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Investigation of the Thermo– and Photo–Chemical Reactivity with Green’s Function

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Investigation of the Thermo– and Photo–Chemical Reactivity with Green’s Function[#]

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Abstract

A theoretical method for thermo– and photo–chemical reactivity is presented in terms of the Green’s function. The results are rewritten by using a concept of effective interaction, which is intuitively appealing. As parameters for reactivity, the bond order is useful for a single–particle perturbation, and polarizability is useful for a couple of the single–particle interaction. Then the screening of the Coulomb potential is investigated by polarizability. Several examples are shown. The modified electron–electron coupling between levels active for photo–irradiation is likely to be attractive.

Keywords. Chemical reactivity, Green’s function; bond order; polarizability; effective interaction.

1 INTRODUCTION

We have already useful theories of chemical reactivity [1–4]. If any perturbation v which is usually of the single–particle character, is put on a system described by the Hamiltonian H^0 , the expected reaction can be presented by using H^0 and v . Several indices useful for describing reactivity were developed: charge density, bond order and polarizability in Coulson’s theory, the HOMO and LUMO orbitals in Fukui’s theory, and symmetry conservation in Woodward–Hoffmann’s theory. Hosoya’s treatment [5] based on the graphical interpretation is also interesting combined with the above theories.

In order to synthesize a new compound from A and B , the theory of chemical reactivity turns out to the theory of orbital interaction [6]. Namely, the Hamiltonians for A and B are already diagonalized, and their eigenvalues and eigenfunctions are prepared. If some interaction between A and B is supposed, the problem is what reaction can be expected. The mechanism responsible for this reaction must be described by couplings between eigenfunctions of A and B . The final feature

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of this reaction is displayed by the modified coupling, or the effective interaction. Even though qualitative, we must fatally expect any possible reaction or a new molecule as a stable substance, from H^0 and v given before reaction.

Recently, elaborate calculations are performed for arbitrarily given conformations, and then the structure optimized energetically is supposed to be the product. This is a computational experiment, and we hesitate to call it a theory.

In our treatment, Coulson's theory is reformulated in terms of Green's function. Coulson's theory is itself an old fashioned Green's function theory. It is now dressed in the latest fashion, then we obtain a unified view over all the established theories.

In chapters 2 and 3, we briefly sketch our general treatment of the chemical reactivity distinguishing thermo- and photo-chemical reactions [6,7,8,9], and give a few illustrative examples. In chapter 4, the concept of effective interaction is introduced to rewrite previous results. This may be more impressive for current chemists. In this chapter, this idea is extended to the two-particle interaction, say, the electron-electron interaction. The deep investigation of electronic correlation is one of the most important problem in the many-particle systems.

2 THERMO-CHEMICAL

The Green's function, $G(z)$ for the system in question is given as:

$$G(z) = \frac{1}{z - H} \quad (2.1)$$

with

$$H = H^0 + v \quad (2.2)$$

where H^0 is the non-interacting part of the Hamiltonian and v is a perturbation. Then $G(z)$ is written as:

$$\begin{aligned} G(z) &= \frac{1}{z - H} \\ &= \frac{1}{z - H^0} + \frac{1}{z - H^0} v \frac{1}{z - H} \\ &= \frac{1}{z - H^0} + \frac{1}{z - H^0} v \frac{1}{z - H^0} + \frac{1}{z - H^0} v \frac{1}{z - H^0} v \frac{1}{z - H^0} + \dots \\ &= G^0(z) + G^0(z)vG^0(z) + G^0(z)vG^0(z)vG^0(z) + \dots \end{aligned} \quad (2.3)$$

where the second line is an identity, called the Dyson equation, and the third line is a perturbation expansion with respect to v . The extra energy due to v is given by:

$$\begin{aligned}
 \Delta E &= \text{Tr} \oint \frac{dz}{2\pi i} z (G(z) - G^0(z)) \\
 &= \text{Tr} \oint \frac{dz}{2\pi i} z (G^0(z) \nu G^0(z) + G^0(z) \nu G^0(z) \nu G^0(z) + \dots) \\
 &= \text{Tr} \oint \frac{dz}{2\pi i} (\nu G^0(z) + \nu G^0(z) \nu G^0(z) + \dots)
 \end{aligned} \tag{2.4}$$

The last line is obtained by integration by parts. The terms up to the second order to ν is enough for studying chemical reactivity.

The non-interacting Green's function is written as the diagonal form:

$$G^0(z) = \frac{|i\rangle\langle i|}{z - \varepsilon_i} \tag{2.5}$$

where $|i\rangle$ is a single particle state and ε_i is its energy. Here and hereafter summation convention for repeated indices is applied. Then Eq. (2.4) is estimated in the site representation:

$$\begin{aligned}
 \Delta E &= \text{Tr} \oint \frac{dz}{2\pi i} z (G(z) - G^0(z)) \\
 &= \oint \frac{dz}{2\pi i} \left[\nu_{rs} \frac{\langle s|i\rangle\langle i|r\rangle}{z - \varepsilon_i} + \nu_{rs} \frac{\langle s|i\rangle\langle i|t\rangle}{z - \varepsilon_i} \nu_{tu} \frac{\langle u|j\rangle\langle j|t\rangle}{z - \varepsilon_j} + \dots \right] \\
 &\equiv \nu_{rs} q_{rs} + \nu_{rs} \Pi_{rs;ut} \nu_{tu} + \dots
 \end{aligned} \tag{2.6}$$

