

## The Variation Principle

The variation theorem states that given a system with a Hamiltonian  $H$ , then if  $\phi$  is any normalised, well-behaved function that satisfies the boundary conditions of the Hamiltonian, then

$$\langle \phi | H | \phi \rangle \geq E_0 \quad (1)$$

where  $E_0$  is the true value of the lowest energy eigenvalue of  $H$ . This principle allows us to calculate an upper bound for the ground state energy by finding the trial wavefunction  $\phi$  for which the integral is minimised (hence the name; trial wavefunctions are varied until the optimum solution is found). Let us first verify that the variational principle is indeed correct.

We first define an integral

$$\begin{aligned} I &= \langle \phi | H - E_0 | \phi \rangle \\ &= \langle \phi | H | \phi \rangle - \langle \phi | E_0 | \phi \rangle \\ &= \langle \phi | H | \phi \rangle - E_0 \langle \phi | \phi \rangle \\ &= \langle \phi | H | \phi \rangle - E_0 \quad (\text{since } \phi \text{ is normalised}) \end{aligned}$$

If we can prove that  $I \geq 0$  then we have proved the variation theorem.

Let  $\psi_i$  and  $E_i$  be the true eigenfunctions and eigenvalues of  $H$ , so  $H \psi_i = E_i \psi_i$ . Since the eigenfunctions  $\psi_i$  form a complete basis set for the space spanned by  $H$ , we can expand any wavefunction  $\phi$  in terms of the  $\psi_i$  (so long as  $\phi$  satisfies the same boundary conditions as  $\psi_i$ ).

$$\phi = \sum_k a_k \psi_k$$

Substituting this function into our integral  $I$  gives

$$\begin{aligned} I &= \langle \sum_k a_k \psi_k | H - E_0 | \sum_j a_j \psi_j \rangle \\ &= \langle \sum_k a_k \psi_k | \sum_j (H - E_0) a_j \psi_j \rangle \end{aligned}$$

If we now use  $H\psi = E\psi$ , we obtain

$$\begin{aligned} I &= \langle \sum_k a_k \psi_k | \sum_j a_j (E_j - E_0) \psi_j \rangle \\ &= \sum_k \sum_j a_k^* a_j (E_j - E_0) \langle \psi_k | \psi_j \rangle \\ &= \sum_k \sum_j a_k^* a_j (E_j - E_0) \delta_{jk} \end{aligned}$$

We now perform the sum over  $j$ , losing all terms except the  $j=k$  term, to give

$$\begin{aligned} I &= \sum_k a_k^* a_k (E_k - E_0) \\ &= \sum_k |a_k|^2 (E_k - E_0) \end{aligned}$$

Since  $E_0$  is the lowest eigenvalue,  $E_k - E_0$  must be positive, as must  $|a_k|^2$ . This means that all terms in the sum are non-negative and  $I \geq 0$  as required.

For wavefunctions that are not normalised, the variational integral becomes:

$$\frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0$$

## Linear variation method

A special type of variation widely used in the study of molecules is the so-called linear variation function, a linear combination of  $n$  linearly independent functions  $f_1, f_2, \dots, f_n$  (often atomic orbitals) that satisfy the boundary conditions of the problem. i.e.  $\phi = \sum_i c_i f_i$ . The coefficients  $c_i$  are parameters to be determined by minimising the variational integral. In this case, we have:

$$\begin{aligned} \langle \phi | H | \phi \rangle &= \langle \sum_i c_i f_i | H | \sum_j c_j f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j \langle f_i | H | f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j H_{ij} \end{aligned} \quad \text{where } H_{ij} \text{ is the Hamiltonian matrix element.}$$

$$\begin{aligned} \langle \phi | \phi \rangle &= \langle \sum_i c_i f_i | \sum_j c_j f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j \langle f_i | f_j \rangle \\ &= \sum_i \sum_j c_i^* c_j S_{ij} \end{aligned} \quad \text{where } S_{ij} \text{ is the overlap matrix element.}$$

The variational energy is therefore

$$E = \frac{\sum_i \sum_j c_i^* c_j H_{ij}}{\sum_i \sum_j c_i^* c_j S_{ij}}$$

which rearranges to give

$$E \sum_i \sum_j c_i^* c_j S_{ij} = \sum_i \sum_j c_i^* c_j H_{ij}$$

We want to minimise the energy with respect to the linear coefficients  $c_i$ , requiring that  $\frac{\partial E}{\partial c_i} = 0$  for all  $i$ .

Differentiating both sides of the above expression gives,

$$\frac{\partial E}{\partial c_k} \sum_i \sum_j c_i^* c_j S_{ij} + E \sum_i \sum_j \left[ \frac{\partial c_i^*}{\partial c_k} c_j + \frac{\partial c_i}{\partial c_k} c_i^* \right] S_{ij} = \sum_i \sum_j \left[ \frac{\partial c_i^*}{\partial c_k} c_j + \frac{\partial c_i}{\partial c_k} c_i^* \right] H_{ij}$$

Since  $\frac{\partial c_i^*}{\partial c_k} = \delta_{ik}$  and  $S_{ij} = S_{ji}$ ,  $H_{ij} = H_{ji}$ , we have

$$\frac{\partial E}{\partial c_k} \sum_i \sum_j c_i^* c_j S_{ij} + 2E \sum_i c_i S_{ik} = 2 \sum_i c_i H_{ik}$$

When  $\frac{\partial E}{\partial c_k} = 0$ , this gives

$$\boxed{\sum_i c_i (H_{ik} - E S_{ik}) = 0} \quad \text{for all } k \quad \text{SECULAR EQUATIONS}$$

We therefore have  $k$  simultaneous *secular equations* in  $k$  unknowns. These equations can also be written in matrix notation, and for a non-trivial solution (i.e.  $c_i \neq 0$  for all  $i$ ), the determinant of the secular matrix must be equal to zero. i.e.

$$|H_{ik} - ES_{ik}| = 0$$

The resulting algebraic equation can be solved to obtain the energies  $E$ . When arranged in order of increasing energy, these provide approximations to the energies of the first  $k$  states (each having an energy higher than the true energy of the state by virtue of the variation theorem). To find the energies of a larger number of states we simply use a greater number of basis functions  $f_i$  in the trial wavefunction  $\phi$ . To obtain the approximate wavefunction for a particular state, we substitute the appropriate energy into the secular equations and solve for the coefficients  $c_i$ .

