Theory of Thermo- and Photo-Chemical Reactivity and Its Applications

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A theory of the chemical reactivity for thermo- and photo-chemical reactions is formulated in terms of the Green's function and applied to recent observations: the photo-magnetization of a molecular crystal obtained by reduction from 2,2'-biindenyl observed by Tanaka et al., and the internal rotation of the methyl group in toluene and *o*-, *m*-, and *p*-fluorotoluenes observed by Ito et al.

Theories of chemical reactivity have been given in various styles: Coulson et al. presented the reactivity indices, namely charge density, bond order, free valence, and so on, which might be quantum-mechanical counterparts of the classical concepts of chemical reactivity.[1] The frontier orbital analysis developed by Fukui is more quantal, since the phases of the highest occupied and lowest vacant orbitals play the central roles.[2] Our theory[3] in terms of the Green's function may be read as follows. If a spacial conformation of the activated complex is assumed, then what type of reaction path is likely is judged by estimating the extra energy associated with the reaction path in question. Recently, some interesting observations have been made, which will be explained separately in the section concerning applications. Now, our theory is reformulated in a fashionable form to make these applications easy.

Theory

The Hamiltonian of the system in question is written as

$$H = H_0 + v. \tag{1}$$

In any one-particle approximation, once we obtain the one-particle state, $|i>$, which diagonalyze the unpeturbed Hamiltonian H_0, we can denote by a suitable choice of the one-particle energy, ϵ_i.

$$H_0 \, | \, i >= \epsilon_i \, | \, i > \text{ or } H_0 = \sum_i | \, i > \epsilon_i < i \, |. \tag{2}$$

Here, the set $\{|i>\}$ is assumed to be complete. The perturbation, v which drives the chemical reaction is imagined by chemists usually to be an action acting on the site or between sites,

$$v = \sum_{rs} | \, r > v_{rs} < s \, |, \tag{3}$$

where the set $\{|r>\}$ is also assumed to be complete. The transformation between $|i>$ and $|r>$ is written as

$$| \, i >= \sum_r | \, r > < r \, | \, i >, \tag{4}$$

of which spacial representation is called the molecular orbital constructed by the linear combination of atomic orbitals; the matrix element of this transformation is the LCAO coefficient.

1. Thermo-Chemical Reaction. The thermal reaction is a ground-state phenomenon, since the thermal energy is in magnitude much less than electronic energy. The resolvent or the Green's operator for H is expanded as

$$
\begin{aligned}
G(z) &= \frac{1}{z - H} = \frac{1}{z - H_0 - v} \\
&= \frac{1}{z - H_0} + \frac{1}{z - H_0} v \frac{1}{z - H_0} + \frac{1}{z - H_0} v \frac{1}{z - H_0} v \frac{1}{z - H_0} + \cdots \\
&= G_0(z) + G_0(z) v G_0(z) + G_0(z) v G_0(z) v G_0(z) + \cdots,
\end{aligned} \tag{5}
$$

where z is the energy parameter, and

$$G_0(z) = \frac{1}{z - H_0} = \sum_i \frac{| \, i > < i \, |}{z - \epsilon_i}. \tag{6}$$

Once we obtain the Green's function, almost all physical quantities can be derived from it.[4] For instance, the bond order, q_{rs} between sites r and s is obtained as

$$
\begin{aligned}
q_{rs} &= \frac{1}{2\pi i} \int_C dz < r \, | \, G_0(z) \, | \, s > \\
&= \frac{1}{2\pi i} \int_C dz \frac{< r \, | \, i > < i \, | \, s >}{z - \epsilon_i} \\
&= \sum_i^{occ} < r \, | \, i > < i \, | \, s >,
\end{aligned} \tag{7}
$$

where the contour integration is carried out enclosing the hole states (so-called the Coulson contour). We assume that the sum in the above also includes the spin sum.

Since the total energy of the system is given by

$$
\begin{aligned}
E &= \text{Tr} \frac{1}{2\pi i} \int_C dz H G(z) \\
&= \text{Tr} \frac{1}{2\pi i} \int_C dz z G(z),
\end{aligned} \tag{8}
$$

the extra energy due to v is

$$\Delta E = \text{Tr} \frac{1}{2\pi i} \int_C dz \, z (G(z) - G_0(z))$$

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$$= \text{Tr}\frac{1}{2\pi i}\int_C dz\ z(G_0 v G_0 + G_0 v G_0 v G_0 + \cdots)$$

$$= \text{Tr}\frac{1}{2\pi i}\int_C dz(G_0 v + \frac{1}{2}G_0 v G_0 v + \cdots + \frac{1}{n}(G_0 v)^n + \cdots)$$

$$= \text{Tr}\frac{-1}{2\pi i}\int_C dz \log(1 - G_0 v)$$

$$= \frac{-1}{2\pi i}\int_C dz \log\det(1 - G_0 v). \tag{9}$$

·The third line is obtained from the second by integration by parts and the invariance character for the circulation inside Tr is used. The integrand in the last line is rewritten as

$$\log(1 - G_0 v) = \log G_0(G_0^{-1} - v) = \log(G_0/G), \tag{10}$$

from which we can clearly understand this yields ΔE. In considering the chemical reactivities, it is sufficient to use the first-order or up to the second-order terms with respect to v in Eq. 9.

