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Use of Propagators in the Hückel Model

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The electronic structures of molecules composed of identical atoms are investigated in terms of propagators under the Hückel approximation. General rules to get propagators for systems under considerations are presented. Then some physical quantities (the charge densities, the bond orders and the total energies) are obtained by making the analysis of the propagators. Expressions for the mutual polarizabilities are also exactly derived. Some discussions about the approximate natures of current results are made.

Quantum mechanical calculations are usually carried out as follows: First, the Shrödinger equation for a system under consideration is solved under a certain approximation, and then the observed quantities are estimated as the expectation values of the corresponding operators by the use of the wave function. It has been pointed out by Coulson and Longuet-Higgins[1] that even in the quantum chemical calculations the procedure mentioned above is not always necessary. They stressed that once the Hückel determinant is given, any physical quantity is directly calculated without solving the secular equation, by making the analysis of this determinant:

Let

$$\Delta(\omega) \equiv \begin{vmatrix} \alpha_1-\omega & \beta_{12} & \beta_{13} & \cdots & \beta_{1n} \\ \beta_{21} & \alpha_2-\omega & \beta_{23} & \cdots & \beta_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \cdots & \alpha_n-\omega \end{vmatrix} \tag{1}$$

where α_i, β_{ik}, and ω are the coulomb integral, resonance integral and energy parameter respectively. Then the bond order q_{rs} (its diagonal term is the charge density) and the total energy E are obtained as

$$q_{rs} = \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z \frac{\Delta_{rs}(z)}{\Delta(z)}, \tag{2}$$

$$E = \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z\, z\frac{\partial}{\partial z}\ln \Delta(z). \tag{3}$$

where $\Delta_{rs}(z)$ is the (r,s) cofactor of $\Delta(z)$ and integration with respect to the complex variable z is performed along the so-called Coulson contour shown in Fig. 1. Integration is assumed to include the spin summation.

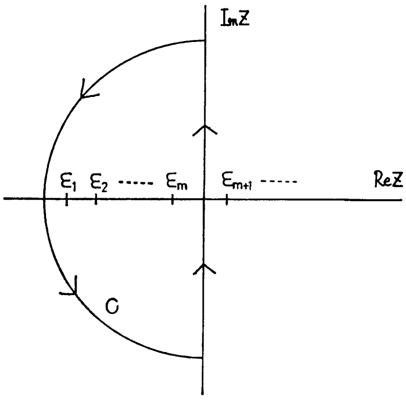

Fig. 1. Coulson contour: ε_1—ε_m are occupied energies and $\varepsilon_{m+1}\cdots$ are unoccupied.

Coulson and Longuet-Higgins have also given similar expressions for mutual polarizabilities. It is needless to say that for these quantities the expressions with LCAO coefficients are commonly used, and that the use of these approximate expressions is only for the convienience of numerical calculations.

In the present work, a theory with propagator is developed in the Hückel model. This is related very closely to the idea of Coulson and Longuet-Higgins. The processes of constructing propagators, however, make clear the physical content of the Hückel model.

Propagator

The Green's function (propagator), corresponding to the linear Hermitian time-independent differential operator $L(r)$ and the complex variable z, is defined as the solution of the equation

$$(z-L(r))G(r,r';z) = \delta(r-r'), \tag{4}$$

subject to certain boundary conditions on the surface of the domain of r and r'. Equation 4 can be considered as the coordinate representation of the operator equation

$$(z-L)G = 1. \tag{5}$$

If $\{|n\rangle\}$ is the complete orthonormal set of the operator L, *i.e.*,

$$L|n\rangle = \lambda_n|n\rangle, \tag{6}$$

$$\langle n|m\rangle = \delta_{nm}, \tag{7}$$

$$\sum_n |n\rangle\langle n| = 1, \tag{8}$$

then one can write

$$G = (z-L)^{-1} = \sum_n \frac{|n\rangle\langle n|}{z-\lambda_n}. \tag{9}$$

$G(r,r';z)$ in Eq. 4 may be regarded as the (r,r') matrix element of the operator G.