where integration is carried out along the Coulson contour [1], enclosing poles for the occupied levels. It is noted that:

$$\begin{aligned}
 q_{sr} &= \oint \frac{dz}{2\pi i} G_{sr}(z) = \oint \frac{dz}{2\pi i} \frac{\langle s|i\rangle\langle i|r\rangle}{z - \varepsilon_i} \\
 &= \sum_i^{occ} \langle s|i\rangle\langle i|r\rangle \\
 \Pi_{rs;ut} &= \oint \frac{dz}{2\pi i} G_{rs}(z) G_{ut}(z) \\
 &= \oint \frac{dz}{2\pi i} \frac{\langle r|i\rangle\langle i|s\rangle}{z - \varepsilon_i} \frac{\langle u|j\rangle\langle j|t\rangle}{z - \varepsilon_j} \\
 &= 2 \sum_i^{occ} \sum_j^{un} \frac{\langle r|i\rangle\langle i|s\rangle\langle u|j\rangle\langle j|t\rangle}{\varepsilon_i - \varepsilon_j}
 \end{aligned} \tag{2.7}$$

These are bond order and polarizability [1]. Note that in the present treatment, spin factors are omitted for simplicity.

3 PHOTO-CHEMICAL

In investigating photo-chemical reactions the Green's function G^0 is modified by interaction with the radiation field, f :

$$G(z) = \frac{1}{z-H}$$

$$= \frac{1}{z-H^0} + \frac{1}{z-H^0} f \frac{1}{z-H^0} + \frac{1}{z-H^0} f \frac{1}{z-H^0} f \frac{1}{z-H^0} + \dots \quad (3.1)$$

This is the Dyson equation, which is explicit up to the second order with respect to f . Here G^0 modified by f is simply written G . It is helpful to define projection operators, P and Q which project out the ground and excited states respectively. These are:

$$|N, n_k \rangle \approx |H, n_k \rangle, \quad |X, n_k - 1 \rangle \approx |L, n_k - 1 \rangle, \quad (3.2)$$

being written symbolically labeled by H (the highest occupied level) and by L (the lowest vacant level), respectively. Then we have:

$$P = |H, n_k \rangle \langle H, n_k|$$

$$Q = |L, n_k - 1 \rangle \langle L, n_k - 1|, \quad (3.3)$$

where the n_K terms represent the *number* of photons. It is needless to say that:

$$P + Q = 1$$

$$PQ = 0$$

$$P^2 = P, \quad Q^2 = Q \quad (3.4)$$

It is clear that:

$$(P + Q)G(P + Q) = G^P + G^Q + G^{PQ} + G^{QP} \quad (3.5)$$

We begin by estimating G^P . Since G^0 is diagonal for P and Q , while f is off-diagonal, the first order term to f in Eq. (3.1) obviously vanishes. We thus obtain:

$$G^P = P \frac{1}{z-H} P$$

$$= P \frac{1}{z-H^0} P + P \frac{1}{z-H^0} P f Q \frac{1}{z-H^0} Q f P \frac{1}{z-H} P. \quad (3.6)$$

This is solved as:

$$G^P = [(G_0^P)^{-1} - f^{PQ} G_0^Q f^{QP}]^{-1}. \quad (3.7)$$

Similarly,

$$G^Q = [(G_0^Q)^{-1} - f^{QP} G_0^P f^{PQ}]^{-1}. \quad (3.8)$$

G^{PQ} may be estimated in a similar manner, but will be neglected because of its small effect. The

matrix element of f is written as, for example,

$$f^{PQ} = \langle H, n_k | f | L, n_k - 1 \rangle = f_{HL} \sqrt{n_k} \quad (3.9)$$

where f^{HL} is the matrix element of the spatial part of f , and the manipulation of photon operators is implicitly carried out.

We thus have:

$$\begin{aligned} f^{PQ} G_0^Q f^{QP} &= \sum_k n_k |f^{HL}|^2 \frac{1}{z - \varepsilon_{LH} - (n_k - 1)\omega_k} \\ &\approx \sum_k n_k |f^{HL}|^2 \frac{1}{\varepsilon_H + n_k \omega_k - \varepsilon_L - (n_k - 1)\omega_k} \\ &\approx |f^{HL}|^2 \int d\omega_k \rho(\omega_k) n_k \frac{1}{\omega_k - (\varepsilon_L - \varepsilon_H)} \end{aligned} \quad (3.10)$$

where $\rho(\omega_k)$ is the state density at ω_k , and in obtaining the second line, z is approximately replaced by the pole of G_0^P , since we are now interested in the ground state.

