Lecture 4. Beyond the Hückel $\pi$-electron theory

4.1 Charge densities and bond orders

Charge density is an important parameter that is used widely to explain properties of molecules. An electron in an orbital $\psi_r = \sum_m c_{rm} \phi_m$ has density distribution $\sum_m c_{rm}^2 \phi_m^2$ (neglecting all overlap density terms such as $\phi_n \phi_m$). We can thus define the $\pi$-electron charge density $q_m$ at atom $m$ as follows:

$$q_m = \sum_r n_r c_{rm}^2, \quad (4.1)$$

where $c_{rm}$ is the coefficient of the basis orbitals $\phi_m$ in the molecular orbital $\psi_r$; the sum is over all the $\pi$ orbitals with $n_r$ electrons in each orbital ($n_r=0, 1, 2$). For the ground state of butadiene (see Fig. 3.2, lecture 3) $n_r=2$ for the two occupied bonding orbitals and $n_r=0$ for the antibonding orbitals, thus the charge densities at atoms $a$ and $b$ are

$$q_a = 2c_{1a}^2 + 2c_{2a}^2 = 2(0.37)^2 + 2(0.60)^2 = 1.00$$
$$q_b = 2c_{1b}^2 + 2c_{2b}^2 = 2(0.60)^2 + 2(0.37)^2 = 1.00 \quad (4.2)$$

By symmetry we know that $q_a=q_d$ and $q_b=q_c$. Thus the $\pi$-electron density is unity at each atom in butadiene. Examination of the orbitals of benzene will show that the same is true for all the carbon atoms in benzene.

To interpret many phenomena in molecules, and it is desirable to estimate the degree of double-bond character in the bond joining two atoms. By analogy with the charge density at an atom $m$, we can define a $\pi$-electron bond order between atoms $m$ and $n$ as follows:

$$p_{mn} = \sum_r n_r c_{rm} c_{rn} \quad (4.3)$$
For ethylene the two electrons in the bonding $\pi$ orbital, whose wavefunction gives a bond order of 1. For butadiene we have
\begin{align*}
p_{ab} &= 2c_{1a}c_{1b} + 2c_{2a}c_{2b} = 0.89, \quad (4.4) \\
p_{bc} &= 2c_{1b}c_{1c} + 2c_{2b}c_{2c} = 0.45. \quad (4.5)
\end{align*}
By symmetry $p_{ab}=p_{cd}$ so that according to Hückel theory the outer bonds in butadiene have much more double-bond character than the central bond but less than that in an isolated ethylene molecule. The conventional representation of butadiene as a single valence structure (CH$_2$=CH-CH=CH$_2$) is in close accord with the Hückel picture but fails to show that there is some double-bond character in the central bond.

![Fig. 4.1 A common representation of $\pi$–electron densities in ethylene, butadiene and benzene.](image)

4.2 Introduction of other atoms into Hückel theory

In the simple Hückel $\pi$-electron theory, it assumes that all the atomic orbitals in an LCAO expansion were similar and had the same energy, so only two parameters, $\alpha$ and $\beta$, are required. The simple Hückel $\pi$-electron theory provides reasonable description of alternant hydrocarbons that
consist of only carbon and hydrogen atoms. If we wish to treat molecules, such as CH$_2$=CH-CH=O, C$_6$H$_5$N=NC$_6$H$_5$ then we have to deal with atoms other than carbon atoms. One way to treat this situation is to express $\alpha_X$ and $\beta_{CX}$ of these other atoms (X) in terms of the values for benzene ($\alpha_C$ and $\beta_{CC}$),

$$\alpha_X = \alpha_C + h_X \beta_{CC} \quad (4.6)$$

and

$$\beta_{CX} = k_{CX} \beta_{CC}, \quad (4.7)$$

where $h_X$ and $k_{CX}$ are empirical parameters.

### 4.3 Extended Hückel $\pi$-electron theory

The Hückel $\pi$-electron theory includes only the $\pi$ orbitals and ignores completely the contribution due to $\sigma$ orbitals and hydrogen atoms. Attempts have been made to include the $\sigma$ and hydrogen orbitals have been developed for hydrocarbons and called all-electron theories. The basic features of the theory are that the atomic orbital basis consists of all the valence atomic orbitals and carbon 2s and 2p orbitals. It is more successful than the simple Hückel $\pi$-electron theory, but it has many limitations and is not very satisfactory for polar molecules. This is because like the Hückel $\pi$-electron theory, the extended Hückel $\pi$-electron theory is based on independent electron model, which ignores electron-electron interactions.

