( i \) or \( j \) for molecular orbitals.
Common types of atomic orbitals

Slater-type orbitals (STOs)

\[ \chi_\mu \propto e^{-\zeta r} \]

The STOs are like hydrogen atom wave functions. The problem with STOs arises in multicenter integrals. The Coulomb and exchange integrals involve electrons on different nuclei and so the distance \( r \) has a different origin.

Gaussian-type orbitals (GTOs)

\[ \chi_\mu \propto e^{-\alpha r^2} \]

Gaussian orbitals can be used to mimic the shape of exponentials, i.e. the form of the solutions for the hydrogen atom. Multicenter Gaussian integrals can be solved analytically.
STOs vs GTOs

GTOs are mathematically easy to work with

![Graph showing the exponential decrease of amplitude with distance, represented as $\exp(-r)$]
STOs vs GTOs

GTOs are mathematically easy to work with, but the shape of a Gaussian is not that similar to that of an exponential.
STOs vs GTOs

Therefore, linear combinations of Gaussians are used to imitate the shape of an exponential. Shown is a representation of the 3-Gaussian model of a STO.
Double-zeta basis sets

Since the remaining atoms have a different exponential dependence than hydrogen it is often convenient to include more parameters.

\[ \chi_\mu = D_{\mu a}e^{-\zeta_a r} + D_{\mu b}e^{-\zeta_b r} \]

The second exponential is a diffuse function. It accounts for properties of a valence electrons involved in bonding.

When GTOs are used there are always multiple Gaussians required because the shape of Gaussians must be matched as closely as possible to that of exponentials. In a double-zeta basis there may be up to 3 Gaussians used to represent the first exponent \( \zeta_a \) and 1 for the second exponent \( \zeta_b \). In a so-called 6-31G basis set in the GAUSSIAN program, there are 6 Gaussians for core electrons and then 3 for \( \zeta_a \) and 1 for \( \zeta_b \).
The variation procedure applied to the HF wave functions

The HF procedure uses the variational method to obtain the value of parameters that minimizes the energy

$$\delta E = \delta \langle \phi | H | \phi \rangle = \delta \int \phi^* H \phi \, d\tau = 0$$

subject to the constraint the wave functions remain orthogonal

$$\langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j \, d\tau = \delta_{ij}$$

The minimization of an equation subject to a constraint is carried out using the method of LaGrange undetermined multipliers.

$$\delta \left[ \langle \phi | H | \phi \rangle - E \left( \langle \phi | \phi \rangle - 1 \right) \right] = 0$$

Note that the multiplier is the energy $E$ and it will be determined during the procedure.
The variational method in HF

The variation can also be viewed as a variation of the function by an infinitesimal amount

\[ \phi = \phi' + \delta \phi' \]

The energy then becomes

\[ E[\phi + \delta \phi] = \langle \phi + \delta \phi | H | \phi + \delta \phi \rangle \]

\[ \approx \langle \phi | H | \phi \rangle + \langle \phi + \delta \phi | H | \phi \rangle + \langle \phi | H | \phi + \delta \phi \rangle \]

\[ = E + \delta E \]

In the variation method we are looking for the wave function \( f \) that will minimize the energy. Here the condition is that the variation in the energy \( \delta E = 0 \) as indicated on the previous slide. This condition assures that \( E \) is stationary. A stationary point is usually a minimum.
Introduction of the basis

At this point we can substitute our trial wave function into the Fock equations.

\[ E = \langle \phi | H | \phi \rangle = \sum_{\mu \nu} C_\mu^* C_\nu \langle \chi_\mu | H | \chi_\nu \rangle \]

The Lagrangian becomes

\[ L = \langle \phi | H | \phi \rangle - E \langle \phi | \phi \rangle - 1 \]

\[ = \sum_{\mu \nu} C_\mu^* C_\nu \langle \chi_\mu | H | \chi_\nu \rangle - E \sum_{\mu \nu} C_\mu^* C_\nu \langle \chi_\mu | \chi_\nu \rangle - 1 \]

The first variation in the Lagrangian is set equal to zero.

\[ \delta L = \sum_{\mu \nu} \delta C_\mu^* C_\nu \langle \chi_\mu | H | \chi_\nu \rangle + \sum_{\mu \nu} C_\mu^* \delta C_\nu \langle \chi_\mu | H | \chi_\nu \rangle - E \sum_{\mu \nu} \delta C_\mu^* C_\nu \langle \chi_\mu | \chi_\nu \rangle - E \sum_{\mu \nu} C_\mu \delta C_\nu \langle \chi_\mu | \chi_\nu \rangle = 0 \]
Expansion in terms of coefficients

