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Use of Propagators in the Hückel Model. IV. Chemical Reactivity in Radiation Field

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The propagator approach is applied to chemical reactivity in the presence of radiation field. The Woodward-Hoffmann's rule in photochemical reactions is generally derived. As an illustrative example, the ring closure or ring opening reactions are discussed.

In the previous work,[1] we have successfully applied the propagator theory to the problem of chemical reactivity and stability in the absence of radiation field. The treatment is fairly general, not restricted to the specified levels, *e.g.*, the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) but whole electrons and levels are involved. The results have been shown analytically and, to some extent, quantitatively even though we are confined to the Hückel Hamiltonian.

In the present paper, we generalize the above theory to the chemical reactivity of photochemical reaction, and derive the Woodward-Hoffmann's rule in the presence of the radiation field.

General

As has been mentioned in early papers,[1,2] the total energy of the electronic system described by the Hamiltonian $\mathbf{H}$ is given as

$$\begin{aligned} E &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\mathbf{G}(z) \\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, \mathbf{HG}(z), \end{aligned} \tag{1}$$

where $\mathbf{G}(z)$ is the Green's function matrix with energy parameter z, and the integration contour, so called the Coulson contour, encloses only poles corresponding to the occupied levels. The second equality of Eq. 1. is obtained by adding and subtracting $\mathbf{H}$ to the right hand side of the first line and by noting that $(z-\mathbf{H})^{-1}=\mathbf{G}(z)$. It should be noticed that the expression of Eq. 1. is independent of the kind of representation.

Let us consider that the original system with Hamiltonian $\mathbf{h}$ is perturbed by a static interaction $\mathbf{v}$, under influence of the radiation field. The Hamiltonians to be considered are

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{v}, \tag{2}$$

$$\mathbf{H}_0 = \mathbf{h} + \mathbf{F}, \tag{3}$$

where $\mathbf{F}$ denotes the radiation field and the interaction between radiation and electron. We now investigate the extra energy defined by

$$\Delta E = \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[\mathbf{HG}(z) - \mathbf{H}_0\mathbf{G}^0(z)]. \tag{4}$$

Substituting Eqs. 2. and 3 into Eq. 4, we obtain

$$\begin{aligned} \Delta E &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[(\mathbf{h}+\mathbf{F}+\mathbf{v})\mathbf{G}(z) - (\mathbf{h}+\mathbf{F})\mathbf{G}^0(z)] \\ &\cong \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[(\mathbf{h}+\mathbf{F}+\mathbf{v})(\mathbf{G}^0(z)+\mathbf{G}^0(z)\mathbf{vG}^0(z)) \\ &\qquad - (\mathbf{h}+\mathbf{F})\mathbf{G}^0(z)] \\ &\cong \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[\mathbf{vG}^0(z) + (\mathbf{h}+\mathbf{F})\mathbf{G}^0(z)\mathbf{vG}^0(z)]. \end{aligned} \tag{5}$$

In this derivation, terms of first order with respect to $\mathbf{v}$ are retained. Further simplification shall be made: If we add and subtract z to the second term in Eq. 5, it yields that

$$\begin{aligned} &\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(\mathbf{h}+\mathbf{F})\mathbf{G}^0(z)\mathbf{vG}^0(z) \\ &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\mathbf{G}^0(z)\mathbf{vG}^0(z) \\ &\quad - \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(z-\mathbf{h}-\mathbf{F})\mathbf{G}^0(z)\mathbf{vG}^0(z). \end{aligned} \tag{6}$$

Noting that $\mathbf{G}^0(z)=(z-\mathbf{h}-\mathbf{F})^{-1}$, we can see that the second term of Eq. 6. cancel the first term by integration by part. Then we obtain

$$\Delta E \cong \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, \mathbf{vG}^0(z). \tag{7}$$

Certainly, Eq. 7. is exactly accordance with the first order term of our previous result (See Eq. 3. of Ref. 1.).