We now recover the imaginary part of orbital energies as:

$$\varepsilon_{LH} = \varepsilon_L - i\eta - (\varepsilon_H + i\eta) = \varepsilon_L - \varepsilon_H - i\eta \quad (3.11)$$

where, for example, the positive imaginary (infinitesimal) part of the hole energy is put so that the hole state vanishes in the infinite past of time. We then can carry out integration over ω_k , replacing the state density and n_k by their appropriate average value, $\overline{n_k \rho(\omega_k)}$,

$$f^{PQ} G_0^Q f^{QP} \} = |f^{HL}|^2 \overline{n_k \rho(\omega_k)} i\pi \quad (3.12)$$

where the relation:

$$\frac{1}{z \pm i\eta} = P \frac{1}{z} \mp i\pi \delta(z)$$

was used. After integration, the principal part is omitted, since it gives merely the energy shift and does not concern with the particle density. Finally we obtain

$$G^P = \sum_i \frac{1}{z - (\varepsilon_i + i\eta) - (\varepsilon_H - iw_{HL}) - n_k \omega_k} \quad (3.13)$$

with:

$$w_{HL} = \pi |f_{HL}|^2 \overline{n_k \rho(\omega_k)}. \quad (3.14)$$

It is noted that without irradiation, the hole (occupied) levels have positive imaginary parts which are rather fictitious, however, upon irradiation, the H level gets a negative imaginary part which is physical.

Similarly, by interchanging $H \leftrightarrow L$ and replacing $n_k \omega_k$ by $(n_k+1)\omega_k$, we obtain:

$$G^Q = \sum_i \frac{1}{z - (\varepsilon_i - i\eta) - (\varepsilon_L + iw_{HL}) - (n_k + 1)\omega_k} \quad (3.15)$$

Note the signs of imaginary parts in G^P and G^Q .

Let us evaluate the bond orders:

$$\begin{aligned} q_{rs}^P &= \oint \frac{dz}{2\pi i} \langle r | G^P | s \rangle \\ &= \sum_i \oint \frac{dz}{2\pi i} \frac{\langle r | H \rangle \langle H | s \rangle + \langle r | i \rangle \langle i | s \rangle}{z - (\varepsilon_i + i\eta) - (\varepsilon_H - iw_{HL}) - n_k \omega_k} \\ &= q^0 - \langle r | H \rangle \langle H | s \rangle = q_{rs}^0 - q_{rs}^H \end{aligned} \quad (3.16)$$

where the integration is carried out on the upper half plane of z , along the contour closing the poles, anti-clockwise. The final result shows that the bond order in the ground state has lost the partial bond order of the highest occupied level. Similarly, we obtain:

$$q_{rs}^Q = \langle r | L \rangle \langle L | s \rangle = q_{rs}^L, \quad (3.17)$$

In this case, the integration carried out on the upper half plane yields only the partial bond order of the lowest vacant level. Therefore we obtain the result:

$$\begin{aligned} q_{rs} &= q_{rs}^P + q_{rs}^Q \\ &= q_{rs}^0 - q_{rs}^H + q_{rs}^L = q_{rs}^0 + q_{rs}^{LH}, \end{aligned} \quad (3.18)$$

where

$$q_{rs}^{LH} = q_{rs}^L - q_{rs}^H$$

is directly concerned with the photo-excitation. Then, if we take into account the perturbation, v driving the chemical reaction, and follow the procedure to arrive at Eq. (2.6), it immediately results:

$$\begin{aligned} \Delta E^{(1)} &= Tr \oint \frac{dz}{2\pi i} G(z) v \\ &= Tr \{ q v + q^{LH} v \} \end{aligned} \quad (3.19)$$

The first term is the extra energy not concerned with the radiation field. Thus, in the photochemical reaction the energy proportional to the first order of v and the photo-excitation, f is:

$$\Delta E_f^{(1)} = \sum_{rs} q_{rs}^{LH} v_{sr}. \quad (3.20)$$

Next we evaluate polarizabilities. The propagators in Eq. (2.7) are now replaced by those in Eqs. (3.19) and (3.21): Indicating the radiation field by superscript by f ,

$$\begin{aligned}
 \Pi_{ru;ts}^f &= \oint \frac{dz}{2\pi i} G_{rs}^f(z) G_{tu}^f(z) \\
 &= \oint \frac{dz}{2\pi i} (G_{rs}^P(z) + G_{rs}^Q(z))(G_{tu}^P(z) + G_{tu}^Q(z)) \\
 &= \oint \frac{dz}{2\pi i} (G_{rs}^P(z) G_{tu}^Q(z) + G_{rs}^Q(z) G_{tu}^P(z)) \\
 &= \oint \frac{dz}{2\pi i} \frac{\langle r | i \rangle \langle i | s \rangle + \langle r | H \rangle \langle H | s \rangle}{z - (\varepsilon_i + i\eta) - (\varepsilon_H + iw_{HL}) + n_k \omega_k} \\
 &\quad \times \frac{\langle t | j \rangle \langle j | u \rangle + \langle t | L \rangle \langle L | u \rangle}{z - (\varepsilon_j - i\eta) - (\varepsilon_L + iw_{HL}) + (n_k + 1)\omega_k} \\
 &\quad + \text{term with } P \leftrightarrow Q
 \end{aligned} \tag{3.21}$$

where the terms as $G^P G^P$ vanish due to double poles arising. Integration is carried out by enclosing the contour on the upper half plane, and for the second term, it is done by enclosing the contour on the lower half plane. We evaluate the first half of Eq. (3.21):