Hückel Model. The Hückel Hamiltonian (the tight-binding approximation in the solid state physics) is written as

$$H = \sum_s |s\rangle\varepsilon_s\langle s| + \sum_{st}{}' |s\rangle v_{st}\langle t|, \tag{10}$$

where s and t are site indices. Keeping in mind that we are dealing with molecules which consist of the same kind of atoms, we put $\varepsilon_s=0$, $v_{st}=v$ and the second summation in Eq. 10 is carried out as usual only for the nearest neighbors. Thus the Hamiltonian becomes simply

$$H = v\sum_{st}{}' |s\rangle\langle t|. \tag{11}$$

In order to perform the forthcoming analysis in the present work, we investigate the diatomic molecule a—b in Fig. 2a in terms of propagators. The diagonal term of the Green's function in the zeroth-order approximation, $G_0(a,a;\ z)$ is simply obtained from Eq. 9 and the first term of Eq. 10 as

$$G_0(a,a;z) = \sum_s \frac{\langle a|s\rangle\langle s|a\rangle}{z-\varepsilon_s} = \frac{1}{z}, \quad (\varepsilon_s=0), \tag{12}$$

where the completeness condition (8) has been used.

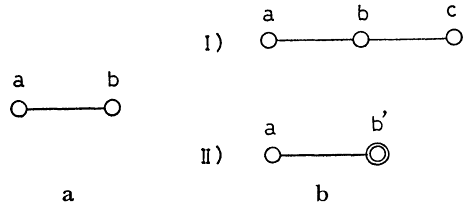

Fig. 2. Schematic diagrams of molecules. a: Diatomic molecule, b: triatomic molecule.

Now we consider the exact propagator $G(a,a;\ z)$ fully dressed by interactions:

$$G(a,a) = G_0(a,a) + G_0(a,a)vG_0(b,b)vG_0(a,a) + G_0(a,a)vG_0(b,b)vG_0(a,a)vG_0(b,b)vG_0(a,a) + \cdots, \tag{13}$$

where the first term is the bare propagator, the second includes the interaction twice, the third four times and so on. Equation 13 is rewritten as

$$\begin{aligned} G(a,a) &= G_0(a,a) + G_0(a,a)vG_0(b,b)v[G_0(a,a) \\ &\quad + C_0(a,a)vG_0(b,b)vG_0(a,a) + \cdots \\ &= G_0(a,a) + G_0(a,a)vG_0(b,b)vG(a,a) \\ &= [G_0(a,a)^{-1} - vG_0(b,b)v]^{-1}. \end{aligned} \tag{14}$$

The last expression is the Dyson equation for our simplest case. Substituting Eq. 12 into Eq. 14, we obtain

$$G(a,a;z) = z/(z^2-v^2). \tag{15}$$

It is obvious that the poles of Eq. 15, *i.e.*, the roots of $z^2-v^2=0$, give us the Hückel orbital energies.

The charge density q_a at site a, the bond order q_{ab} and the total energy E are obtained with the propagators as,

$$q_a = \frac{1}{2\pi i}\int_C dz\, G(a,a;z), \tag{16}$$

$$\begin{aligned} q_{ab} &= \frac{1}{2\pi i}\int_C dz\, G(a,b;z) \\ &= \frac{1}{2\pi i}\int_C dz\, G(a,a;z)vG_0(b,b;z), \end{aligned} \tag{17}$$

$$E = \frac{1}{2\pi i}\sum_a\int_C dz\, zG(a,a;z), \tag{18}$$

where the integration is made along the Coulson contour and is assumed to include the spin summation. Thus we can easily get the well-known results, $q_a=q_{ab}=1$ and $E=2v$.

General Rules to Get Propagators

We generalize the method in the previous section to the arbitrary finite network. This procedure is called the renormalization perturbation expansion which has been investigated by Anderson[2,3] for the infinite lattice. Generalization will be done step by step in the following.

End Point Propagator. Consider the edge atom a in the triatomic molecule shown in Fig. 2b. If we replace b and c in (I) by b' as in (II), the propagator $G(a,a)$ can be immediately obtained as has been done in the previous section:

$$G(a,a) = [G_0(a,a)^{-1} - vG(b',b')v]^{-1} \tag{19}$$

in which $G(b',b')$ is the propagator dressed only by the interaction between b and c, since the interaction between a and b is alreadly taken into account, that is,

$$G(b',b') = [G_0(b,b)^{-1} - vG_0(c,c)v]^{-1}. \tag{20}$$

In this sense, $G(b',b')$ is rewritten as $G(b,b[a])$ indicating that the effect of site a should be excluded. We rewrite Eq. 19 as

$$G(a,a) = [G_0(a,a)^{-1} - vG(b,b[a])v]^{-1}. \tag{21}$$

This relation is itself a generalized expression for an arbitrary chain molecule, as seen from Fig. 3.