The Green's function, $\mathbf{G}^0(z)$ which describes the electronic structure of the system interacting with radiation, but without $\mathbf{v}$ is derived in the appendix as

$$\begin{aligned} \mathbf{G}^0(z) = [z-\mathbf{h}- &\sum_k \mathbf{f}^k n_k(z+\omega_k-\mathbf{h})^{-1}\mathbf{f}^k \\ &-\sum_k \mathbf{f}^k(1+n_k)(z-\omega_k-\mathbf{h})^{-1}\mathbf{f}^k]^{-1}. \end{aligned} \tag{8}$$

Here $\mathbf{f}^k$ is the interaction (matrix) between electron and radiation with the mode k, n_k, and ω_k are, respectively, number and angular frequency of photon with the mode k. The term with n_k is to do with absorption and the term with $(1+n_k)$ does emission.

First, if we confine ourselves, for simplicity, to the case of absorption with a single mode, it follows that

$$\mathbf{G}^0(z) = (z-\mathbf{h})^{-1} + (z-\mathbf{h})^{-1}\mathbf{f}n(z+\omega-\mathbf{h})^{-1}\mathbf{f}(z-\mathbf{h})^{-1}, \tag{9}$$

where we omitted the mode index k.

Substituting this into Eq. 7, and picking up the term relating with the radiation field, we obtain

$$\Delta E_f^a = n\,\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, \mathbf{v}(z-\mathbf{h})^{-1}\mathbf{f}(z+\omega-\mathbf{h})^{-1}\mathbf{f}(z-\mathbf{h})^{-1}. \tag{10}$$

The Green's function, $(z-\mathbf{h})^{-1}$ has been precisely investigated in II[3] of this series for the case of the Hückel model.

Remembering that Eq. 10 has an expression independent of the kind of representation, we can manipulate this by the representation that the Green's functions are diagonal, namely by the MO representation. Thus

$$\Delta E_f^a = n \sum_{i,j,k} v_{ij} f_{jk} f_{ki} \frac{1}{2\pi \mathrm{i}} \int_c \mathrm{d}z \frac{1}{(z-\varepsilon_i)(z-\varepsilon_j)(z+\omega-\varepsilon_k)}, \tag{11}$$

where ε_i is the orbital energy or the eigenvalue of **h**. Now we impose an experimental condition usually met in the laboratory: suppose that the radiation field has a strong intensity at the frequency

$$\omega \cong \varepsilon_L - \varepsilon_H, \tag{12}$$

where ε_L and ε_H are orbital energies of LUMO and HOMO, respectively, and the electronic carries the oscillator strength only between LUMO and HOMO. Then Eq. 11 becomes

$$\begin{aligned}\Delta E_f^a &= n v_{HH} |f_{HL}|^2 \frac{1}{2\pi \mathrm{i}} \int_c \mathrm{d}z \frac{1}{(z-\varepsilon_H)^2 (z+\omega-\varepsilon_L)} \\ &+ n v_{LL} |f_{LH}|^2 \frac{1}{2\pi \mathrm{i}} \int_c \mathrm{d}z \frac{1}{(z-\varepsilon_L)^2 (z+\omega-\varepsilon_H)}. \end{aligned} \tag{13}$$

The contour integration using the Coulson contour (Fig. 1) is easily carried out to yield

$$\begin{aligned}\Delta E_f^a &= n |f_{HL}|^2 \left\{ \frac{v_{LL}}{(\varepsilon_H-\varepsilon_L-\omega)^2} - \frac{v_{HH}}{(\varepsilon_L-\varepsilon_H-\omega)^2} \right\} \\ &\cong -n |f_{HL}|^2 v_{HH} / (\varepsilon_L-\varepsilon_H-\omega)^2, \end{aligned} \tag{14}$$

where the condition 12 is used to get the final result, neglecting the first term.

If we deal with the emission part of Eq. 8, the similar treatment gives rise to

$$\Delta E_f^e = (1+n) |f_{HL}|^2 \frac{v_{LL}}{(\varepsilon_L-\varepsilon_H-\omega)^2}. \tag{15}$$

Therefore, the net effect is

$$\begin{aligned}\Delta E_f &= \Delta E_f^a + \Delta E_f^e \\ &= |f_{HL}|^2 \{-n v_{HH} + (1+n) v_{LL}\} / (\varepsilon_L-\varepsilon_H-\omega)^2, \end{aligned} \tag{16}$$

the value of which should be negative for the photochemical reaction to take place. An analytical expression of the Woodward-Hoffmann's rule in the radiation field[4)] is thus obtained.