$$\begin{aligned}
 &\oint \frac{dz}{2\pi i} \langle r | i \rangle \langle i | s \rangle \langle t | j \rangle \langle j | u \rangle \\
 &\quad \times \frac{1}{[z - (\varepsilon_i + i\eta) - (\varepsilon_H - iw_{HL}) + n_k \omega_k][z - (\varepsilon_j - i\eta) - (\varepsilon_L + iw_{HL}) + (n_k - 1)\omega_k]} \\
 &= \oint \frac{dz}{2\pi i} \frac{\langle r | i \rangle \langle i | s \rangle \langle t | j \rangle \langle j | u \rangle}{\varepsilon_i - \varepsilon_j - iw_{HL} + \omega_k} \\
 &\quad \times \left\{ \frac{1}{z - (\varepsilon_i + i\eta) - (\varepsilon_H - iw_{HL}) + (n_k + 1)\omega_k} - \frac{1}{z - (\varepsilon_j - i\eta) - (\varepsilon_L + iw_{HL}) + n_k \omega_k} \right\} \\
 &= \sum_i^{occ} \sum_j^{un} (1 - \delta_{iH} - \delta_{iL}) \frac{\langle s | i \rangle \langle i | t \rangle \langle u | j \rangle \langle j | r \rangle}{\varepsilon_i - \varepsilon_j - iw_{HL} + \omega_k}
 \end{aligned} \tag{3.22}$$

Note that ε_{i_s} indicates to exclude ε_H , ε_{ϕ_s} indicates to exclude ε_L , and in the denominator of the third line the physical imaginary part only retained.

We now assume that ω_k extends some region so that we take average over this region, obtaining

$$\begin{aligned}
 &\sum_k \frac{1}{\varepsilon_i - \varepsilon_j - iw_{HL} + \omega_k} \\
 &\approx \int d\omega_k \rho(\omega_k) \frac{1}{\varepsilon_i - \varepsilon_j - iw_{HL} + \omega_k} \\
 &\sim i\pi \delta(\varepsilon_i - \varepsilon_j - iw_{HL} + \omega_k)
 \end{aligned} \tag{3.23}$$

where $\rho(\omega_k)$ is the state density. If we rewrite δ function more accurately,

$$i\pi \delta(x) = \left(\frac{1}{x} - \frac{d}{dx} \log x \right)$$

this gives oscillating factor. Due to the relation (3.23), levels taking part in may be restricted to H and L orbitals,

$$\begin{aligned}\Pi_{rst;u}^f &= \rho(\omega_{\kappa})_{(\omega_{\kappa}=\varepsilon_{\Lambda}-\varepsilon_{\text{H}})} \langle s | H \rangle \langle H | t \rangle \langle u | L \rangle \langle L | r \rangle \\ &= \rho(\omega_{\kappa})_{(\omega_{\kappa}=\varepsilon_{\Lambda}-\varepsilon_{\text{H}})} \mathbf{q}_{st}^H \mathbf{q}_{ur}^L\end{aligned}\quad (3.24)$$

where we use partial bond orders. In the later chapter this will be used for the screened Coulomb potential in the radiation field.

As to applications, numerous examples have been already published except the polarizability in the radiation field [7-10].

4 EFFECTIVE INTERACTIONS

It is known that if the exact single particle Green's function were obtained the total energy of the system could be evaluated accurately [11].

Keeping this in mind, we rewrite Eq. (2.3):

$$\begin{aligned}G(z) &= G^0(z) + G^0(z)vG(z)G(z) \\ &= G^0(z) + G^0(z)\tilde{v}G^0\end{aligned}\quad (4.1)$$

where the effective interaction $\tilde{v}(z)$ is z dependent:

$$\tilde{v}(z) = v + vG^0(z)v + vG^0(z)vG^0(z)v + \dots = v + vG^0(z)\tilde{v},\quad (4.2)$$

or

$$\tilde{v}(z) = \frac{v}{1 - vG^0(z)}\quad (4.3)$$

Namely, the property of the integral equation for the propagator transfers to the interaction.

4.1 Single-Particle Interaction

It may be helpful for a schematic understanding to use the perturbation expansion of Eq. (3.1). Up to the first order, we have:

$$\begin{aligned}\tilde{v}_{rs}(z) &= v_{rs} + v_{rt}G_{tu}^0(z)v_{us} \\ &= v_{rs} + v_{rt} \frac{\langle t | i \rangle \langle i | u \rangle}{z - \varepsilon_t} v_{us}.\end{aligned}\quad (4.4)$$

As an illustrative example, we employ the Hückel Hamiltonian for butadiene,

$$H = \begin{pmatrix} 0 & v_{12} & 0 & 0 \\ v_{21} & 0 & v_{23} & 0 \\ 0 & v_{32} & 0 & v_{34} \\ 0 & 0 & v_{43} & 0 \end{pmatrix} \quad (4.5)$$

Note that $v_{14} = 0$. Now we want to obtain $\tilde{v}_{14}(z)$. Eq. (3.4) yields:

$$\begin{aligned} \tilde{v}_{14}(z) &= v_{14} + v_{12} \frac{\langle 2 | i \rangle \langle i | 3 \rangle}{z - \varepsilon_i} v_{34} \\ &= v_{12} \frac{\langle 2 | i \rangle \langle i | 3 \rangle}{z - \varepsilon_i} v_{34} \end{aligned} \quad (4.6)$$