From the first term in the third line of Eq. 9, we obtain

$$\Delta E^{(1)} = \sum_{rs} q_{rs} v_{sr}, \tag{11}$$

where v is assumed not to depend on z. Thus, the first-order energy correction is expressed by combining the bond order and coupling. The second-order energy correction is obtained from the second term in Eq. 9 as

$$\Delta E^{(2)} = \sum_{rs}\sum_{tu} v_{rs}\pi_{rs;tu} v_{tu}, \tag{12}$$

where $\pi_{rs;tu}$ is the polarizability.[1,5] The bond order or the polarizability is a kind of correlation function with a wave character, which changes its phase from place to place. The bond order is sometimes misunderstood as if it were the charge density at the bond reagion. The importance of the long-range bond order should be stressed, whose sign, positive or negative, is crucial for the chemical reactivity, combined with the coupling parameter, v.

2. Photo-Chemical Reaction. First of all, we introduce the radiative pertubation, f inducing the electronic excitation in a molecule, before taking into account v which causes the chemical reaction. We then rewrite Eq. 4 as[6]

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

$$= \frac{1}{z - H_0} + \frac{1}{z - H_0}f\frac{1}{z - H_0} + \frac{1}{z - H_0}f\frac{1}{z - H_0}f\frac{1}{z - H}. \tag{13}$$

This is the Dyson equation, which is explicit up to the second order with respect to f. The Dyson equation is an integral equation, since on the right-hand side we have $G(z)$ itself. The reason why the Dyson equation is employed here instead of the perturbational expansion in the previous section is to carry out an infinite summation with respect to f, we can then naturally obtain the transiton probability, as shown in the following. It is instructive to employ projection operators, P and Q, which project out the ground and excited states respectively. Namely,

$$P + Q = 1,$$

$$P = |P\rangle\langle P|, \quad Q = |Q\rangle\langle Q|, \tag{14}$$

and

$$|P\rangle = |N, n_k\rangle \approx |H, n_k\rangle$$

$$|Q\rangle = \sum_i |X_i, n_k - 1\rangle \approx |L, n_k - 1\rangle, \tag{15}$$

where N and X_i are the group of levels occupied in the respective states, the states symbollically labeled with the highest occupied level H and the lowest vacant level L, implicitly assume transitions between these two levels. The terms n_k and $n_k - 1$ are the corresponding photon numbers.

It is clear that

$$(P + Q)\frac{1}{z - H}(P + Q) \equiv (P + Q)G(P + Q)$$

$$= G^P + G^Q + G^{PQ} + G^{QP}. \tag{16}$$

We begin by estimating G^P. Since for P and Q, G_0 is diagonal, while f is off-diagonal, it is obvious that the second term in Eq. 13 vavishes. We thus obtain

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

$$= P\frac{1}{z - H_0}P + P\frac{1}{z - H_0}PfQ\frac{1}{z - H_0}QfP\frac{1}{z - H}P. \tag{17}$$

This is easily solved as

$$G^P = [(G_0^P)^{-1} - f_{PQ}G_0^Q f_{QP}]^{-1}. \tag{18}$$

Similarly,

$$G^Q = [(G_0^Q)^{-1} - f_{QP}G_0^P f_{PQ}]^{-1}. \tag{19}$$

In order to evaluate G^{PQ}, the Dyson equation,

$$\frac{1}{z - H} = \frac{1}{z - H_0} + \frac{1}{z - H_0}f\frac{1}{z - H}. \tag{20}$$

is used to obtain

$$G^{PQ} = G_0^P f_{PQ}G^Q.$$

Using Eq. 15, we obtain

$$f_{PQ} = \langle H, n_k|f|L, n_k - 1\rangle = f_{HL}\sqrt{n_k}, \tag{21}$$

where f_{HL} is the matrix element of the spacial part of f, and the manipulation of photon operators is implicitly carried out. Thus it proceeds that

$$f_{PQ}G_0^Q f_{QP} = \sum_k n_k|f_{HL}|^2\frac{1}{z - \epsilon_L - (n_k - 1)\omega_k}$$

$$\approx \sum_k n_k|f_{HL}|^2\frac{1}{\epsilon_H + n_k\omega_k - \epsilon_L - (n_k - 1)\omega_k}$$

$$\approx |f_{HL}|^2\int d\omega_k\rho(\omega_k)n_k\frac{1}{\omega_k - \epsilon_{LH}}, \tag{22}$$

where $\rho(\omega_k)$ is the state density at ω_k, then the energy parameter z in the first line is approximately replaced by the pole of G_0^P in the second line. We now recover the imaginary parts of orbital energies as

$$\epsilon_{LH} = (\epsilon_L - i\eta) - (\epsilon_H + i\eta) = \epsilon_L - \epsilon_H - i\eta, \tag{23}$$

where, for example, the positive imaginary (infinitesimal) part of the hole state energy is put so that the hole state vanishes in the infinite past of time. We then can carry

out integration with ω_k, replacing the state density by its appropriate average value, $n_k\overline{\rho(\omega_k)}$,

$$f_{PQ}G_0^Q f_{QP} = |f_{HL}|^2 n_k\overline{\rho(\omega_k)}\,i\pi, \tag{24}$$

where the relation

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

was used. After integration, the real part is omitted, since it gives merely the energy shift and does not concern the particle density.