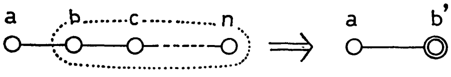

Fig. 3. Renormalization of the propagator of a linear molecule.

The off-diagonal term $G(a,c)$ in Fig. 2b is given by

$$G(a,c) = G(a,a)vG(b,b[a])vG(c,c[a,b]), \tag{22}$$

where it is apparent that $G(c,c[a,b])=G_0(c,c)$. Generalization of Eq. 22 to an arbitrary path is straightforward.

Branching Point Propagator. Consider the propagator $G(b,b)$ at site b in Fig. 2b. Since we have two paths arrived at site b, $G(b,b)$ can be expressed as

$$G(b,b) = [G_0(b,b)^{-1} - vG_0(a,a)v - vG_0(c,c)v]^{-1}. \tag{23}$$

This result is easily generalized to the branching point at which many paths end as shown in Fig. 4:

$$G(b,b) = [G_0(b,b)^{-1} - \sum_i vG(a_i,a_i[b])v]^{-1}. \tag{24}$$

It should be noted that there is no interactions among branches in this case.

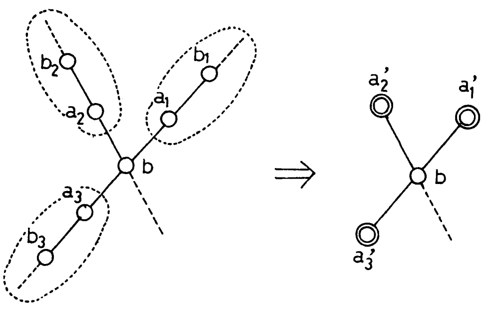

Fig. 4. Schematic diagram of a branched molecule and renormalization of its propagator.

Ring Propagator. We consider a ring of three members as shown in Fig. 5a. In order to obtain $G(a,a)$, we first follow the path $a \to b \to c \to a$. If there were no interaction between a and c, we would simply have

$$G(a,a) = [G_0(a,a)^{-1} - vG(b,b[a])v]^{-1}. \tag{25}$$

Actually we need a new term $G(b,c[a])$ to enclose the loop, and obtain

$$G(a,a) = [G_0(a,a)^{-1} - vG(b,b[a])v - vG(b,c[a])v]^{-1}. \tag{26}$$

This procedure should be performed also along the path $a \to c \to b \to a$. Thus we obtain

$$\begin{aligned} G(a,a) = [G_0(a,a)^{-1} &- vG(b,b[a])v - vG(b,c[a])v \\ &- vG(c,c[a])v - vG(c,b[a])v]^{-1}, \end{aligned} \tag{27}$$

where for example

$$G(b,c[a]) = G(b,b[a])vG(c,c[a,b]) \tag{28}$$

is the off-diagonal term of the b—c subsystem.

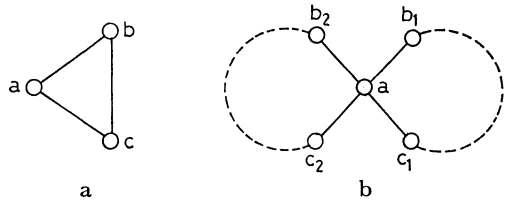

Fig. 5. Schematic diagrams of ring molecules. a: Triatomic ring molecule, b: two rings joinning at site a.

The physical meanings of Eq. 27 are as follows: The propagator $G(a,a)$ is the sum of the quantum mechanical probability amplitude for all the possible ways the electron can propagate in a ring from site a to itself interacting with various sites on the way. The first term is the free propagator given by Eq. 12. The second term represents the process that the electron interacts with site b, propagates many times in the b—c subsystem and finally returns to site a through site b. This process is schematically shown in Fig. 6a. The third term represents a new process due to the ring character. The electron propagates in the b—c subsystem as before, but comes back to site a through site c. This process is also shown in Fig. 6b. The last two terms are the counterparts of the above processes.