The value of $\tilde{v}_{rs}(z)$ depends on what state we are now interested in. If we are interested in the ground state, ε_i should correspond to one of the hole state and z is replaced by the energy of the particle state. We then estimate $z - \varepsilon_i$ by an average of the excitation energy $\Delta E_{AV} > 0$. Then we have:

$$\tilde{v}_{14}(z) = \frac{1}{\Delta E_{AV}} v_{12} q_{23} v_{34}. \quad (4.7)$$

Observing that $v_{12}, v_{34} < 0$ and $q_{23} = 0.447 > 0$, we find unexpectedly that \tilde{v}_{14} is positive, or repulsive. This implies that the ring closure of cyclo-butadiene is unlikely to happen, as is explained by the current theory [2,3].

On the other hand, if we are interested in the excited state, the lowest vacant level with ε_L is occupied by an electron and $\Delta E_{AV} < 0$ or the negative of the average excitation energy. We then have”

$$\tilde{v}_{14}(z) = \frac{1}{\Delta E_{AV}} v_{12} q_{23}^L v_{34}. \quad (4.8)$$

Here we know that the partial bond order $q_{23}^L = 0.138 > 0$, so that in this case $\tilde{v}_{14}(z)$ is negative or attractive. We conclude that in the presence of radiation field, the cyclo-butadiene is likely to perform ring closure.

One of the most interesting example for Eq. (4.7) is the additive reaction between ethylene and H₂ molecule. In Figure 1, on sites 1 and 2 representing H₂ molecule there are 1s orbitals, while on sites 3 and 4 representing C₂H₄ molecule, there are 2pπ orbitals. The model Hamiltonian for this system is written similarly as Eq. (4.5) and the effective interaction \tilde{v}_{14} is also given by Eq. (4.7). It is obvious that in this case, v_{12} and v_{34} are both negative. However if $q_{34} < 0$, it results that $\tilde{v}_{14} < 0$, so that we can expect the ring compound being formed. That $q_{34} < 0$ is achieved from $v_{23} > 0$ as is shown below.

For the Hamiltonian:

$$H = \begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

we have $q_{23} = -0.447$. In order to establish $v_{23} > 0$, $1s(2)$ and $2p\pi(3)$ must be mutually out of phase, schematically speaking, the lines indicating bonds of H_2 and C_2H_4 should cross as shown in Figure 1. This is the (smallest) Möbius band.

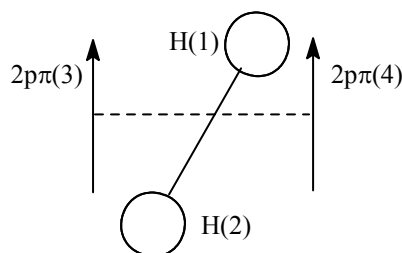


Figure 1. Molecular compound between ethylene and H_2 molecule. The arrows represent the $2p\pi$ AOs of carbon atoms, while the circles the $1s$ AOs of the hydrogen molecule.

4.2 Electron–Electron Interaction

We rewrite the perturbation expansion of the Green’s function, (2.3),

$$G(z) = G^0 + G^0(z)vG^0(z) + G^0(z)vG^0(z)vG^0(z) + \dots \quad (4.9)$$

When v is the two–particle interaction, the approximation procedure may be complicated. We now write:

$$v = \int d^3x_1 d^3x_2 \varphi_{\alpha}^{+}(x_1) \varphi_{\beta}^{+}(x_2) v(1.2) \varphi_{\beta}(x_2) \varphi_{\alpha}(x_1), \quad (4.10)$$

where $v(1,2)$ is the quantum mechanical operator. The field operators are developed in terms of single–particle orbitals with creation or annihilation operators, and these turn into the Green’s function. The HF (Hartree–Fock) potential is obtained through a mean field average:

$$v^{HF} = \int d^3x_1 \varphi_{\alpha}^{+}(x_1) \varphi_{\alpha}(x_1) \times \int d^3x_2 v(1.2) \left\{ \langle \varphi_{\beta}^{+}(x_2) \varphi_{\beta}(x_2) \rangle - \langle \varphi_{\beta}(x_2) \varphi_{\alpha}^{+}(x_2) \rangle \delta_{\alpha\beta} \right\} \quad (4.11)$$

The treatment $\langle \dots \rangle$ is the ground state average and carried out self–consistently. The HF potential is a single–particle potential, so the infinite sum in Eq. (4.9) is now possible. This is the usual HF procedure.