Since both $E$ and $L$ are real we can collect terms and exchange indices to obtain

$$
\sum_{\mu=1}^{N} \delta C_{k\mu}^* \left( \sum_{i} H_{k\mu} C_{\mu i} - E_i S_{k\mu} C_{\mu i} \right) \quad k = 1,2,3,\ldots, N
$$

$$
H_{k\mu} = \langle \chi_{k}\mid H\mid\chi_{\mu} \rangle = \int \chi_{k}^{*} H \chi_{\mu} d\tau
$$

$$
S_{k\mu} = \langle \chi_{k}\mid\chi_{\mu} \rangle = \int \chi_{k}^{*} \chi_{\mu} d\tau
$$

In other words:

$$
\left( H_{11} - E_i S_{11} \right) C_{1i} + \left( H_{12} - E_i S_{12} \right) C_{2i} + \ldots + \left( H_{1N} - E_i S_{1N} \right) C_{Ni} = 0
$$

$$
\left( H_{21} - E_i S_{21} \right) C_{1i} + \left( H_{22} - E_i S_{22} \right) C_{2i} + \ldots + \left( H_{2N} - E_i S_{2N} \right) C_{Ni} = 0
$$

$$
\ldots
$$

$$
\left( H_{N1} - E_i S_{N1} \right) C_{1i} + \left( H_{N2} - E_i S_{N2} \right) C_{2i} + \ldots + \left( H_{NN} - E_i S_{NN} \right) C_{Ni} = 0
$$
The secular determinant

There are \(N\) equations and \(N + 1\) unknown variables: \(C_{1i}, C_{2i}, C_{3i}, \ldots, C_{Ni}\), and \(E_i\).

In order for the equations to have meaningful (non-zero) solutions they must comprise a secular determinant

\[
\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & \cdots \\
H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & \cdots \\
H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots \\
\end{vmatrix} = 0
\]

which leads to \(N\) eigenvalues, \(E_i\) (\(i = 1,2,3,\ldots,N\)).

The solutions for the \(\phi_i = C_{1i} \chi_1 + C_{2i} \chi_2 + \ldots C_{Ni} \chi_N\) under the constraint:

\[
\sum_{\mu=1}^{N} \sum_{v=1}^{N} C_{\mu i} C_{v r} S_{\mu v} = 1
\]
Matrix representation

The fock hamiltonian is an effective one-electron hamiltonian

\[ H^\text{eff} \phi_i = E_i \phi_i \quad \quad H^\text{eff} \equiv f(r) \]

AOS: \( \{\chi_1, \chi_2, \chi_3, \ldots, \chi_N\} \)

MOs: \( \phi_i = \sum_{\mu=1}^{N} C_{\mu i} \chi_i \)

The matrix representation for the overlap and interaction energies is:

\[
S = \begin{pmatrix}
S_{11} & S_{12} & S_{13} & \ldots & S_{1N} \\
S_{21} & S_{22} & S_{23} & \ldots & S_{2N} \\
& \ddots & \ddots & \ddots & \ddots \\
S_{N1} & S_{N2} & S_{N3} & \ldots & S_{NN}
\end{pmatrix}
\quad 
H = \begin{pmatrix}
H_{11} & H_{12} & H_{13} & \ldots & H_{1N} \\
H_{21} & H_{22} & H_{23} & \ldots & H_{2N} \\
& \ddots & \ddots & \ddots & \ddots \\
H_{N1} & H_{N2} & H_{N3} & \ldots & H_{NN}
\end{pmatrix}
\quad 
C_i = \begin{pmatrix}
C_{1i} \\
C_{2i} \\
\vdots \\
C_{Ni}
\end{pmatrix}
\]
Matrix representation

Thus, \( HC_i = E_i SC_i \)

Define the matrices of coefficients and eigenvalues as:

\[
C = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & \ldots & C_{1N} \\
C_{21} & C_{22} & C_{23} & \ldots & C_{2N} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
C_{N1} & C_{N2} & C_{N3} & \ldots & C_{NN}
\end{pmatrix},
\]

\[
E = \begin{pmatrix}
E_{11} & 0 & 0 & \ldots & 0 \\
0 & E_{22} & 0 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & E_{NN}
\end{pmatrix}
\]

Then the matrix form is \( HC = SCE \). This system of equations is diagonalized if \( \det |H - ES| = 0 \). However, this is possible only in the MO basis.

