

What Does the Hückel MO Method Calculate?

The Hückel molecular orbital (HMO) method has played the unfathomable role in organic chemistry since it was adapted in the problems of chemistry about 50 years ago. Recent days, the HMO method has played the main role of the Woodward-Hoffmann rule. In spite of such an important method, the very few organic chemists seem to understand the answer to "what does the Hückel MO method calculate?"

The HMO method was introduced by E. Hückel (1896-1980, Germany) in order to explain the special stability of benzene (Fig. 1). It was the 1930s. Since no computers were available, bold approximations and abbreviations were taken in and the method was made such a simple one that hand calculation can be carried out if it is a small system. Since it was so much simplified, the energy obtained by the HMO method is not clear in what is expressed.

The meaning of the HMO method has been studied.^{1, 2)} I will explain it based on the literature 2. Since the HMO method is a simplification of a Schrödinger equation, one may grasp the physical meaning of simplification and the results of calculation by knowing the ways of simplification. Therefore, I will start explaining from the theory of the molecular orbital method.

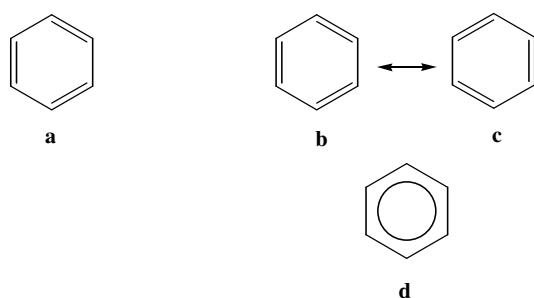


Fig. 1. Structure of benzene.

A Brief Theory of the Molecular Orbital Method

The General Theory

First, let me explain the general method of how to form a Schrödinger equation. (Those who feel unnecessary may skip this section.)

Let me go ahead with the story imagining a hydrogen atom as a model (Fig. 2). In quantum mechanics, momentum (p) is a more fundamental quantity than velocity (v). Here, $p = mv$ (m is mass). The energy (E) of a system consists of the sum of kinetic energy (T) and potential energy (V). That is, $E = T + V$. For example, a hydrogen atom has an electron in the surroundings of a nucleus (proton). Since the Born-Oppenheimer (BO) approximation³⁾ (any nucleus does not move) is used, the kinetic energy of the nucleus is 0. This is omitted from the start. If the nucleus is put on the origin, using the distance of the electron from the origin ($r = \sqrt{x^2 + y^2 + z^2}$) and electron's velocity (v), E is

expressed as the center formula in Eq. 1. E is also expressed, using momentum (p), as the bracketed formula.

$$E = T + V = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \left(\equiv \mathbf{H} = \frac{1}{2m} p^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \quad 1$$

Here, m and ϵ_0 are mass of electron and the vacuous dielectric constant. Especially the bracketed formula that expresses E with coordinates (generally expressed as q) and the momentum p is called the Hamilton function. This function is show as $\mathbf{H}(q, p)$ (the variables q and p are not shown in many cases.).

The procedure of formulating the Schrödinger equation of an arbitrary system is simply packed as,

Procedure 1: Express the energy of a system on the classical mechanics (Newtonian mechanics), and denote the energy of the electron by momenta (for example, p_x, p_y, p_z) and coordinates (x, y, z) (formulation of the Hamilton function).

$$E \equiv \mathbf{H} = T(p_x, p_y, p_z) + V(x, y, z) \quad 2$$

Procedure 2: Concerning every momentum, next transformation is carried out,

$$\begin{aligned} p_x &\rightarrow -i\hbar \frac{\partial}{\partial x} \\ p_y &\rightarrow -i\hbar \frac{\partial}{\partial y} \\ p_z &\rightarrow -i\hbar \frac{\partial}{\partial z} \end{aligned} \quad 3$$

As for coordinates,

$$\begin{aligned} x &\rightarrow x \\ y &\rightarrow y \\ z &\rightarrow z \end{aligned} \quad 4$$

In the above transformations, i is the imaginary unit and \hbar is the constant of Planck's constant divided by 2π . The operator H formed as above procedures is called a Hamiltonian. Here, $\frac{\partial}{\partial x}$ expresses partial differentiation. That is, for example, if the function $f(x,y)=x^2+3xy+y^3$ is partial-differentiated with respect to x ,

$$\frac{\partial}{\partial x}(x^2 + 3xy + y^3) = 2x + 3y$$

is given. And the quantum mechanical operator for p_x^2 is,

$$p_x^2 = p_x p_x \rightarrow -i\hbar p_x \frac{\partial}{\partial x} \rightarrow -\hbar^2 \frac{\partial}{\partial x} \frac{\partial}{\partial x} \equiv -\hbar^2 \frac{\partial^2}{\partial x^2}$$

Here, $\frac{\partial^2}{\partial x^2}$ is second partial-derivative as you know.