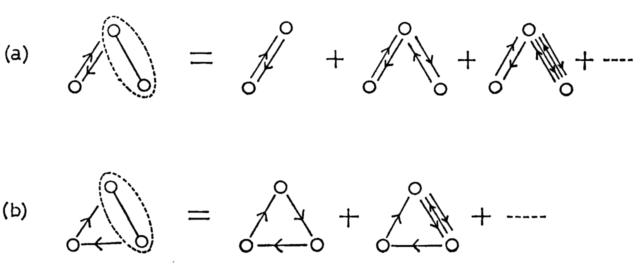

Fig. 6. Renormalization of the interactions between a and b—c subsystem.

The generalization to a more complicated ring shown in Fig. 5b is straightforward. The three types of the processes mentioned above suffice to obtain the propagator for an arbitrary network.

Illustrative Examples

Triatomic Linear Molecule. Substituting Eqs. 12 and 15 into Eqs. 21 and 23, we have

$$G(a,a;z) = G(c,c;z) = \frac{z^2 - v^2}{z^3 - 2zv^2}, \tag{29}$$

$$G(b,b;z) = \frac{z^2}{z^3 - 2zv^2}, \tag{30}$$

The off-diagonal elements are also easily estimated as

$$G(a,b;z) = \frac{zv}{z^3 - 2zv^2}, \tag{31}$$

$$G(a,c;z) = \frac{v^2}{z^3 - 2zv^2}. \tag{32}$$

The Hückel orbital energies are obtained from the poles of these propagators, as $z = \pm\sqrt{2}v$, 0. We can estimate the bond order matrix and the total energy, using Eqs. 17 and 18, respectively, as

$$q = \begin{pmatrix} 1 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 1 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 1 \end{pmatrix}, \tag{33}$$

$$E = 2\sqrt{2}v. \tag{34}$$

It is noted that in this case the Coulson contour has to include the origin.

Triatomic Ring Molecule (Positive Ion). We consider only the case of positive ion for the sake of simplicity. Using Eqs. 12 and 20 in Eq. 27, we get

$$G(a,a;z) = \frac{z^2 - v^2}{z^3 - 3zv^2 - 2v^2}. \tag{35}$$

The off-diagonal element, $G(a,b)$, can be calculated by taking into account two paths, that is, $a \to b$ and $a \to c \to b$:

$$\begin{aligned} G(a,b;z) &= G(a,a)vG(b,b[a]) + G(a,a)vG(c,c[a])vG(b,b[a,c]) \\ &= \frac{zv + v^2}{z^3 - 3zv^2 - 2v^2}. \end{aligned} \tag{36}$$

The poles of these propagators determine the Hückel orbital energies as $z = 2v$, $-v$(doubly degenerate). If we consider the positive ion case, the contour goes around only the pole, $z = 2v$. Then we obtain the bond order and total energy as

$$q_{ij} = 2/3 \text{ for all } i,j, \qquad E = 4v. \tag{37}$$

Chain Molecule; Recurrence Formulae. We have seen in the preceding treatment that any kind of matrix element of the propagator can be constructed from the diagonal elements at the edge of the chain molecule. It is useful at this stage to provide a simple way to obtain them. In this section, G_N denotes the diagonal matrix element at the edge of the chain molecule of N atoms.

It is a simple task to estimate G_N as a continued fraction, *i.e.*,

$$\begin{aligned} G_N(z)^{-1} &= z - \cfrac{1}{z - \cfrac{1}{z - \cfrac{1}{z - \cdots}}} \\ &\equiv z - \frac{1}{z\,+}\,\frac{1}{z\,-}\,\frac{1}{z\,+}\cdots, \end{aligned} \tag{38}$$

where we put $v = 1$. If there is a more general continued fraction

$$S_N = b_1 + \frac{1}{b_2\,+}\,\frac{1}{b_3\,+}\cdots\frac{1}{+\,b_N}, \tag{39}$$

this is expressed as

$$S_N = P_N/Q_N, \tag{40}$$

where, for P_N and Q_N, the following recurrence relations hold:

$$\begin{aligned} P_N &= b_N P_{N-1} + P_{N-2}, \\ Q_N &= b_N Q_{N-1} + Q_{N-2}, \end{aligned} \tag{41}$$

with

$$\begin{aligned} P_0 &= 1, \quad P_{-1} = 0, \\ Q_0 &= 0, \quad Q_{-1} = 1. \end{aligned} \tag{42}$$