**AO basis:** \( \{ \chi_1, \chi_2, \chi_3, \ldots, \chi_N \} \)

\( S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \) : Not orthogonal

\( H_{\mu\nu} = \langle \chi_\mu | H^{\text{eff}} | \chi_\nu \rangle \) : Not diagonal

**MO basis:** \( \{ \phi_1, \phi_2, \phi_3, \ldots, \phi_N \} \)

\( \delta_{ij} = \langle \phi_i | \phi_j \rangle \) : Orthogonal

\( E_i \delta_{ij} = \langle \phi_i | H^{\text{eff}} | \phi_j \rangle \) : Diagonal
Eigenvalues are energies and eigenvectors are MOs

The procedure is carried out until a self-consistent minimum energy is found. The resulting self-consistent field (SCF) energy is the Hartree-Fock procedure.

The values for the coefficients that give the SCF energies for the electronic states give the MOs. As shown previously we can think of these as linear combinations of atomic orbitals.

The linear combinations have distinctive shapes such as those shown for the MOs of N\textsubscript{2} in the following.
Summary of methods

1. Determine the optimum atomic orbitals. This is done by a variational procedure for each atom. The exponent of the STO or GTO is optimized. More than one STO can be used per atomic orbital (e.g. double-zeta basis). The GTO requires parameterization of multiple Gaussian functions.
2. Form linear combinations of the atomic orbitals at the positions indicated by a molecular geometry. Note that this is initially just a guess and that the geometry, which gives the lowest energy must be calculated in a number of tries (cycles) of the HF procedure.
3. Perform the HF procedure repeatedly until a self-consistent solution of the equations for the coefficients is obtained. This is the self-consistent field (SCF) method.
Example of the Variation Method: Screening of Electrons in He
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:

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

\( n \) is the principal quantum number. \( a_0 \) is the Bohr radius.
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.

\[ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}} - \frac{\hbar^2}{2m} \nabla_2^2 \]
The hydrogen 1s wave functions for electrons 1 and 2 are:

\[ f_1 = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_1/a_0}, \quad f_2 = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_2/a_0} \]

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:

\[ \varphi = f_1 f_2 \]

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 $\zeta$.

$$\varphi = \frac{1}{\pi} \left( \frac{\zeta}{a_0} \right)^3 e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0}$$

$\zeta$ 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:

$$H = \left( -\frac{\hbar^2}{2m} V_1^2 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} V_2^2 - \frac{\zeta e^2}{r_2} \right) + \left( \zeta - Z \right) \frac{e^2}{r_1} + \left( \zeta - Z \right) \frac{e^2}{r_2} + \frac{e^2}{r_{12}}$$
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.

\[
\left( -\frac{\hbar^2}{2m} \nabla^2_1 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} \nabla^2_2 - \frac{\zeta e^2}{r_2} \right) \phi = -\frac{\zeta^2 e^2}{a_0} \phi
\]

where the right hand side is twice the energy of a 1s electron. Using this result we have:

\[
\int \phi^* H \phi d\tau = -\frac{\zeta^2 e^2}{a_0} \int \phi^* \phi d\tau + (\zeta - Z)e^2 \int \frac{\phi^* \phi d\tau}{r_1} + (\zeta - Z)e^2 \int \frac{\phi^* \phi d\tau}{r_2} + e^2 \int \frac{\phi^* \phi d\tau}{r_{12}}
\]

The integrals have the following values:

\[
\int \phi^* \phi d\tau = 1 , \quad \int \frac{\phi^* \phi d\tau}{r_1} = \int \frac{\phi^* \phi d\tau}{r_2} = \frac{\zeta}{a_0} , \quad e^2 \int \frac{\phi^* \phi d\tau}{r_{12}} = \frac{5\zeta e^2}{8a_0}
\]
Evaluation of the variational parameter $\zeta$

We have:

$$\int \varphi^* H \varphi d\tau = \left( \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) \frac{e^2}{a_0}$$

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

$$\frac{\partial}{\partial \zeta} \int \varphi^* H \varphi d\tau = \frac{\partial}{\partial \zeta} \left( \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) \frac{e^2}{a_0} = 0$$

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

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

The variational energy is:

$$\int \varphi^* H \varphi d\tau = \left( -Z^2 + \frac{5}{8}Z - \frac{25}{256} \right) \frac{e^2}{a_0} = - \left( Z - \frac{5}{16} \right)^2 \frac{e^2}{a_0}$$
The variational energy: comparison with experiment

The experimental ionization energy of He is –24.5 eV.

Our first guess would be to calculate the energy of the 1s Electron in He using the hydrogen energy level with a nuclear charge $Z = 2$, $E = -Ze^2/a_0$.
This 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 value is much closer to the true value. In accord with the variational theorem, the true ground state energy is less than that given by variational method.
Summary

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.