Electrocyclic Reaction

As an illustrative example, we want to apply the general result 16 to the electrocyclic reaction. The ring closure and ring opening reactions are to be discussed, based on the same model that has been explained in III[2)] of this seres. In Fig. 2 we display the model of the closure reaction of the conjugated chain molecule with N number of atoms; when the reaction path is con-rotatory the interaction between two ends, $v_{0,N-1}$ is positive, while when dis-rotatory, $v_{0,N-1}$ is negative.

In order to determine which of these two is likely to take place, it suffice to examine v_{HH} and v_{LL} in Eq. 16. As is shown in Fig. 2, the non-vanishing matrix elements of v are only $v_{0,N-1}$ and $v_{N-1,0}$, and then we can decompose these as follows

$$\begin{aligned} v_{AA} = \langle A|\mathbf{v}|A\rangle &= \sum_{s,t}^{\text{sites}} \langle A|s\rangle\langle s|\mathbf{v}|t\rangle\langle t|A\rangle, \ (A{=}L \text{ and } H) \\ &= 2v_{0,\,N-1}\langle 0|A\rangle\langle A|N-1\rangle \\ &= 2v_{0,\,N-1}\frac{1}{2\pi \mathrm{i}}\int_A \mathrm{d}z\, g(0, N-1;\ z). \end{aligned} \tag{17}$$

The final expression is obtained by the use of the definition of the Green's function; $g(0,N-1;z)$ being the $(0,N-1)$ matrix element of the propagator. The contour A encloses only the pole at ε_A. In other words, the partial bond order between the 0-th and $(N-1)$-th atoms of the chain molecule is given by the pole strength of the corresponding propagator (except for the spin factor). The propagator $g(0, N-1;\ z)$ is given in II as

$$\begin{aligned} &g(0, N-1;\ z) = \sin\theta / \sin(N+1)\theta, \\ &z = 2\cos\theta. \end{aligned} \tag{18}$$

Using these in Eq. 17, and noticing that

$$\theta_A = \pm \pi A/(n+1), \tag{19}$$

we obtain

$$v_{AA} = (-1)^{A+1} \frac{4v}{N+1} \sin^2 \pi A/(N-1), \tag{20}$$

when v is the abbreviation of $v_{0,N-1}$.

Here if we put $A=H$, and note that $L=H+1$, we obtain

$$\begin{aligned} \Delta E_f &= (-1)^H v \frac{4}{N+1} \frac{|f_{HL}|^2}{(\varepsilon_L-\varepsilon_H-\omega)^2} \\ &\times \left\{ n \sin^2 \frac{\pi H}{N+1} + (1+n) \sin^2 \frac{\pi(H+1)}{N+1} \right\} \\ &\propto (-1)^H v. \end{aligned} \tag{21}$$

This is the selection rule for the electrocyclic reaction in the presence of the radiation field. We shall examine in more detail conditions that the reaction takes place, or $\Delta E_f < 0$.

i) If H is even, the sign of v should be negative. In this case, the HOMO is designated to be the $2m$-th level (m is integer). If levels are doubly occupied up to the HOMO, namely concerned with $4m$ electrons system, the dis-rotatory reaction path is probable both for the ring closure and ring opening reaction.

ii) If H is odd, the sign of v should be positive. In this case, the HOMO is designated to be the $(2m+1)$-th level. If levels are doubly occupied up to the HOMO, namely concerned with $4m+2$ electrons system, the con-rotatory reaction path is probable both for the ring closure and the ring opening reaction. These selection rules are also tabulated in Table 1.

It should be mentioned that the above statements for the photochemical reaction give reverse prediction comparing with rules of the thermal electrocyclic reaction.[3)]

Concluding Remarks

We have explained that even for the photochemical reaction the propagator approach works as well as for the ground state properties. In our theory the excited state are *virtually* taken into account, so that not only the absorption process but also the emission process are involved to photochemical reactivity. In

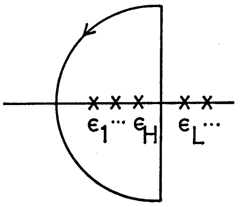

Fig. 1. Coulson contour and eigenvalues.