In the case of Eq. 38, observing that $b_N = (-1)^{N-1}z$, we can easily calculate the first few series for P_N and Q_N. Then we use the mathematical induction to obtain the general formula and get

$$\begin{aligned} P_N &= \varepsilon_N p_N \\ &= \varepsilon_N \left[\sum_k (-1)^k \binom{N-k}{k} z^{N-2k} \right] \end{aligned} \tag{43}$$

where ε_N is the phase factor defined by

$$\varepsilon_N = \begin{cases} (-1)^{(N-1)/2} & \text{for odd } N, \\ (-1)^{N/2} & \text{for even } N. \end{cases} \tag{44}$$

We also obtain

$$Q_N = (-1)^{N-1} P_{N-1}. \tag{45}$$

Combining Eqs. 43 and 45, we have

$$G_N(z)^{-1} = p_N(z)/p_{N-1}(z). \tag{46}$$

It is obvious that p_N is nothing but the Hückel determinant. We list up some p_N in the following:

$$\begin{aligned} p_1 &= z, \\ p_2 &= z^2 - 1, \\ p_3 &= z^3 - 2z, \\ p_4 &= z^4 - 3z^2 + 1, \\ p_5 &= z^5 - 4z^3 + 3z, \\ p_6 &= z^6 - 5z^4 + 6z^2 - 1. \end{aligned} \tag{47}$$

Perturbation Theory

In order to express the various polarizabilities in terms of propagators, we provide an alternative method in the perturbation expansion of the propagator. In the matrix notation,

$$\begin{aligned} \boldsymbol{G}(z) &= \boldsymbol{G}_0(z) + \boldsymbol{G}_0(z)\boldsymbol{v}\boldsymbol{G}_0(z) + \boldsymbol{G}_0(z)\boldsymbol{v}\boldsymbol{G}_0(z)\boldsymbol{v}\boldsymbol{G}_0(z) + \cdots \\ &= \boldsymbol{G}_0(z) + \boldsymbol{G}_0(z)\boldsymbol{T}(z)\boldsymbol{G}_0(z), \end{aligned} \tag{48}$$

where

$$\begin{aligned} \boldsymbol{T}(z) &= \boldsymbol{v} + \boldsymbol{v}\boldsymbol{G}_0(z)\boldsymbol{v} + \boldsymbol{v}\boldsymbol{G}_0(z)\boldsymbol{v}\boldsymbol{G}_0(z)\boldsymbol{v} + \cdots \\ &= \boldsymbol{v}[1 - \boldsymbol{G}_0(z)\boldsymbol{v}]^{-1}. \end{aligned} \tag{49}$$

In the above, $\boldsymbol{v}$ is the perturbation whose magnitude is arbitrary in our treatment, so that the full propagators previously obtained are rewritten $\boldsymbol{G}_0$ in this section.

The Perturbation of the Coulomb Potential at Site m. In this case, the perturbation becomes

$$v_{ij} = \begin{cases} \varepsilon_m & \text{for } i = j = m, \\ 0 & \text{for others,} \end{cases} \tag{50}$$

so that $\boldsymbol{T}(z)$ is given by

$$T(i,j;\, z) = \begin{cases} \varepsilon_m/(1 - G_0(m,\, m;\, z)\varepsilon_m) & \text{for } i = j = m \\ 0 & \text{for others.} \end{cases} \tag{51}$$

Substituting this into Eq. 48, we get

$$G(a,a) = G_0(a,a) + G_0(a,m)T(m,m)G_0(m,a). \tag{52}$$

Hence, the change in charge density at site a becomes

$$\begin{aligned} \delta q_a &= \frac{1}{2\pi i}\int_C \mathrm{d}z(G(a,a;\, z) - G_0(a,a;\, z)) \\ &= \varepsilon_m \frac{1}{2\pi i}\int_C \mathrm{d}z|G_0(a,m;\, z)|^2/(1 - G_0(m,m;\, z)\varepsilon_m) \\ &\equiv \varepsilon_m \cdot \Pi_{a:m}, \end{aligned} \tag{53}$$

where the last equation defines the atom-atom polarizability. Remember that we have assumed the integration includes the spin summation. If we neglect $G_0(m,m)\varepsilon_m$ as a small quantity compared to unity, Eq. 53 reproduces the result of the elementary perturbation theory:

$$\Pi^0_{a:m} = \frac{1}{2\pi i}\int_C \mathrm{d}z|G_0(a,m;\, z)|^2. \tag{54}$$

It should be noted that in our exact expression, ε_m is replaced by the effective interaction

$$\begin{aligned} \tilde{\varepsilon}_m &= T(m,m;\, z) \\ &= \varepsilon_m/(1 - G_0(m,m)\varepsilon_m). \end{aligned} \tag{55}$$

