

The Variation Principle

The variation theorem states that given a system with a Hamiltonian H , then if ϕ 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 ϕ 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

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

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

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

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

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

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

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 ϕ . 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 π systems. We assume σ - π separability, which means that the nuclei, electrons of the atomic inner shells and localised σ bonds provide an effective field in which the remaining π 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 π molecular orbitals as linear combinations of atomic orbitals. In a minimal basis set calculation of a planar conjugated hydrocarbon, the only atomic orbitals with π symmetry are the 2p orbitals on carbon. The π orbitals can therefore be written

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

where f_j is a 2p π 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:

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

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

α and β 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 π 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 π 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.