The Method of Solving Constrained Schrödinger Equation

Solving the constrained Schrödinger equation is a strong method that has no theoretical defects. According to one's idea, the method can apply to the analyses of a wide variety of chemical phenomena.

Electronic Structure and Chemical Property of Molecule

An important theme of a theoretical study of a chemical phenomenon is to seek the relationship between the electronic structure of a molecule and its chemical property. Particularly it can be said that most of theoretical studies of organic-chemical properties of a system by quantum chemistry are in this region.

Let us consider the problem of resonance/conjugation as a concrete instance. It is theoretically impossible by the molecular orbital methods to know how much the conjugation energy between double bonds of butadiene is. Someone may say "What if the energies of structures **A** and **B** on figure 1 are compared?" But this method is completely erroneous.
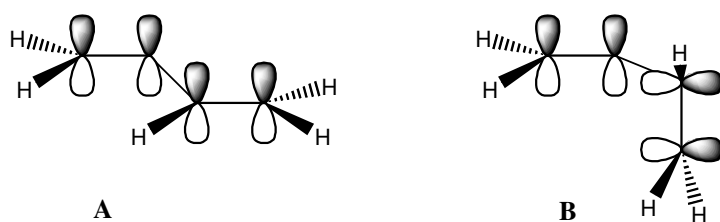

Fig.1. Chemical expression of conjugate and non-conjugate structures of butadiene

Although chemically Structures **A** and **B** are the same as butadiene, they are completely different systems in the molecular orbital theories which is based on the Born-Oppenheimer approximation. Even if the positions of the nuclei are changes in a very small quantity, the system is different from the former one. Namely, chemically same structures are not always the same in molecular orbital theories.
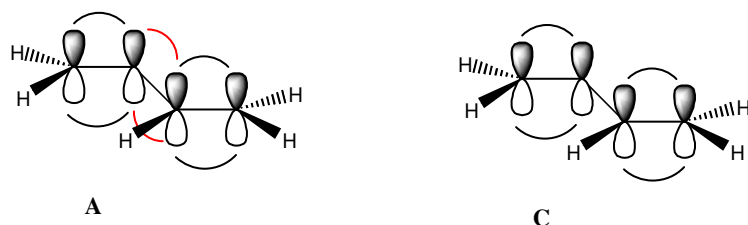

Fig.2. The true conjugate and non-conjugate structures of butadiene.

The desired electronic structure of non-conjugated structure of butadiene is the one in which only π electrons do not exist between on C_2 and C3 of the same geometry as shown in figure 2. If one

obtains the total energy in this state (**C**), it is possible to determine the energy of decline of energy by conjugation. The vertical resonance energy corresponds to this decline energy. It is a by-talk, but the lowest total energy won't be by electronic structure of **C**. The geometry changes to give the lowest total energy. The energy difference of this structure and the original structure (**A**) is the adiabatic resonance energy.

To find the resonance energy of benzene, one may determine the energy difference of the total energies between usual conjugate benzene and the one of the electronic structure which has no π electronic delocalization (**E** of Fig. 3), without changing the locations of the atomic nuclei. Then, one may know the cause of the resonance phenomenon by analyzing changes in partitioned energies of the total energy.
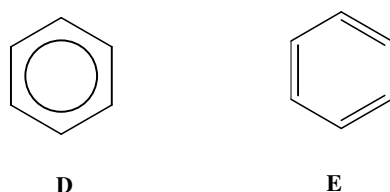

D   **E**

Fig.3. Conjugate benzene and non-conjugate benzene.

Now, the problem comes to be how to obtain the wavefunction of structure **C**. In fact, this is equivalent to solve the constrained Schrödinger equation in terms of quantum mechanics. If it is rewritten in molecular orbital theories, it will be the problem of solving the constrained Hartree-Fock equation.

The Constrained Hartree-Fock Equation

The Schrödinger equation of the stationary state is shown as $H\Psi=E\Psi$. As this formula shows, the wavefunction Ψ depends on the Hamilton operator H. If one wants to get the wavefunction which gives a specific electronic structure, the simple procedure is that H should be so changed that the desired electronic structure may be given. If "change" is expressed as λ, the equation is $(H + \lambda)\Psi=E\Psi$. This is called the constrained Schrödinger equation. Since this equation is also an eigenvalue problem, <u>the obtained wavefunction is that of the stationary state</u>.