Next, evaluating the off-diagonal element of Eq. 48, we get

$$G(a,b) = G_0(a,b) + G_0(a,m)T(m,m)G_0(m,b), \tag{56}$$

from which the change in bond order is derived;

$$\begin{aligned} \delta q_{ab} &= \frac{1}{2\pi i}\int_C \mathrm{d}z(G(a,b;\, z) - G_0(a,b;\, z)) \\ &= \varepsilon_m \frac{1}{2\pi i}\int_C \mathrm{d}z G_0(a,m;\, z)G_0(m,b;\, z)/(1 - G_0(m,m;\, z)\varepsilon_m) \\ &\equiv \varepsilon_m \cdot \Pi_{ab:m}, \end{aligned} \tag{57}$$

where the last equation defines the bond-atom polarizability. If we replace $\tilde{\varepsilon}_m$ by ε_m as before, we get

$$\Pi^0_{ab:m} = \frac{1}{2\pi i}\int_C \mathrm{d}z\, G_0(a,\, m;\, z)G_0(m,b;\, z). \tag{58}$$

*The Perturbation of the Resonance Energy at the Bond (*m,n*).* Here we consider the case that

$$v_{ij} = \begin{cases} v & \text{for } (i,j) = (n,m) \text{ or } (m,n) \\ 0 & \text{otherwise.} \end{cases} \tag{59}$$

In this case, as seen from Eq. 49, non-vanishing part of $\boldsymbol{T}$ becomes a 2×2 matrix and its explicit form may be calculated as follows:

$$\begin{aligned} \boldsymbol{T}(z) &= (\boldsymbol{v}^{-1} - \boldsymbol{G}_0(z))^{-1} \\ &= \begin{pmatrix} -G_0(m,m) & 1/v - G_0(m,n) \\ 1/v - G_0(n,m) & -G_0(n,n) \end{pmatrix}^{-1} \\ &= \frac{\tilde{v}}{1 - \tilde{v}^2 G_0(m,m)G_0(n,n)} \begin{pmatrix} \tilde{v}G_0(n,n) & 1 \\ 1 & \tilde{v}G_0(m,m) \end{pmatrix}, \end{aligned} \tag{60}$$

where

$$\tilde{v}(z) = v/(1 - G_0(m,n)v). \tag{61}$$

Substituting Eq. 60 into Eq. 48, we obtain

$$\begin{aligned} G(a,a) &= G_0(a,a) + \sum_{k,l}^{m,n} G_0(a,k)T(k,l)G_0(l,a) \\ &= G_0(a,a) + \frac{\tilde{v}}{1 - \tilde{v}^2 G_0(m,m)G_0(n,n)} \\ &\quad \times [G_0(a,m)\tilde{v}G_0(n,n)G_0(m,a) + G_0(a,m)G_0(n,a) \\ &\quad + G_0(a,n)G_0(m,a) + G_0(a,n)\tilde{v}G_0(m,m)G_0(n,a)]. \end{aligned} \tag{62}$$

Thus, the change in the charge density at site a is

$$\begin{aligned}\delta q_a &= v\frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z\frac{1}{(1-vG_0(m,n))(1-\tilde{v}^2G_0(m,m)G_0(n,n))}\\ &\quad\times[G_0(a,m)\tilde{v}G_0(n,n)G_0(m,a)+G_0(a,m)G_0(n,a)\\ &\quad+G_0(a,n)G_0(m,a)+G_0(a,n)\tilde{v}G_0(m,m)G_0(n,a)]\\ &\equiv v\Pi_{a:mn},\end{aligned} \tag{63}$$

where the final equation defines the atom-bond polarizability.

