APPROXIMATED METHODS

The Hamiltonian operator for an n-electron atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze'^2}{r_i} + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e'^2}{r_{ij}}$$

where the last term is the interelectronic repulsion. If repulsion were absent, the Hamiltonian would be the sum of single-electron terms and the associated eigenvalue problem would be exactly solvable (the wave function would be the product of single-electron wave functions and the energy the sum of the single-electron energies). However, **the presence of the interelectronic terms makes the Schrödinger equation not solvable exactly**. This requires the use of approximation methods

APPROXIMATED METHODS

Approximation methods are needed to get the solutions of the time-independent Schrödinger equation for systems (atoms or molecules) that contain interacting electrons

There are two main methods of approximation. The **perturbation theory** and the **variation method**

We will study the variation method, which allows to approximate the ground-state energy of a system without solving the Schrödinger equation. The variation method is based on the variation theorem

VARIATION METHOD

Variation Theorem

Given a system whose Hamiltonian operator is time independent and the lowest energy eigenvalue is E_1, if ϕ is any, well-behaved function of the coordinates of the system's particles that satisfies the boundary conditions of the problem, then

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1$$

The variation theorem allows to calculate (1) an upper bound for the ground-state energy of a system and (2) an approximated wave function

Note that ϕ is not a wave function, but an approximation to it

VARIATION METHOD

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1$$

The function ϕ is called **trial variation function** (or simply trial function)

The ratio of integrals is called **variation integral** (denoted as W)

$$W = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau}$$

To get a good approximation to the ground-state energy E_1, we have to try many trial functions and look for the one that gives the lowest value of W

VARIATION METHOD

If we are lucky enough to choose a trial function equal to the wave function for the ground state, then we find that the variation integral is equal to E_1

$$\frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\int \psi^* E_1 \psi \, d\tau}{\int \psi^* \psi \, d\tau} = E_1$$

We therefore expect that the lower the value of the variational integral, the closer the trial function will approach the true ground-state wave function

VARIATION METHOD

Example: Verify the variation method for the trial function reported below considering the one-particle system moving in a box of length l

Trial function

$$\begin{cases} \phi(x) = x(l-x) \quad \text{for} \quad 0 \le x \le l \\ \phi(x) = 0 \qquad \text{for} \quad x \le 0 \qquad x \ge l \end{cases}$$

Ground-state energy of a one-particle $\rightarrow \quad E_1 = \dfrac{h^2}{8ml^2}$

$$\int \phi^* \hat{H} \phi \, dx = \frac{l^3 \, h^2}{24\pi^2 m} \qquad \int \phi^* \phi \, dx = \frac{l^5}{30}$$

$$\frac{\int \phi^* \hat{H} \phi \, dx}{\int \phi^* \phi \, dx} = \frac{10}{\pi^2} \frac{h^2}{8ml^2} \simeq 1{,}013 \frac{h^2}{8ml^2}$$

VARIATION METHOD

In practice, one usually puts several parameters into the trial function ϕ, and then varies these parameters so as to minimize the variation integral

VARIATION METHOD (linear variation functions)

A special kind of trial function widely used in the study of molecules is the **linear variation function**. A linear variation function is a linear combination of n linearly independent functions $f_1, f_2, \ldots, f_n$

$$\phi = c_1 f_1 + c_2 f_2 + \cdots + c_n f_n = \sum_{j=1}^{n} c_j f_j$$

where ϕ is the trial function and the coefficients c_j are parameters to be determined by minimizing the variation integral. The functions f_j (which are called **basis functions**) must satisfy the boundary conditions of the problem. We shall restrict ourselves to real c_j and real f_j

VARIATION METHOD (linear variation functions)

We now apply the variation theorem

$$\int \phi^* \phi \, d\tau = \int \sum_{j=1}^{n} c_j f_j \sum_{k=1}^{n} c_k f_k \, d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \int f_j f_k \, d\tau$$

We define the overlap integral S_{jk} as $S_{jk} = \int f_j f_k \, d\tau$

Therefore we get $$\int \phi^* \phi \, d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k S_{jk}$$

Note that S_{jk} is not necessarily equal to 0 or 1, because there is no reason to suppose that the functions f_j and f_k are orthogonal and normalized

VARIATION METHOD (linear variation functions)

The numerator of the variation integral is

$$\int \phi^* \hat{H} \phi \, d\tau = \int \sum_{j=1}^{n} c_j f_j \hat{H} \sum_{k=1}^{n} c_k f_k \, d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \int f_j \hat{H} f_k \, d\tau$$

and using the abbreviation $H_{jk} = \int f_j \hat{H} f_k \, d\tau$

We write $$\int \phi^* \hat{H} \phi \, d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k H_{jk}$$

The variation integral is $$W \equiv \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = \frac{\sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k H_{jk}}{\sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k S_{jk}}$$

VARIATION METHOD (linear variation functions)

We now minimize W, *the variation integral,* so as to approach to E_1 as closely as we can. The variation integral W is a function of the n independent variables $c_1, c_2, \ldots, c_n$

$$W = W(c_1, c_2, \ldots, c_n)$$

A necessary condition for a minimum in a function W of several variables is that its partial derivatives with respect to each of the variables must be zero at the minimum

$$\frac{\partial W}{\partial c_i} = 0, \qquad i = 1, 2, \ldots, n$$

VARIATION METHOD (linear variation functions)