If we look at Eq. (4.10), a particle–hole pair arises at x_1 and then this pair sinks at x_2 . It may be considered that such processes occur infinite times. This is called vacuum polarization, since the ground state of many particle system is thought a kind of vacuum. We can consider a few different

types for them, and among them select the most effective one, which is called the ring approximation [10]. This procedure is written as follows, obtaining the effective HF potential \tilde{v}^{HF} :

$$\begin{aligned}\tilde{v}^{HF} &= v^{HF} + v^{HF} \Pi v^{HF} + v^{HF} \Pi v^{HF} \Pi v^{HF} + \dots \\ &= v^{HF} + v^{HF} \Pi \tilde{v}^{HF},\end{aligned}\tag{4.12}$$

where Π is called the polarization part and consists of two propagators. It might be instructive to write \tilde{v} in the site representation:

$$\begin{aligned}\tilde{v}_{rs;tu} &= v_{rs;tu} + v_{rs;t'u'} \Pi_{t'u';t''u''} v_{t''u'';tu} + \dots \\ &= v_{rs;tu} + v_{rs;t'u'} \oint \frac{dz}{2\pi i} \frac{\langle t' | i \rangle \langle i | t'' \rangle \langle u'' | j \rangle \langle j | u' \rangle}{z - \epsilon_i} v_{t''u'';tu} + \dots \\ &= v_{rs;tu} + 2v_{rs;t'u'} \sum_i^{occ} \sum_j^{un} \frac{\langle t' | i \rangle \langle i | t'' \rangle \langle u'' | j \rangle \langle j | u' \rangle}{\epsilon_j - \epsilon_i} v_{t''u'';tu} + \dots\end{aligned}\tag{4.13}$$

where

$$v_{rs;tu} = \int d^3x_1 d^3x_2 r(x_1) s(x_1) v(1,2) t(x_2) u(x_2),\tag{4.14}$$

so that

$$\Pi_{t'u';t''u''} = 2 \sum_i^{occ} \sum_j^{un} \frac{\langle t' | i \rangle \langle i | u'' \rangle \langle t'' | j \rangle \langle j | u' \rangle}{\epsilon_j - \epsilon_i}\tag{4.15}$$

This is nothing but the polarization part in Eq. (2.7). We understand that the HF procedure with \tilde{v}^{HF} might be a pretty good approximation for evaluating the energy of any state. In the presence of the radiation field, Π of Eq. (3.21) is employed.

5 APPLICATIONS

For completeness, we summarize our theory of chemical reactivity. Let v be the perturbation. The extra-energy due to v is in dark:

$$\begin{aligned}\Delta E^{(1)} &= v_{rs} q_{sr} \\ \Delta E^{(2)} &= v_{rs} \Pi_{rs;tu} v_{tu},\end{aligned}\tag{5.1}$$

and photo-chemically:

$$\begin{aligned}\Delta E^{f(1)} &= v_{rs} q_{sr}^{LH} \\ \Delta E^{f(2)} &= v_{rs} \Pi_{rs;tu}^f v_{tu}.\end{aligned}\tag{5.2}$$

Notice that summation convention, and:

$$q_{sr}^{LH} = q_{sr}^L - q_{sr}^H.\tag{5.3}$$

Before beginning applications we want to stress the meanings of the bond order or the polarizability. These are correlation functions made from propagators. When we have v_{rs} , this combines with q_{sr} and then closes a path. If we deal with v_{rs} and v_{tu} , $\Pi_{rs;tu}$ combines with these and closes a path, the latter being understandable in terms of the Green's functions as described in Eq. (2.7).

5.1 Stability

5.1.1 Naphthalene vs azulene

Let us consider a ring composed of ten members. Each of them is labeled from 1 to 10. If we have a bond between sites 1 and 6, this corresponds to naphthalene, while the bond 1–5 displays azulene. For naphthalene:

$$\begin{aligned}\Delta E^{(1)} &= v_{16}q_{61} = -1. \times 0.20 \\ \Delta E^{(2)} &= v_{16}\Pi_{16;61}v_{61} = -1. \times (-0.187) \times (-1.).\end{aligned}\tag{5.4}$$

for azulene:

$$\begin{aligned}\Delta E^{(1)} &= v_{15}q_{51} = -1. \times 0.0 \\ \Delta E^{(2)} &= v_{16}\Pi_{16;61}v_{61} = -1. \times (-0.220) \times (-1.).\end{aligned}\tag{5.5}$$

The case of naphthalene is as expected, while azulene is stable due to the second order effect.

5.1.1 Anthracene vs phenanthrene

We consider a ring of 14 members. The compounds with bonds (0–9) and (2–7) corresponds to anthracene, while one with bonds (1–10) and (2–7) corresponds to phenanthrene. We cannot distinguish these from the first order effect, since

$$q_{0,9} = q_{1,10} = q_{2,7} = 0.159\tag{5.6}$$

However observing that

$$\begin{aligned}\Pi_{0,9;2,7} &= -0.0631 \\ \Pi_{1,10;2,7} &= -0.0854\end{aligned}\tag{5.7}$$

we can see that phenanthrene is a little more stable due to the second order effect, than anthracene is. Examples of interesting photochemical reactivity are presented in the literature [8,9].

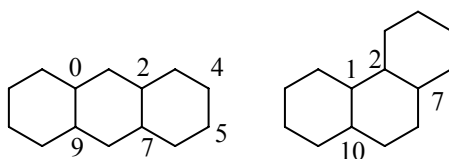


Figure 2. Anthracene and phenanthrene.