### 4.4 PPP method

The Pariser-Parr-Pople (PPP) method is similar to Hückel $\pi$-electron theory, except that it includes electron-electron repulsion. We can write

$$H_{PPP} = H_{Hückel} + \text{repulsion}. \quad (4.8)$$
4.5 *Ab-initio* Calculations

*Ab-initio* is a Latin term and means *from the beginning* or from *first-principle*. The first *ab-initio* calculation was probably the one on H\textsubscript{2} molecule by Heitler-London in 1927, but it was not attempted to any larger molecules until the development of electronic computers in the 1950s. The extensive production of *ab-initio* calculations began in 1960s with the widespread availability of programs for Self-Consistent Field (SCF) calculations on polyatomic molecules. Interestingly, the ever-increasing computer power allows us to understand molecular electronics that could ultimately produce even more powerful computers.

Hartree-Fock SCF method is one of widely used *ab initio* methods. To understand the theory, let us start with a two-electron molecule. The two electrons have orbitals (wavefunctions), \( \phi_a \) and \( \phi_b \), respectively. The wavefunction of the two electron system, \( \Psi(1,2) \), maybe written as \( \Psi(1,2) = \phi_a(1)\phi_b(2) \), where numbers 1 and 2 represent the two electrons. This wavefunction is used in the Hartree SCF, but it has a serious problem. Since the electron is a Fermion (spin is a half-integer), it has to obey the Pauli Exclusion Principle, which requires an antisymmetric wavefunction when electrons 1 and 2 exchange positions. Clearly the wavefunction given above is not antisymmetric. A simple way to construct an antisymmetric wavefunction for the many electron system is to use the Slater determinant, which takes the form of

\[
\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)],
\]

for the two electron system. The prefactor in the expression is required for normalization. It is easy to verify that \( \Psi(1,2) = -\Psi(2,1) \) as expected for antisymmetric wavefunction. Also we note that \( \Psi(1,1) = -\Psi(1,1) = 0 \), which means the two electrons cannot occupied the same state, a result of the Pauli exclusion principle. The above considerations ignore electron spin and the molecular orbitals \( \phi_a \) and \( \phi_b \) are functions of space only. It is rather straightforward to include it in the
wavefunction. Electrons can have either spin up (+1/2) or down (-1/2), which can be described by two spin functions, $\alpha$ and $\beta$, as follows

$$\begin{align*}
\alpha(\uparrow) &= 1, \quad \alpha(\downarrow) = 0 \\
\beta(\uparrow) &= 0, \quad \beta(\downarrow) = 1.
\end{align*}$$

(4.10)

The molecular orbitals now have both space and spin parts and take the forms of, $\alpha\phi_a$, $\beta\phi_a$, $\alpha\phi_b$ and $\beta\phi_b$, which are often referred to as spin-orbitals. If the two-electron system has only one molecular orbital, $\phi_a$, available, then the wavefunction is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{bmatrix} \alpha(1)\phi_a(1) & \beta(1)\phi_a(1) \\ \alpha(2)\phi_a(2) & \beta(2)\phi_a(2) \end{bmatrix},$$

(4.11)

which reflects the fact that the first electron takes spin up state, the second electron must take spin down, vice versa. The wavefunction given by 4.11 is often called restricted Hartree-Fock wavefunction, which is typically applied to close-shell molecules (electrons are paired). Unrestricted Hartree-Fock wavefunction does not require the two electrons to occupy the same orbitals (space-part of the wavefunction). For example,

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{bmatrix} \alpha(1)\phi_a(1) & \beta(1)\phi_a(1) \\ \alpha(2)\phi_a(2) & \beta(2)\phi_a(2) \end{bmatrix}$$

(4.12)

is an unrestricted Hartree-Fock wavefunction. For open-shell molecules, both restricted and unrestricted Hartree-Fock wavefunctions are used.