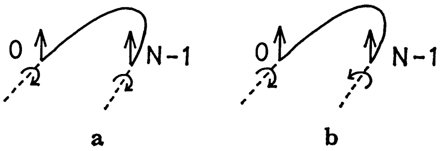

Fig. 2. Model for the ring closure reaction.
a: Con-rotatory, $v_{0,N-1}>0$, b: dis-rotatory, $v_{0,N-1}<0$.

TABLE 1. SELECTION RULES OF THE ELECTROCYCLIC REACTION IN THE PRESENCE OF RADIATION FIELD

Number of electron	Condition	Path	Type of ring
$4m$	$v<0$	dis	Hückel ring
$4m+2$	$v>0$	con	Möbius ring

order to derive the Woodward-Hoffmann's rule as is written in a usual way, we have impose a special (laboratory) condition such as the relation (12) and the comments following it. However this restriction does not harm our general procedure, which ensures possibilities to analyze the more complicated phenomena and to get clear cut results.

Appendix

We derive $\mathbf{G}^0(z)$, the propagator of the electronic system in the radiation field, in a field theoretical way by means of the equation of motion method, combined by the decoupling procedure.[5,6] The Hamiltonian of the system under investigation is

$$H_0=\sum_s \alpha_s a_s^+ a_s+\sum_{s,t}\beta_{st}a_s^+a_t+\sum_{s,t,k}f_{st}^k a_s^+ a_t(c_k^+ + c_k) + \sum_k \omega_k c_k^+ c_k. \tag{A1}$$

Here matrix elements are written in the AO representation, indices s and t indicate atomic sites, and a_s^+ (a_s) is the creation (annihilation) operator of electron at the site s, c_k^+ (c_k) is the creation (annihilation) operator of photon with mode k, f_{st}^k, and ω_k being the electron-photon coupling constant and the photon frequency, respectively. The representation used above is only for convenience. The final result will be independent of the kind of representation.

We investigate the Green's function defined by

$$G_{rs}^0(t) = -\mathrm{i}\langle T[a_r(t)a_s^+(0)]\rangle, \tag{A2}$$

where $\langle\cdots\rangle$ denotes the ground state average, and T is the time ordering operator. The equation of motion of $G_{rs}^0(t)$ is Fourier transformed with respect to time as

$$zG_{rs}^0(z) = \delta_{rs} + \langle\langle [a_r, H_0];\ a_s^+\rangle\rangle_z \tag{A3}$$

where

$$G_{rs}^0(z) \equiv \langle\langle a_r;\ a_s^+\rangle\rangle_z = \int_{-\infty}^{\infty}\mathrm{d}t\ e^{izt}\langle\langle a_r(t);\ a_s^+\rangle\rangle = \int_{-\infty}^{\infty}\mathrm{d}t\ e^{izt}G_{rs}^0(z). \tag{A4}$$

The commutator in Eq. A3 is evaluated as

$$[a_r, H_0] = \alpha_r a_r + \sum_u \beta_{ru}a_u + \sum_{u,k} f_{ru}^k(c_k^+ + c_k)a_u. \tag{A5}$$

Using this in Eq. A3, we obtain

$$zG_{rt}^0(z) = \delta_{rs} + \alpha_r G_{rs}^0(z) + \sum_u \beta_{ru}G_{us}^0(z) + \sum_{u,k} f_{ru}^k\langle\langle c_k^+ a_u;\ a_s^+\rangle\rangle_z + \sum_{u,k} f_{ru}^k\langle\langle c_k a_u;\ a_s^+\rangle\rangle_z. \tag{A6}$$

If we want to evaluate $G_{rs}^0(z)$ utilizing this equation, we have to evaluate the higer order Green's functions:

$$M_{us}^{k+}(z) = \langle\langle c_k^+ a_u;\ a_s^+\rangle\rangle_z,$$
$$M_{us}^{k}(z) = \langle\langle c_k a_u;\ a_s^+\rangle\rangle_z. \tag{A7}$$