5.2 Screened Coulomb Interaction

It is well known that the Coulomb interactions are screened in many electron systems, as was first investigated by Moffit and Scanlan [11]. In investigating the T – V (triplet–singlet) separation in the π –excitation spectra in the ethylene molecule, the molecular integral $\langle 11;11 \rangle$ is estimated nearly 10 eV from the spectroscopic data of the carbon atom. Other integrals are calculated by using the Slater $2p$ atomic orbitals. This idea is extended over whole range of inter–atomic distance, by Pariser–Par–Pople or Nishimoto–Mataga [12], and the latter is widely used, say:

$$v_{rs} = \frac{14.4}{r_{rs} + 14.4/10.8} \text{ (eV)}, \quad r_{rs} (\text{\AA}^\circ), \quad (5.8)$$

where $v_{rs} = \langle r(1)r(1) | s(2)s(2) \rangle$. In the present parameterization, the direct terms are retained and the exchange terms are disregarded. For example in butadiene (in the unit eV):

$$v_{rs} = \begin{pmatrix} 10.800 & 5.407 & 3.766 & 2.794 \\ 5.407 & 10.800 & 5.775 & 3.766 \\ 3.766 & 5.775 & 10.800 & 5.407 \\ 2.794 & 3.766 & 5.407 & 10.800 \end{pmatrix} \quad (5.9)$$

This parametrization has no physical foundation, but may be considered to be screening by the sigma–electron polarization.

5.3 Screening in Dark

The screened Coulomb potential is given, in dark, by [4,12]:

$$\begin{aligned} \tilde{v} &= \frac{v}{1 - \Pi v} \\ &\approx v + v \Pi v \end{aligned} \quad (5.10)$$

If it is written in the site representation:

$$\tilde{v}_{rs} \approx v_{rs} + v_{rt} \Pi_{tu} v_{ut}. \quad (5.11)$$

Here it should be noted that since we are now using the Pariser–Parr–Pople procedure, the polarization part is diagonal,

$$\Pi_{tu} = \Pi_{tu;ut}.$$

However, the approximation (5.11) is too poor to demonstrate the result. It is preferable to employ the procedure in the first line. This requires the matrix inversion, which is an easy task for the computers. Then we obtain:

$$\tilde{v}_{rs} = \begin{pmatrix} 8.466 & 6.311 & 4.474 & 4.989 \\ 6.311 & 8.902 & 4.816 & 4.474 \\ 4.474 & 4.816 & 8.902 & 6.311 \\ 4.989 & 4.474 & 6.311 & 8.466 \end{pmatrix} \quad (5.12)$$

Comparing this with v in Eq. (5.9), even though we deal with a small molecule, the essential feature of screening is realized: Some of them are screened, and others are descreened, and they oscillate [13].

5.4 Screening for the Combined System

Let us consider the case two species are combined by some bonds. A famous model was presented by Little [14]. He considered a π long chain molecule combined with similar dye molecules at every sites of the chain. The former is called spine, and the latter the side chain. Each species is polarized through bonds between them, so that the electron–electron interaction in the spine might be attractive. If this happens, the spine becomes superconductor at even room temperature.

Here the method of P, Q projection method introduced in Eq. (2.2) is again useful. Let P refer to the spine, and Q to the side chain. If we are interested in the spine, it follows that:

$$\begin{aligned} P\tilde{v}P &= PvP + Pv(P+Q)\Pi(P+Q)\tilde{v}P \\ &= PvP + (PvP + PvQ)(P\Pi P + Q\Pi Q)(P\tilde{v}P + Q\tilde{v}P) \\ &= PvP + (PvP)(P\Pi P)(P\tilde{v}P) + (P\tilde{v}Q)(Q\Pi Q)(Q\tilde{v}P). \end{aligned} \quad (5.13)$$

We now require to know $Q\tilde{v}P$,

$$\begin{aligned} Q\tilde{v}P &= QvP + Qv(P+Q)\Pi(P+Q)\tilde{v}P \\ &= QvP + (QvP + QvQ)(P\Pi P + Q\Pi Q)(P\tilde{v}P + Q\tilde{v}P) \\ &= QvP + (QvP)(P\Pi P)(P\tilde{v}P) + (QvQ)(Q\Pi Q)(Q\tilde{v}P) \end{aligned} \quad (5.14)$$

Namely:

$$Q\tilde{v}P = [1 - (QvQ)(Q\Pi Q)]^{-1} [QvP + (QvP)(P\Pi P)(P\tilde{v}P)]. \quad (5.15)$$

Substituting this into Eq. (5.13) yields:

$$\tilde{v}^P = \frac{1}{1 - v^P \Pi^P - v^{PQ} \Pi^Q \frac{1}{1 - v^Q \Pi^Q} v^{QP} \Pi^P} \left[v^P + v^{PQ} \Pi^Q v^{QP} \right] \quad (5.16)$$

where notations are simplified:

$$\tilde{v}^P = P\tilde{v}P, \quad v^{PQ} = PvQ, \quad \Pi^P = P\Pi P, \quad \text{but } \Pi^{PQ} = 0. \quad (5.17)$$

Equation (5.16) is exact. If we employ the first order approximation with respect to Π , it results that:

$$\tilde{v}^P = \frac{v^P}{1 - v^P \Pi^P} + v^{PQ} \Pi^Q v^{QP}. \quad (5.18)$$

The first term arises from the polarization in the P -part, and the second term is due to interaction with the Q -part. If we observe the exact expression (5.16), the third term of the denominator takes into account the effect of polarization in the Q -part through interaction between.