Using this method, let us obtain the Schrödinger equation of hydrogen. As the classical model,

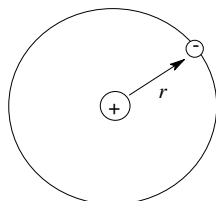


Fig.2. Classical model of a hydrogen atom

an electron assumed to run in a circle around the non-moving proton. The classical expression of E is, putting the proton on the origin and using mass m and velocity u , shown as,

$$E = \frac{m}{2}(u_x^2 + u_y^2 + u_z^2) - \frac{e^2}{4\pi\epsilon_0 r} \quad r = \sqrt{x^2 + y^2 + z^2} \quad 5$$

If momentum, $p=mu$, is used, the Hamilton function is obtained as,

$$\mathbf{H} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \frac{e^2}{4\pi\epsilon_0 r} \quad 6$$

Transformations due to Eqs. 3 and 4 on Eq. 6 give the Hamiltonian (H) as,

$$H \equiv \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \left(\equiv \frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{4\pi\epsilon_0 r} \right) \quad 7$$

Thus, the Schrödinger equation of hydrogen atom is,

$$E\psi = H\psi \quad 8$$

Here, the contents of H are as shown in Eq. 7. Next, let us apply this method to molecule.

Consider a molecule that consists of N number of nuclei and n number of electrons. The classical total energy (E) is expressed as,

$$E = \frac{1}{2} \sum_{A=1}^N M_A U_A^2 + \frac{m}{2} \sum_{i=1}^n u_i^2 - \sum_{A=1}^N \sum_{i=1}^n k \frac{Z_A e^2}{r_{iA}} + \sum_{i>j}^n k \frac{e^2}{r_{ij}} + \sum_{A>B}^N k \frac{Z_A Z_B}{R_{AB}} \quad 8$$

If the BO approximation is introduced in Eq. 8, the kinetic energy of nuclei (the first term of right-hand side of the equation) is set to be 0. The nuclear repulsion energy is obtained classically as well leading the following formula.

$$E = E^{el} + \sum_{A>B}^N k \frac{Z_A Z_B}{R_{AB}} \quad 9$$

$$E^{el} = \frac{m}{2} \sum_{i=1}^n u_i^2 - \sum_{A=1}^N \sum_{i=1}^n k \frac{Z_A e^2}{r_{iA}} + \sum_{i>j}^n k \frac{e^2}{r_{ij}}$$

Then, E^{el} is transformed to the classical Hamilton function (\mathbf{H}^{el}) as,

$$\mathbf{H}^{el} = -\frac{1}{2m} \sum_{i=1}^n p_i^2 - \sum_{A=1}^N \sum_{i=1}^n k \frac{Z_A e^2}{r_{iA}} + \sum_{i>j}^n k \frac{e^2}{r_{ij}} \quad 10$$

According to transformation procedures (Eqs. 3 and 4), one may obtain quantum mechanical Hamiltonian as,

$$H^{el} = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^n k \frac{Z_A e^2}{r_{iA}} + \sum_{i>j}^n k \frac{e^2}{r_{ij}} \quad 11$$

And using this Hamiltonian, the Schrödinger equation is $E^{el}\Psi^{el} = H^{el}\Psi^{el}$. Solving this equation to obtain E^{el} and adding the nuclear repulsion energy, one may get the total energy of the considered system.