The derivative

$$\frac{\partial W}{\partial c_i} = \frac{\partial}{\partial c_i}\left[\frac{\sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k H_{jk}}{\sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k S_{jk}}\right] = 0$$

For simplicity, we set

$$h(c_1,\ldots,c_n) = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k H_{jk}$$

$$s(c_1,\ldots,c_n) = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k S_{jk}$$

VARIATION METHOD (linear variation functions)

The derivative can be written as

$$\frac{\partial W}{\partial c_i} = \frac{\partial}{\partial c_i}\left[\frac{h(c_1,\ldots,c_n)}{s(c_1,\ldots,c_n)}\right] = 0$$

$$s^{-1}\left(\frac{\partial h}{\partial c_i} - \frac{h}{s}\frac{\partial s}{\partial c_i}\right) = 0$$

$$\sum_{k=1}^{n} c_k \left(H_{ik} + H_{ki}\right) - W \sum_{k=1}^{n} c_k \left(S_{ik} + S_{ki}\right) = 0$$

VARIATION METHOD (linear variation functions)

By definition we have

$$S_{ik} = \int f_i f_k \, d\tau$$

$$S_{ki} = \int f_k f_i \, d\tau$$

Thus $\boxed{S_{ik} = S_{ki}}$

Moreover $H_{ik} = \int f_i \hat{H} f_k \, d\tau$ $H_{ki} = \int f_k \hat{H} f_i \, d\tau$

For real functions, it is possible to show that

$$\boxed{H_{ik} = H_{ki}}$$

VARIATION METHOD (linear variation functions)

Thus we get $$2\sum_{k=1}^{n} c_k H_{ik} - 2W\sum_{k=1}^{n} c_k S_{ik} = 0$$

$$\sum_{k=1}^{n}\left[c_k\left(H_{ik} - WS_{ik}\right)\right] = 0, \quad i = 1, 2, \ldots, n$$

The eq above is a system of n simultaneous, linear, homogeneous equations in the n unknowns $c_1, c_2, \ldots, c_n$
Writing explicitly the system of equations we obtain

$$\begin{cases} (H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 + \cdots + (H_{1n} - S_{1n}W)c_n = 0 \\ (H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 + \cdots + (H_{2n} - S_{2n}W)c_n = 0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ (H_{n1} - S_{n1}W)c_1 + (H_{n2} - S_{n2}W)c_2 + \cdots + (H_{nn} - S_{nn}W)c_n = 0 \end{cases}$$

VARIATION METHOD (linear variation functions)

The system of linear homogeneous equations has a non trivial solution if the determinant of the coefficients vanishes (the trivial solution is: $c_1 = c_2 = \cdots = c_n = 0$, not physically acceptable)

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & \cdots & H_{1n} - S_{1n}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W & \cdots & H_{2n} - S_{2n}W \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ H_{n1} - S_{n1}W & H_{n2} - S_{n2}W & \cdots & H_{nn} - S_{nn}W \end{vmatrix} = 0$$

This is a n-degree linear equation in the variable W. It has n real solutions. The above equation is called **secular equation**

DETERMINANTS

The (n-1)-order determinant obtained by striking out the i-th row and the j-th column of the n-th order determinant is called the minor of the element a_{ij}. We define the cofactor of a_{ij} as the minor of a_{ij} times the factor $(-1)^{i+j}$. The determinant is evaluated by multiplying each element of the top row by its cofactor and adding up the products.

Examples:

determinant of order 3

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

Determinant of order 2

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$$

VARIATION METHOD (linear variation functions)

Arranging these n roots of the secular equation in order of increasing value, we have $W_1 \leq W_2 \leq \cdots \leq W_n$. If we number the states of the system in order of increasing energy, we have $E_1 \leq E_2 \leq \cdots \leq \cdots$, where the E's denote the true energies of various states. From the variation theorem, we know that $E_1 \leq W_1$. Moreover, it can be proved that

$$E_1 \leqslant W_1, \quad E_2 \leqslant W_2, \quad E_3 \leqslant W_3, \ldots, \quad E_n \leqslant W_n$$

Thus, **the linear variation method provides upper bounds to the energies of the lowest *n* bound states of the system**. If approximations to the energies of more states are wanted, we add more functions to the trial function. The addition of more functions can be shown to increase (or cause no change in) the accuracy of the previously calculated energies

VARIATION METHOD (linear variation functions)

In the simplest case of $n = 2$ the system of equations is

$$\begin{cases} (H_{11} - WS_{11})c_1 + (H_{12} - WS_{12})c_2 = 0 \\ (H_{21} - WS_{21})c_1 + (H_{22} - WS_{22})c_2 = 0 \end{cases}$$

Secular equation

$$\begin{vmatrix} H_{11} - WS_{11} & H_{12} - WS_{12} \\ H_{21} - WS_{21} & H_{22} - WS_{22} \end{vmatrix} = 0$$

$$(H_{11} - WS_{11})(H_{22} - WS_{22}) - (H_{12} - WS_{12})^2 = 0$$

We denote the 2 solutions as W_1 and W_2. The approximation to the wave-function of the ground state is obtained by substituting W_1 in the system above and solving for c_1 and c_2.
The same should be done for the first excited state