We will try a pilot calculation. The system is benzene mono-substituted by butadiene, say, P refers to benzene and Q to butadiene. The electron-electron interactions among π electrons are (in the unit of $-\beta = 3$ eV)

$$v^P = \begin{pmatrix} 3.50 & 1.73 & 1.15 & 0.86 & 0.69 & 0.57 \\ 1.73 & 3.50 & 1.73 & 1.15 & 0.86 & 0.69 \\ 1.15 & 1.73 & 3.50 & 1.73 & 1.15 & 0.86 \\ 0.86 & 1.15 & 1.73 & 3.50 & 1.73 & 1.15 \\ 0.69 & 0.86 & 1.15 & 1.73 & 3.50 & 1.73 \\ 0.57 & 0.69 & 0.86 & 1.15 & 1.73 & 3.50 \end{pmatrix} \quad (5.19)$$

and

$$v^Q = \begin{pmatrix} 3.50 & 1.73 & 1.15 & 0.86 \\ 1.73 & 3.50 & 1.73 & 1.15 \\ 1.15 & 1.73 & 3.50 & 1.73 \\ 0.86 & 1.15 & 1.73 & 3.50 \end{pmatrix} \quad (5.20)$$

We have a single interaction between P and Q , which is expressed by the 4–6 matrix with a single matrix element:

$$H^{QP} = \begin{pmatrix} -1.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \end{pmatrix} \quad (5.21)$$

Note that H^{QP} is the transpose of the above. This is extremely simplified without lack of essentiality.

In the followings we present results. The result with the first order with respect to Π is [14]:

$$\tilde{v}^P(\text{Little}) = \begin{pmatrix} 2.77 & 2.01 & 1.67 & 1.63 & 1.67 & 2.01 \\ 2.01 & 3.08 & 2.01 & 1.67 & 1.63 & 1.67 \\ 1.67 & 2.01 & 3.08 & 2.01 & 1.67 & 1.63 \\ 1.63 & 1.67 & 2.01 & 3.08 & 2.01 & 1.67 \\ 1.67 & 1.63 & 1.67 & 2.01 & 3.08 & 2.01 \\ 2.01 & 1.67 & 1.63 & 1.67 & 2.01 & 3.08 \end{pmatrix} \quad (5.22)$$

and

$$\tilde{v}^Q(\text{Little}) = \begin{pmatrix} 2.64 & 1.96 & 1.32 & 1.44 \\ 1.96 & 3.02 & 1.51 & 1.32 \\ 1.32 & 1.51 & 3.02 & 1.96 \\ 1.44 & 1.32 & 1.96 & 2.84 \end{pmatrix} \quad (5.23)$$

Ours are

$$\tilde{v}^P(\text{our}) = \begin{pmatrix} 3.01 & 2.01 & 1.67 & 1.63 & 1.67 & 2.01 \\ 2.01 & 3.07 & 2.00 & 1.66 & 1.63 & 1.66 \\ 1.67 & 2.00 & 3.08 & 2.00 & 1.67 & 1.63 \\ 1.63 & 1.66 & 2.00 & 3.08 & 2.00 & 1.66 \\ 1.67 & 1.63 & 1.67 & 2.00 & 3.08 & 2.00 \\ 2.01 & 1.66 & 1.63 & 1.66 & 2.00 & 3.07 \end{pmatrix} \quad (5.24)$$

and

$$\tilde{v}^Q(\text{our}) = \begin{pmatrix} 2.79 & 1.95 & 1.33 & 1.43 \\ 1.95 & 3.00 & 1.50 & 1.30 \\ 1.33 & 1.50 & 3.02 & 1.96 \\ 1.43 & 1.30 & 1.96 & 2.83 \end{pmatrix} \quad (5.25)$$

Both the equations display slight differences except the position where the substitution takes place. At this position, the effect is larger in Little’s treatment than in ours because the effect from the backflow is not taken into account.

Our elaborate investigations for realistic systems to establish the room temperature superconductivity were in vain [16,17].

5.5 Screening, Photochemical

The screening of the Coulomb potential in the presence of the radiation field is given by the equation similar to Eq. (5.11) by using Π^f ,

$$\begin{aligned} \tilde{v}_{rs}^f &\approx v_{rs} + v_{rt} \Pi_{tu}^f v_{ut} \\ &= v_{rs} + v_{rt} \rho(\omega_k)_{\omega_k = \epsilon_\lambda - \epsilon_H} q_{tu}^H q_{ut}^L v_{us} \end{aligned} \quad (5.26)$$

In order to compare this with one in the dark, it is preferable to estimate the latter by an approximation such that

$$\begin{aligned} \Pi_{tu} &\approx 2 \sum_i^{occ} \sum_j^{un} \frac{\langle t | i \rangle \langle i | u \rangle \langle u | j \rangle \langle j | t \rangle}{\varepsilon_i - \varepsilon_j} \\ &\approx 2 \frac{q_{tu}^H q_{ut}^L}{\varepsilon_H - \varepsilon_L}. \end{aligned} \quad (5.27)$$

Since the denominator of Eq. (5.27) is negative, this gives the opposite sign to that of Eq. (5.16). We thus have a possibility that the electron–electron interaction becomes attractive in the radiation field. In studying the photo–superconductivity of two level system, this phenomenon might be used [18].

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