By the way, since the right-hand side of Eq. 11 consists of the sum of operators of the kinetic energy and Coulombic energy (potential energy), H is expressed as the sum of T and V as,

$$H = T + V \quad 12$$

$$T = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \quad 13$$

$$V = -\sum_{A=1}^N \sum_{i=1}^n k \frac{Z_A e^2}{r_{iA}} + \sum_{i>j}^n k \frac{e^2}{r_{ij}} \quad 14$$

Since the Hamiltonian for a general system (Eq.11) looks complicated, a special unit system called “atomic units” may be introduced. The length unit of atomic units is the distance of the maximum distribution of electron from the nucleus of hydrogen atom (a_0) and is set to 1 (au). The mass of electron (m), elementary charge (*i.e.*, the absolute charge quantity of an electron or a proton), and Planck’s constant (\hbar) are all set to 1 (au). By doing so, \hbar , e , and m in the Schrödinger equation disappear.

Length

$$1au = a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529167 \times 10^{-10} m \quad 15$$

Charge

$$1au = e = 1.60219 \times 10^{-19} C \quad 16$$

Energy (this unit is called a Hartree also)

$$1au = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.35942 \times 10^{-18} J \quad 17$$

Using atomic units, Eq. 11 turns out to be a very simple form as,

$$H^{el} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^n \frac{Z_A}{r_{iA}} + \sum_{i>j}^n \frac{1}{r_{ij}} \quad 18$$

Hückel Molecular Orbital Method

A carbon-carbon bond is either σ -bond or π -bond. σ -Bond is that with the axial symmetry, in which the character of the bond by rotation around the bond axis is not changed. All bonds that include s atomic orbital in organic compounds are usually σ bonds. Hydrocarbons which consist only of σ bonds are called saturated hydrocarbons. They are chemically non-reactive and do not have special physiological activity, either. This is because the reactivity is in a low state as the energy of σ electrons is low and stable if compared with π electrons.

On the other hand, a π bond is that with plane-symmetric nature, and has a plane (symmetry plane) which divides two bonding atomic orbitals equally in accordance with a bond axis. In organic compounds, one double bond or triple bond consists of one σ bond, and one or two π bonds, respectively. Hydrocarbons which include π bond(s) are called unsaturated hydrocarbons. It is known that a compound including an unsaturated bond is active in a chemical reaction and physiological activity is also strong. This is because π electrons (electrons in π bonds) are in an energetic high state. Although a σ bond includes 2 s orbitals, a π bond consists only of 2 p orbitals. Since a 2 p orbital is in a level higher energy than 2 s , the energy of most π electrons becomes higher than that of σ electron.

The benzene (C₆H₆) has a circular configuration among double bonds and shows specific stability. Benzene has three double bonds with the structure of Fig. 1. Generally, an unsaturated bond (especially double bond) between carbons is rich in chemical reactivity. For example, when the solution of bromine (Br₂) is added to a solution of an unsaturated hydrocarbon, it is well-known that bromine adds to a double bond and the color of bromine is decolorized immediately. However, such a reaction does not occur in benzene. Benzene rarely causes the addition reaction. Instead, a displacement reaction takes place: H is replaced by another substituent group. That is, benzene tends to maintain the structure of the double bonds conjugated. There is a series of unsaturated hydrocarbons with the similar character, and they have a circular configuration of double bonds and are called aromatic hydrocarbons (aromatic compounds). These chemical features originated in conjugation of double bonds. The Hückel molecular orbital (HMO) method has played important roles in the characterization study of aromatic hydrocarbons.

Approximations in the HMO Method

Assumptions used for the HMO method are enumerated and the meaning is verified as follows.

- (1) The conjugated π electronic system is only considered. The system in which conjugation broke

off as shown in Fig. 3 is considered as two π electronic systems. They are treated separately.

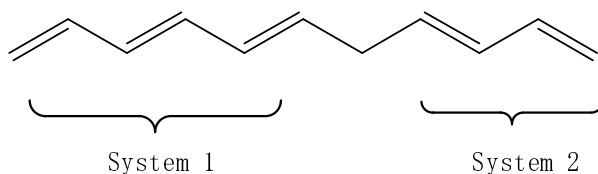


Fig. 3. The system in which conjugation is broke off. It is considered as two π electronic systems

- (2) Influence of σ electrons and inner-shell electrons to the π system is taken in as an average potential.