The Hamiltonian of the two-electron molecule is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V_{11} + V_{12} + \frac{1}{r_{12}} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}},$$

(4.13)

where $\hat{H}_1 = -\frac{1}{2}\nabla_1^2 + V_{11}$ and $\hat{H}_2 = -\frac{1}{2}\nabla_2^2 + V_{12}$ are the so-called core Hamiltonians of electrons 1 and 2, respectively; each consists of the kinetic energy of the electron and electrostatic
attraction between the electron and all the nuclei in the molecule. The energy of the wavefunction 4.9 or 4.11 is

\[ E = \iint \Psi(1,2)^* \hat{H} \Psi(1,2) dv_1 dv_2 \]

\[ = \frac{1}{2} \iint [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)](\hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}})[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] dv_1 dv_2. \]  

(4.14)

Note that spin-orbitals in Eqs. 4.11 and 4.12 are denoted as \( \psi_a(1) \equiv \alpha(1)\phi_a(1) \), \( \psi_b(1) \equiv \beta(1)\phi_b(1) \), \( \psi_a(2) \equiv \alpha(2)\phi_a(2) \) and \( \psi_b(2) \equiv \beta(2)\phi_b(2) \), respectively.

Expanding the above equation, we can express the energy as

\[ E = H_{aa} + H_{bb} + J_{ab} - K_{ab}, \]  

(4.15)

where

\[ H_{aa} = \psi_a(1)\hat{H}_1\psi_a(1) dv_1, \]  

(4.16)

\[ H_{bb} = \psi_b(2)\hat{H}_2\psi_b(2) dv_2 \]  

(4.17)

\[ J_{ab} = \iint \psi_a(1)\psi_b(2)\left(\frac{1}{r_{12}}\right)\psi_a(1)\psi_b(2) dv_1 dv_2 \]  

(4.18)

called Coulomb integral, representing electrostatic repulsion between the two electrons, and

\[ K_{ab} = \iint \psi_a(1)\psi_b(2)\left(\frac{1}{r_{12}}\right)\psi_a(2)\psi_b(1) dv_1 dv_2, \]  

(4.19)

called exchange integral, a purely quantum mechanical effect. For a n-electron molecule, we can generalize 4.15 as

\[ E = \sum_{r=a}^{n} H_{rr} + \frac{1}{2} \sum_{r=a}^{n} \sum_{s=a}^{n} (J_{rs} - K_{rs}). \]  

(4.20)

If we apply the variation theorem to the above equation and vary the molecular orbitals then there is, in principle, a minimum energy that can be reached and the wavefunction associated with this is called the Hatree-Fock wavefunction.
The mathematical procedure to obtain the Hatree-Fock wavefunction is summarized as follows. The first step is to express the molecular orbitals as linear combinations of a pre-defined set of one-electron function known as basis functions, similar to what we have seen in LCAO approximation. These basis functions are usually centered on the atomic nuclei and so bear some resemblance to atomic orbitals. However, the mathematical treatment is more general than this and any set of appropriately defined functions may be used. We define a molecular orbital as

$$\phi_i = \sum_\mu c_{i\mu} \chi_\mu$$  \hspace{1cm} (4.21)

where $c_{i\mu}$ are the molecular orbital expansion coefficients. The basis functions, $\chi_1, \chi_2, \ldots \chi_N$ are normalized. The roman subscripts are for different molecular orbitals and Greek subscripts are for different basis functions. Many \textit{ab initio} methods use Gaussian-type function as basis functions, which have the general form,

$$g(\alpha, x, y, z) = c x^n y^m z^l e^{-\alpha r^2}$$  \hspace{1cm} (4.22)

where $r^2 = x^2 + y^2 + z^2$, and $n$, $m$ and $l$ are integers. The constant $c$ can be determined by normalizing the function,

$$\int g^2 dv = 1.$$  \hspace{1cm} (4.23)

The next step is to determine the molecular orbital expansion coefficients, $c_{i\mu}$, which is achieved with the variation theorem in Hartree-Fock theory. The theorem states: \textbf{If the expectation value of the energy is calculated from an approximation solution of the Schrodinger equation, then this energy is always greater than the exact ground state energy from that Hamiltonian.} In other words, the energy of the exact wavefunction serves as a lower bound to the energies calculated by any other normalized approximated wavefunction. Thus the problem becomes one of finding the set of coefficients that minimize the energy of the resultant wavefunction. The variation
theorem leads to the following equations describing the molecular orbital expansion coefficients, $c_{\nu i}$, derived by Roothaan and Hall:

$$\sum_{\nu=1}^{N} (F_{\mu \nu} - \epsilon_{\nu} S_{\mu \nu}) c_{\nu i} = 0 \quad \mu = 1, 2, \ldots N \quad (4.24)$$

where $\epsilon_{\nu}$ is the energy of an electron in molecular orbital, $\chi_{\nu} F_{\mu \nu}$ is the called Fock matrix and it represents the average field of all the electrons on each orbital. For a close shell system it is given by

$$F_{\mu \nu} = H_{\mu \nu}^{\text{core}} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} P_{\lambda \sigma} \left[ (\mu \nu | \lambda \sigma) - \frac{1}{2} (\mu \lambda | \nu \sigma) \right] \quad (4.25)$$

where $H_{\mu \nu}^{\text{core}}$ is matrix representing the energy of a single electron in the field of the bare nuclei, and $P$ is the density matrix, given by

$$P_{\lambda \sigma} = 2 \sum_{\text{occupied}}^{\infty} c_{\mu i}^{*} c_{\nu i} \quad (4.26)$$

The coefficients are summed over the occupied orbitals only, and the factor two comes from the fact that each orbital holds two electrons. $S_{\mu \nu}$ is the overlap matrix, as we have seen already.

Both the Fock and overlap matrices depend on the molecular orbital expansion coefficients, so equation 8.16 must be solved iteratively. The procedure is called self-consistent field (SCF) method. $(\mu \nu | \lambda \sigma)$ in the above equation is a short notation of

$$\langle \mu \nu | \lambda \sigma \rangle = \int \int \phi_{\mu} (1) \phi_{\nu} (2) \frac{1}{r_{12}} \phi_{\lambda} (1) \phi_{\sigma} (2) dv_{1} dv_{2}, \quad (4.27)$$

which represents two electron repulsion. Under Hartree-Fock treatment, each electron sees all of the other electrons as an average distribution, so the instantaneous electron-electron interaction or correlation is neglected. For example, the Hartree-Fock wavefunction for the ground state of H$_2$ gives a probability density of one electron which is independent of the position of the other.
electron. In reality, if the first electron is near one nucleus then there should be a greater chance of finding the second electron near the other nucleus; that is, the positions of the two electrons should be correlated. Higher level theories, such as Density Functional Theory, have been developed to include the electron-electron correlation.

4.6 Density Functional Theory (DFT)

The DFT approach is based on a strategy of modeling electron correlation via general functionals of the electron density. A functional is a function of a function. Such methods owe their origins to the Hohenberg-Kohn theorem, which demonstrated the existence of a unique functional which determines the ground state energy and density exactly. The theorem itself does not provide the form of the functional. Following the work by Kohn and Sham, the ground state energy of a molecular system (excluding the nuclear-nuclear repulsions) can be written as a unique functional of the ground state density, \( n(\mathbf{r}) \),

\[
E[n(\mathbf{r})] = T[n(\mathbf{r})] - \sum_{\mathbf{R}} Z e \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}|} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}^* \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}^*|} + E_{\text{XC}}[n(\mathbf{r})], \tag{4.28}
\]

In the expression, \( T \) is the kinetic energy term, the second term describes the potential energy of the electron-nuclear attraction and the third term is the repulsion between electrons. The last term, \( E_{\text{XC}} \), is the so-called the exchange-correlation term, which includes: the exchange energy arising from the anti-symmetry of the quantum mechanical wavefunction and dynamic correlation in the motions of the individual electrons. Hohenberg and Kohn demonstrated that \( E_{\text{XC}} \) is determined entirely by the electron density. Practical implementation of DFT requires good approximation of \( E_{\text{XC}} \). Many approximations for \( E_{\text{XC}} \) have been developed. Once the functional of \( E_{\text{XC}} \) is obtained, one can determine the ground state energy and electron density by minimizing the expression 4.28.
Both the HF and DFT methods have been used to compute electron transport through molecules, but they suffer a similar problem – the inherent inaccuracy in computing the LUMO energy and wavefunctions. The errors are, however, different. For example, HF method overestimates the HOMO-LUMO gap since the LUMO energy is too high, while DFT underestimates the gap. So it is clear that both methods give better results if a process is dominated by the HOMO of the molecule than that dominated by the LUMO.

**Homework**

4.1 Determine the charge density and bond order of benzene.

4.2 Derive Eq. 4.15 from Eq. 4.14.