NB: Using this method it is possible to find all the coefficients  $c_1 \dots c_k$  in terms of one coefficient; normalising the wavefunction provides the absolute values for the coefficients.

## Huckel Molecular Orbital Theory

Huckel theory is a simplified version of the linear variation method which can be applied to conjugated  $\pi$  systems. We assume  $\sigma$ - $\pi$  separability, which means that the nuclei, electrons of the atomic inner shells and localised  $\sigma$  bonds provide an effective field in which the remaining  $\pi$  electrons move. We then average the effective field.

$$H_{\pi} = \sum_{i=1}^{n_{\pi}} H_{\text{eff}}(i)$$

The next simplification is to approximate the  $\pi$  molecular orbitals as linear combinations of atomic orbitals. In a minimal basis set calculation of a planar conjugated hydrocarbon, the only atomic orbitals with  $\pi$  symmetry are the 2p orbitals on carbon. The  $\pi$  orbitals can therefore be written

$$\sigma_i = \sum_{j=1}^n c_{ij} f_j$$

where  $f_{ij}$  is a 2p $\pi$  orbital on the  $j$ th carbon atom. The optimum values for the  $n$  lowest p orbitals satisfy the secular equations

$$\sum_{k=1}^n (H_{jk}^{\text{eff}} - S_{jk}E_i)c_{kj} = 0$$

in which the  $E_i$ 's are the roots of the secular determinant

$$|H_{jk}^{\text{eff}} - S_{jk}E_i| = 0$$

The key assumptions in Huckel theory involve the integrals  $H$  and  $S$ . We assume that  $H_{ii}$  has the same value for every carbon atom in the molecule, and also for carbon atoms in different planar hydrocarbons. The integral  $H_{ij}$  is assumed to have the same value for any two carbons bonded to each other and to vanish for two non-bonded atoms. The overlap integral  $S_{ij}$  is assumed to be equal to zero unless  $i=j$ , in which case it will be equal to unity since the atomic orbitals  $f_i$  are normalised. This can be summarised as:

$$\begin{aligned} H_{ii} &= \langle f_i | H^{\text{eff}} | f_i \rangle \equiv \alpha \\ H_{ij} &= \langle f_i | H^{\text{eff}} | f_j \rangle \equiv \beta \quad \text{for atoms } i, j \text{ bonded} \\ H_{ij} &= \langle f_i | H^{\text{eff}} | f_j \rangle = 0 \quad \text{for atoms } i, j \text{ not bonded} \end{aligned}$$

$$S_{ij} = \langle f_i | f_j \rangle = \delta_{ij}$$

$\alpha$  and  $\beta$  are called the *Coulomb* and *bond* (sometimes *resonance*) integrals. Since non-bonded carbon atoms are usually well separated, the third assumption of Huckel theory is reasonable, but assuming an overlap integral of zero for bonded atoms is a poor approximation (in practice, the theory is often modified to improve on this assumption).

As an example, consider butadiene,  $H_2C=CH-CH=CH_2$ . For the purposes of Huckel theory, only the connectivity of the carbon framework is important; no distinction is made between the *cis*- and *trans*-conformations. The Huckel assumptions give:

$$\begin{aligned} H_{11} &= H_{22} = H_{33} = H_{44} = \alpha \\ H_{12} &= H_{23} = H_{34} = \beta \\ H_{13} &= H_{14} = H_{24} = 0 \end{aligned}$$

The secular equations are:

$$\begin{pmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{pmatrix} = 0$$

Solving the secular determinant gives the four roots  $E_1 = \alpha - 1.618\beta$ ,  $E_2 = \alpha - 0.618\beta$ ,  $E_3 = \alpha + 0.618\beta$  and  $E_4 = \alpha + 1.618\beta$ . Substituting each of these energies into the secular equations in turn and solving for the coefficients gives the normalised molecular orbitals:

$$\begin{aligned} \phi_1 &= 0.372f_1 + 0.602f_2 + 0.602f_3 + 0.372f_4 \\ \phi_2 &= 0.602f_1 + 0.372f_2 - 0.372f_3 - 0.602f_4 \\ \phi_3 &= 0.602f_1 - 0.372f_2 - 0.372f_3 + 0.602f_4 \\ \phi_4 &= 0.372f_1 - 0.602f_2 + 0.602f_3 - 0.372f_4 \end{aligned}$$

The molecular orbital coefficients can be used to determine a range of molecular properties. As an example, one quantity that is sometimes quoted in relation to Huckel theory is the  $\pi$  electron or charge density on an atom. The charge density on atom  $j$  is given by  $q_j = \sum_i n_i |c_{ij}|^2$ . While this is not a true electron density, measuring neither charge nor probability density, but merely the number of  $\pi$  electrons in the vicinity of atom  $i$ , it can sometimes be used to give at least a rough indication of the reactivity of particular atoms with nucleophiles and electrophiles.