The total electronic Hamiltonian (H^{el}) of the system that consists of N number of nuclei and n number of electrons is written as,

$$H^{el} = \sum_{i=1}^n -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^n \frac{Z_A}{r_{Ai}} + \sum_{i<j} \frac{1}{r_{ij}} \quad 18$$

Here, ∇_i^2 is the Laplacian with respect to electron i , Z_A is the nuclear charge of nucleus A ,

r_{Ai} is the distance between nucleus A and electron i , and $\sum_{i<j} \frac{1}{r_{ij}}$ means taking the sum of

electron repulsion energy between electrons i and j without duplication. Eq.18 is partitioned into the π electron and other electron (σ electrons and inner-shell electrons) terms. If the number of π electrons is set p , Eq.18 is rewritten as,

$$H^{el} = \sum_{i=1}^p -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^p \frac{Z_A}{r_{Ai}} + \sum_{i<j} \frac{1}{r_{ij}} + \left(\sum_{k=1}^{n-p} -\frac{1}{2}\nabla_k^2 - \sum_{A=1}^N \sum_{k=1}^{n-p} \frac{Z_A}{r_{Ak}} + \sum_{k<l} \frac{1}{r_{kl}} \right) \quad 19$$

In Eq.19, subscripts i and j concern π electrons while k and l do other electrons. Terms in the bracket are concerning σ electrons and inner-shell electrons. They are treated as a constant potential and replace by constant K .

- (3) The electron repulsion between π electrons ($\sum_{i<j} \frac{1}{r_{ij}}$) are averaged and included in K .

$$H^{\pi} = \sum_{i=1}^p -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^N \sum_{i=1}^p \frac{Z_A}{r_{Ai}} + K \quad 20$$

This Hamiltonian is written as H^{π} .

- (4) The potentials of each nucleus ($\sum_{A=1}^N \sum_{i=1}^p \frac{Z_A}{r_{Ai}}$) are averaged and included in K . As a consequence,

H^{π} is,

$$H^\pi = \sum_{i=1}^p -\frac{1}{2}\nabla_i^2 + K \quad 21$$

The Schrödinger equation of Hamiltonian 21 turns out as,

$$\varepsilon\psi = H^\pi\psi = \left(\sum_{i=1}^p -\frac{1}{2}\nabla_i^2 + K \right)\psi = \sum_{i=1}^p -\frac{1}{2}\nabla_i^2\psi + K\psi$$

Here, $K\psi$ is moved to the left-hand side giving,

$$(\varepsilon - K)\psi = \left(\sum_{i=1}^p -\frac{1}{2}\nabla_i^2 \right)\psi \quad 22$$

Again, the following rewriting is carried out.

$$\begin{aligned} (\varepsilon - K) &\Rightarrow \varepsilon \\ \sum_{i=1}^p -\frac{1}{2}\nabla_i^2 &\equiv H^\pi \end{aligned} \quad 23$$

- (5) The total wavefunction is expressed by the product of each molecular orbital in terms of Linear Combination of Atomic Orbitals (LCAO).

The Hückel molecular orbital is obtained by solving Eq.22. We have two ways to solve Eq.22: The HMO method is to use the LCAO method and the other is to solve it analytically (mathematically). The meaning of a Hückel molecular orbital becomes clearer by comparing with the analytical results. For the time being, let us continue to explain the HMO method.

The total wavefunction is expressed by the product of each molecular orbital.⁴⁾

$$\Psi(1,2,\dots,n) = \psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p) \quad 24$$

The Schrödinger equation turns out,

$$E\psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p) = \left(\sum_{i=1}^p -\frac{1}{2}\nabla_i^2 \right)\psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p) \quad 25$$

On both sides, $\psi(1)\psi(2)\psi(3)\dots\psi(p)$ is multiplied and integration is carried out concerning all electrons and all spaces to give,