Comparing Eq. 57 with Eq. 63, we see

$$\Pi_{a:mn} \neq 2\Pi_{mn:a} \tag{64}$$

which is aginst the result of Coulson and Longuet-Higgins.[1] However, if we neglect $vG_0(m,n)$ and $vG_0(n,m)$ as very small quantities compared to unity, the relation $\Pi_{a:mn}=2\Pi_{mn:a}$ approximately holds. (We assume propagators here are real).

Next, by evaluating $G(a,b)$, the similar calculation yields the bond-bond polarizability as

$$\begin{aligned}\Pi_{ab:mn} &= \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z\frac{1}{(1-vG_0(m,n))(1-\tilde{v}^2G_0(m,m)G_0(n,n))}\\ &\quad\times[G_0(a,m)\tilde{v}G_0(n,n)G_0(m,b)+G_0(a,m)G_0(n,b)\\ &\quad+G_0(a,n)G_0(m,b)+G_0(a,n)\tilde{v}G_0(m,m)G_0(n,b)]\\ &\cong \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z(G_0(a,m)G_0(n,b)+G_0(a,n)G_0(m,b)).\end{aligned} \tag{65}$$

The Poles of T Matrix. It should be noted that the poles of the $\boldsymbol{T}$ matrix exactly give new eigenvalues, since the present theory takes into account the effect of the perturbation to the infinite order. As an illustrative example, we put the perturbation v between a and c in the triatomic linear molecule (see Fig. 7). Then the poles of $\boldsymbol{T}$ matrix in this case are given by the roots of the equation

$$1-\left[\frac{1}{1-vG_0(a,c;\,z)}\right]^2G_0(a,a;\,z)G_0(c,c;\,z) = 0. \tag{66}$$

Using Eqs. 29 and 32, we obtain $z=2v,\ -v$ (degenerate). Thus, we successfully reproduce the eigenvalues of the triatomic ring molecule.

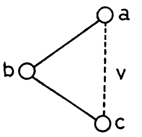

Fig. 7. Interaction v between a and c in the triatomic linear molecule.

Double Perturbations at Site m *and* n. Let us consider a couple of perturbation, ε_m and ε_n at sites m and n. In this case the required interaction is given by

$$\boldsymbol{v} = \begin{pmatrix}\varepsilon_m & 0\\ 0 & \varepsilon_n\end{pmatrix}. \tag{67}$$

For this system we obtain

$$\begin{aligned}\boldsymbol{T}(z) &= \begin{pmatrix}1/\varepsilon_m-G_0(m,m) & -G_0(m,n)\\ -G_0(n,m) & 1/\varepsilon_n-G_0(n,n)\end{pmatrix}^{-1}\\ &= \frac{1}{1-\tilde{\varepsilon}_m\tilde{\varepsilon}_n|G_0(m,n)|^2}\begin{pmatrix}\tilde{\varepsilon}_m & \tilde{\varepsilon}_m\tilde{\varepsilon}_nG_0(m,n)\\ \tilde{\varepsilon}_n\tilde{\varepsilon}_mG_0(n,m) & \tilde{\varepsilon}_n\end{pmatrix},\end{aligned} \tag{68}$$

where $\tilde{\varepsilon}_m$ is defined in Eq. 55. Thus we can estimate the change of the bond order by evaluating the (a,b) element of Eq. 48, as

$$\begin{aligned}\delta q_{ab} &= \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z[G(a,b;\,z)-G_0(a,b;\,z)]\\ &= \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z\frac{1}{1-\tilde{\varepsilon}_m\tilde{\varepsilon}_n|G_0(m,n)|^2}[\tilde{\varepsilon}_mG_0(a,m)G_0(m,b)\\ &\quad+\tilde{\varepsilon}_nG_0(a,n)G_0(n,b)+\tilde{\varepsilon}_m\tilde{\varepsilon}_n\{G_0(a,m)G_0(m,n)G_0(n,b)\\ &\quad+G_0(a,n)G_0(n,m)G_0(m,b)\}].\end{aligned} \tag{69}$$

The first two terms of the square bracket are direct effects separately arisen from two sites, while the remaining terms are indirect ones caused by the perturbation at site $m(n)$ *via* site $n(m)$. If $G_0(m,n)\varepsilon_m$ and $G_0(n,m)\varepsilon_n$ are negligibly small compared to unity, it follows that

$$\delta q_{ab} \cong \frac{1}{2\pi \mathrm{i}}\int_C \mathrm{d}z[\varepsilon_mG_0(a,m)G(m,b)+\varepsilon_nG_0(a,n)G(n,b)]. \tag{70}$$

This shows the additivity of two perturbing effects in a crude approximation.