I will show the way to get the wavefunction which has no conjugation between double bonds by using the Hartree-Fock method. H will be replaced by F in the Hartree-Fock equation, so the constrained Hartree-Fock equation is $(F+\lambda)\Psi=E\Psi$. λ is the operator which makes π electrons between double bond return to their original π bonds. More concretely, the problem is to solve Eq. 1.

$$\begin{cases} P_{rs} = 2\sum_{i}^{occ} C_r^{*i} C_s^i = p_k \\ (F + \lambda)C = \varepsilon' SC \end{cases} \qquad 1$$

Here, F, C, and S are matrices of the Fock operator, coefficients of molecular orbitals, and overlap integrals. Matrix λ is a parameter that controls the distribution of π electrons. Since the π bond order between atomic orbitals r and s is a function of the element λ_{rs} of λ, by choosing it as it gives $P_{rs}=0$ ($p_k=0$), one can sweep out the π electrons between r and s. The detail may be shown in the literature.[1] On the other hand, ε' is the molecular orbital energy of the wavefunction which received the constrained condition, so it is not possible to use. Necessary orbital energy (ε) is the expectation value of the constrained wavefunction to F, not to ($F+\lambda$), and is obtained as Eq. 2.[1]

$$\varepsilon_i = \varepsilon_1' - \sum_{r,s} C_{ir}\lambda_{rs}C_{is} \qquad 2$$

How Molecular Orbitals Change by Imposition of Constraint

Let us see the changes in molecule orbitals by imposing constraint on the usual wave function. Table 1 shows the coefficients of the resultant molecule orbitals for π electrons by imposing constraint that makes the distribution of p electrons on C_2-C_3 zero in butadiene. This is quoted from Literature 1. The basis function is ST-3G.

Table 1. Changes of Coefficients of π Molecular Orbitals in Butadiene

C_1-C_2-C_3-C_4

ε^a	C_1	C_2	C_3	C_4
normal				
-0.39908	0.37137	0.47496	0.47496	0.37137
-0.27625	0.52078	0.40400	-0.40400	-0.52078
0.25602	0.62831	-0.47530	-0.47530	0.62831
0.42034	-0.51252	0.69854	-0.69854	0.51252
constrained				
-0.30325	0.40518	0.44825	0.44825	0.40518
-0.27995	0.48660	0.44825	-0.44825	-0.48660
0.26202	0.60706	-0.50057	-0.50057	0.60706
0.41559	-0.54507	0.67100	-0.67100	0.54507

[a] Corrected orbital energy   (see Eq.3).

Now, let us examine what happens to the bond order of C_2-C_3. Concerning the molecule orbitals without constraint is,

$$2 \times 0.47496 \times 0.47496 + 2 \times 0.4040 \times (-0.40400) = 0.12474$$

On the other hand, that of the constrained molecular orbitals is,

$$2 \times 0.44825 \times 0.44825 + 2 \times 0.44825 \times (-0.44825) = 0$$

See the bond order turns out zero!

Application of Constrained Hartree-Fock Method

This method seems to give a strong means to solve a variety of chemical phenomena. First of all, the application to the problem of resonance/conjugation may be brought forth.

Though mentioned, it is important to understand the concepts of "vertical" and "adiabatic". See Fig. 3. "Vertical" means that the locations of nuclei of the system are not changed at all, i.e., the relationship between **D** and **E** is vertical. "Adiabatic" is a thermodynamical term that means there is no exchange of heat between the considered system and its outside (but the geometry of the system may change to give the lowest energy).

Benzene has its optimized (lowest energy) geometry according to the electron distribution. Namely, the geometries of D and E are different and the difference of the total energies between optimized D and E is the adiabatic resonance energy. This may correspond to the observed resonance energy. However, if one seeks the role of π electrons, one must use the vertical resonance energy. For the adiabatic resonance energy includes the influence of the nuclear positions. The analysis on this line has been carried out already.[2]

Similarly, if one wants to determine the cause of the conjugation of nitrobenzene and aniline, one may analyze the energy increase when flows of π electrons between benzene and its substituents is stopped. The changed of the total energy can rationally be divided into the kinetic energy (T) one-electronic potential energy (V_{eN}), two-electronic potential energy (V_{ee}) and the repulsion energy between nuclei (V_{NN}). These energies except V_{NN} can also be divided into contribution of σ electrons and contribution of π electrons. Thus, it is possible to analyze the chemical phenomenon from the very fundamental laws of physics.

1. Ichikawa, H; Kagawa, H., Inter. J. Quantum Chem. 1994, 52, 575-591.
2. Ichikawa, H.; Kagawa, H., Bull. Chem. Soc. Jpn. 1997, 70, 61-70.