$$\begin{aligned} E \int (\psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p))^2 d\tau_1 d\tau_2 d\tau_3 \dots d\tau_p &= \\ \int \psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p) \left(\sum_{i=1}^p -\frac{1}{2}\nabla_i^2 \right) \psi_1(1)\psi_2(2)\psi_3(3)\dots\psi_p(p) d\tau_1 d\tau_2 d\tau_3 \dots d\tau_p &= \\ = \int \psi_1(1) \left(-\frac{1}{2}\nabla_1^2 \right) \psi_1(1) d\tau_1 \int \psi_2(2)^2 \psi_3(3)^2 \dots \psi_p(p)^2 d\tau_2 d\tau_3 \dots d\tau_p + \int \psi_2(2) \left(-\frac{1}{2}\nabla_2^2 \right) \psi_2(2) d\tau_2 \int \psi_1(1)^2 \psi_3(3)^2 \dots \psi_p(p)^2 d\tau_1 d\tau_3 \dots d\tau_p &= \\ + \int \psi_3(3) \left(-\frac{1}{2}\nabla_3^2 \right) \psi_3(3) d\tau_3 \int \psi_1(1)^2 \psi_2(2)^2 \dots \psi_p(p)^2 d\tau_1 d\tau_2 \dots d\tau_p &= \\ = \int \psi_1(1) \left(-\frac{1}{2}\nabla_1^2 \right) \psi_1(1) d\tau_1 + \int \psi_2(2) \left(-\frac{1}{2}\nabla_2^2 \right) \psi_2(2) d\tau_2 + \dots + \int \psi_p(p) \left(-\frac{1}{2}\nabla_p^2 \right) \psi_p(p) d\tau_p = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \dots + \varepsilon_p \end{aligned}$$

If one uses that all atomic orbitals are normalized, E will become the sum of the energy (ε) of each molecular orbital. Since an electron is independent, the following series of formula are obtained.

$$\int \psi_1(1) \left(-\frac{1}{2} \nabla_1^2 \right) \psi_1(1) = \varepsilon_1$$

$$\int \psi_2(2) \left(-\frac{1}{2} \nabla_2^2 \right) \psi_2(2) = \varepsilon_2$$

$$\vdots$$

These correspond to solving next formulas.

$$\varepsilon_1 \psi_1(1) = \left(-\frac{1}{2} \nabla_1^2 \right) \psi_1(1)$$

$$\varepsilon_2 \psi_2(2) = \left(-\frac{1}{2} \nabla_2^2 \right) \psi_2(2)$$

$$\vdots$$

They have the same type; one only needs to solve any one of them.

$$\varepsilon \psi = h \psi \quad h \equiv -\frac{1}{2} \nabla^2 \quad 26$$

The above is a brief theory of the HMO method.

Schrödinger Equation of Free Electron and Hückel Molecular Orbital Method

The equation which gives the Hückel molecular orbitals was obtained as Eq.26. Let us examine the Schrödinger equation of a free electron. Since a free electron is an electron which moves in the non-potential space, the Hamiltonian of the system of n free electrons (H^{free}) corresponds to the equation excluding the potential terms in Eq.18. Namely,

$$H^{free} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 \quad 27$$

Since the potential does not exist and since electrons are independent, the procedures which give the Hückel molecular orbitals can apply to this case (24, 25 formulas). The resultant formula is Eq.26. That is, a Hückel molecular orbital method is equal to solving the Schrödinger equation of free electrons.

Then, what is the difference between the Hückel molecular orbital method and the free electron model? It is only the difference in a way to solve. The Hückel molecular orbital method presupposes that molecular orbitals are expressed by the linear combination of atomic orbitals (LCAO) and it determines the degree (coefficient) of each atomic orbital to the molecular orbital using the conditions of "standing wave."⁶⁾ Contrary to it, the free electron model solves the Schrödinger equation analytically. Since the difference is only that much, the both methods give the same conclusion. Conclusively, the HMO method obtains the relative kinetic energy of π electrons.

1. Ruedenberg, K.; Scheer, C. W., *J. Chem. Phys.*, **21**, 1565 (1953); *ibid.*, **21**, 1582 (1953).

2. Ichikawa, H.; Sakata, K., *Int. J. Quantum Chem.*, **87**, 135 (2002).
3. If the Born-Oppenheimer approximation is said simply, it is assumed that nuclei do not move since electron movement is so fast compared with nuclear movement. The usual molecular orbital method adopts this assumption. Concerning this, it is very important to know that in chemistry, even if the interatomic distance of benzene changes a little, it is still regarded as the same benzene, but it becomes a completely different system (a different molecule) in a molecular orbital theory.
4. This is called "independent electron model". There are the phenomena A and B, and if probabilities are expressed as P_A and P_B , the probability that A and B will happen simultaneously is denoted by $P_A \times P_B$. If each wave function is independent (independent electronic model), the whole wavefunction (the total wavefunctions) is denoted by those products.
5. It does not receive the potential (electrostatic repulsions) from other electrons, either.
6. Many textbooks claim "the coefficients are so decided to make the energy of the system lowest." But this is absolutely erroneous.