Discussion

In the present work, the renormalized perturbation theory had been used to build up propagators for the Hückel model. If we confine ourselves to discuss the obtained results, we have nothing new more than the simple LCAO MO theory does. However, in the course of constructing propagators, we visualize how interactions work in the Hückel model.

Recently, Hosoya[4–8] introduced the topological index as a quantity characterizing the physical properties of hydrocarbons. This is, simply speaking, the sum of absolute values of the Hückel polynomials corresponding to the molecule in question. The value of the topological index increases almost monotonously with the molecular size, and varies as molecular shapes change. Hosoya displayed some parallel trends between topological indices and physical properties. He also found a convenient procedure to calculate the topological indices other than the simple summation mentioned above. His rule which is found in Eq. 7 in reference 5 is almost analogous to the rules indicated by Eqs. 21, 24, and 27. Therefore we are inclined to say that our work has presented some physical basis for Hosoya's intuition, though we have not yet obtained any direct physical interpretation of the topological index.

We turn to discussion of the polarizabilities. The pioneering work of Coulson and Longuet-Higgins has been followed by Fukui *et al.*[9–11] These works including Coulson's are manipulated mainly by the use of properties of the Hückel determinant, but the final expressions of polarizabilities are given in terms of the LCAO coefficients of the zeroth order molecular orbitals. Their results are not beyond the elementary perturbation theory. Here we rewrite the treatment of Coulson and Longuet-Higgins to derive the relationship

$$\Pi_{a:mn} = 2\Pi_{mn:a}. \tag{71}$$

The orbital energy ε_i is given by

$$\varepsilon_i = \sum_a c_{ia}^2\alpha_a + \sum_{mn} c_{im}c_{in}\beta_{mn}, \tag{72}$$

with the optimized LCAO coefficients c_{im} (assumed to be real). Then it follows that

$$\frac{\partial \varepsilon_i}{\partial \alpha_a} = c_{ia}^2, \quad \frac{\partial \varepsilon_i}{\partial \beta_{mn}} = c_{im}c_{in}. \tag{73}$$

The charge density q_a at site a, and the bond order q_{mn} are given as

$$q_a = 2\sum_i^{\text{occ}} c_{ia}^2 = 2\sum_i^{\text{occ}} \frac{\partial \varepsilon_i}{\partial \alpha_a} = \frac{\partial E}{\partial \alpha_a}, \tag{74}$$

$$q_{mn} = 2\sum_i^{\text{occ}} c_{im}c_{in} = 2\sum_i^{\text{occ}} \frac{\partial \varepsilon_i}{\partial \beta_{mn}} = \frac{\partial E}{\partial \beta_{mn}}, \tag{75}$$

where the factor 2 arises from the spin sum, and E is the total energy. Now we get the polarizabilities

$$\Pi_{a:mn} \equiv \frac{\partial q_a}{\partial \beta_{mn}} + \frac{\partial q_a}{\partial \beta_{nm}} = 2\frac{\partial}{\partial \beta_{mn}}\left(\frac{\partial E}{\partial \alpha_a}\right) \qquad (\beta_{mn}=\beta_{nm}), \tag{76}$$

$$\Pi_{mn:a} \equiv \frac{\partial q_{mn}}{\partial \alpha_a} = \frac{\partial}{\partial \alpha_a}\left(\frac{\partial E}{\partial \beta_{mn}}\right). \tag{77}$$

From these expressions, we can conclusively get Eq. 71. The above derivation looks quite general, but is not beyond the elementary perturbation theory, since Eq. 73 is valid only for infinitesimal variations of α or β.

On the other hand, the present theory works even for an arbitrary magnitude of perturbing interaction. The resultant expressions are exact in the Hückel model, so that we can perform any order of perturbation expansion. In order to explain what we mean, we give a simple example shown by Eq. 53. As was mentioned there, the bare interaction ε_m is replaced by the effective interaction $\bar{\varepsilon}_m$ which is obtained by the infinite repetition of interaction with site m. From the viewpoint of practical use, our theory is not so bad, since propagators in our expressions are easily obtainable from the simple algebra by means of the recurrence formula.

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