Again we set the equation of motions for these: this time the Kronecker delta does not appear, calculation being a little tedious, but straigtforward, and we obtain

$$zM_{us}^{k+}(z) = (a_u-\omega_k)M_{us}^{k+}(z) + \sum_v \beta_{uv}M_{vs}^{k+}(z) + \sum_{v,l} f_{uv}^l\langle\langle c_k^+ c_l^+ a_v;\ a_s^+\rangle\rangle_z + \sum_{v,l} f_{uv}^l\langle\langle c_k^+ c_l a_v;\ a_s^+\rangle\rangle_z - \sum_{v,t} f_{vt}^k\langle\langle a_v^+ a_t a_u;\ a_s^+\rangle\rangle_z. \tag{A8}$$

At this stage we apply decoupling procedure as follows:

$$\langle\langle c_k^+ c_l a_v;\ a_s^+\rangle\rangle_z = \langle c_k^+ c_l\rangle\langle\langle a_v;\ a_s^+\rangle\rangle_z = \delta_{kl}n_k G_{vs}^0(z). \tag{A9}$$

Further we might assume that

$$\langle\langle c_k^+ c_l^+ a_v;\ a_s^+\rangle\rangle_z = 0, \tag{A10}$$

since the two photon process described by this Green's function should be negligibly important, and we assume also

$$\langle\langle a_v^+ a_t a_u;\ a_s^+\rangle\rangle_z = 0,$$

since this is a higher order correction to the electronic process. Accordingly Eq. A8 is approximately rewritten as

$$zM_{us}^{k+}(z) = (\alpha_u-\omega_k)M_{us}^{k+}(z) + \sum_v \beta_{uv}M_{vs}^{k+}(z) + n_k\sum_v f_{uv}^k G_{vs}^0(z), \tag{A11}$$

or in the matrix notation

$$z\mathbf{M}^{k+}(z) = (\mathbf{h}-\omega_k)\mathbf{M}^{k+}(z) + n_k\mathbf{f}^k\mathbf{G}^0(z),$$

or

$$\mathbf{M}^{k+}(z) = n_k(z-\mathbf{h}+\omega_k)^{-1}\mathbf{f}^k\mathbf{G}^0(z), \tag{A12}$$

where

$$\mathbf{h} = \boldsymbol{\alpha} + \boldsymbol{\beta}. \tag{A13}$$

In a similar way,

$$\mathbf{M}^{k}(z) = (1+n_k)(z-\mathbf{h}-\omega_k)^{-1}\mathbf{f}^k\mathbf{G}^0(z). \tag{A14}$$

Substituting Eqs. A12 and A14 into Eq. A6, we obtain

$$\begin{aligned} z\mathbf{G}^0(z) &= \mathbf{1} + \mathbf{h}\mathbf{G}^0(z) + \sum_k \mathbf{f}^k\mathbf{M}^{k+}(z) + \sum_k \mathbf{f}^k\mathbf{M}^{k}(z) \\ &= \mathbf{1} + \mathbf{h}\mathbf{G}^0(z) + \sum_k \mathbf{f}^k n_k(z-\mathbf{h}+\omega_k)^{-1}\mathbf{f}^k\mathbf{G}^0(z) \\ &\quad + \sum_k \mathbf{f}^k(1+n_k)(z-\mathbf{h}-\omega_k)^{-1}\mathbf{f}^k\mathbf{G}^0(z), \end{aligned}$$

or

$$\mathbf{G}^0(z) = [z-\mathbf{h}-\sum_k \mathbf{f}^k n_k(z-\mathbf{h}+\omega_k)^{-1}\mathbf{f}^k - \sum_k \mathbf{f}^k(1+n_k)(z-\mathbf{h}-\omega_k)^{-1}\mathbf{f}^k]^{-1}. \tag{A15}$$

References

1) T. Ohmae, K. Nishikawa, K. Deguchi, and S. Aono, *Bull. Chem. Soc. Jpn.*, **54**, 2857 (1981).

2) S. Aono and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **53**, 3418 (1980).

3) S. Aono, T. Ohmae, and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **54**, 1645 (1981).

4) R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Academic Press, New York and London (1970).

5) D. N. Zubarev, *Soviet. Phys. Uspekhi.*, **3**, 320 (1960).

6) K. Nishikawa and S. Aono, *Prog. Theoret. Phys. (Kyoto)*, **50**, 830 (1973).