Finally, we obtain

$$G^P = \sum_i \frac{1}{z - (\epsilon_i + i\eta) - (\epsilon_H - iw_{HL}) - n_k\omega_k} \tag{25}$$

with

$$w_{HL} = \pi|f_{HL}|^2 n_k\overline{\rho(\omega_k)}. \tag{26}$$

Similarly we obtain

$$G^Q = \sum_i \frac{1}{z - (\epsilon_i - i\eta) - (\epsilon_L + iw_{HL}) - (n_k + 1)\omega_k} \tag{27}$$

by interchanging $H\leftrightarrow L$ and replacing ω_k by ω_k+1. Notice the signs of imaginary parts in G^P and G^Q.

Let us evaluate the bond orders:

$$\begin{aligned}
q_{rs}^P &= \int \frac{dz}{2\pi i} <r|G^P|s> \\
&= \sum_i \int \frac{dz}{2\pi i} \frac{<r|H><H|s> + <r|i><i|s>}{[z - (\epsilon_i + i\eta) - (\epsilon_H - iw_{HL}) - n_k\omega_k]} \\
&= q_{rs}^0 - <r|H><H|s> = q_{rs}^0 - q_{rs}^H, \tag{28}
\end{aligned}$$

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

$$q_{rs}^Q = <r|L><L|s> = q_{rs}^L, \tag{29}$$

In this case, the integration carried out on the upper half plane yields only the partial bond order of the lowest vacant level. The off-diagonal terms in Eq. 27 give negligible contributions proportional to f_{HL} divided by energy difference. Therefore we obtain the result,

$$\begin{aligned}
q_{rs} &= q_{rs}^P + q_{rs}^Q \\
&= q_{rs}^0 - q_{rs}^H + q_{rs}^L = q_{rs}^0 + q_{rs}^{LH}. \tag{30}
\end{aligned}$$

The last term is the partial bond order of LUMO substrated by that of HOMO, and directly concerns the photo-excitation, f. If we take into account the perturbation, v driving the chemical reaction, and follow the procedure to arrive at Eq. 11, it immediately results that

$$\Delta E^{(1)} = \text{Tr}\int_C dz G(z)v, = \text{Tr}\{qv + q^{LH}v\}, \tag{31}$$

where, as previously mentioned, v is independent of z. 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-exitaion, f is

$$\Delta E_f^{(1)} = \sum_{rs} q_{rs}^{LH} v_{sr}. \tag{32}$$

Other physical quantities than the energy can be obtained in a similar way. This is a double-perturbational approach. We now proceed to analyze the observations.

Photo-Magnetization

K. Tanaka et al.[7] have reported their experimental work as follows: The reduction of 2,2'-biindenyl with Zn–ZnCl₂ reagent gives the corresponding compounds (**A** in Fig. 1) of yellow needles. This yellow needles are turned to reddish-purple crystals upon exposure to sunlight for a short time. In the dark, the reddish-purple crystals return to yellow ones. In an ESR spectrum, the reddish-purple crystals give strong signals which are assignable to a triplet biradical, such as (D=13.78 G, E=1.377 G, g_{xx}=2.0026, g_{yy}=2.0027, g_{zz}=2.0030). These D and E tell that the distance between the triplet electrons is about 12.6Å, so that each electron almost localizes at the aromatic rings on both sides of this molecule. However, N,N'-dimethyl-indigo, which is a nitrogene analogue of **A**, is unexpectedly photo-stable; namely it is unable to induce the photochemical magnetization.

The addition of hydrogen to the five-membered ring of **A** does not necessarily spoils the aromaticity of this compound. We would rather consider a hyperconjugation at that site; in other words, even if the orbital hyblidization of carbon changes from sp₂ to sp₃, the π component still remains.

In the following, we examine the mechanism of these phenomena, concentrating on the double bond-character of the central bond. In this respect, we employ the prototype species, **I** and **II**, for **A** and its nitrogene analogue, respectively, and further employ **III** (biphenyl) as a reference species (see Fig. 1).

Analysis. The above-mentioned observations can be explained by a conformation change, namely, twisting around the central bond of **A** or **B**. From this view point, we are reminded of the electronic structure of twisted ethylene.

As is well known, the excitation energies from the ground state to the singlet or the triplet exited states in which the excitation takes place from the i-th occupied level to the j-th vacant level, are given respectively as

$$E_{ij}^1 = \epsilon_j - \epsilon_i - <ii|jj> +2 < ij|ji > \tag{33}$$

and

$$E_{ij}^3 = \epsilon_j - \epsilon_i - <ii|jj>, \tag{34}$$

where ϵ_i and ϵ_j are the orbital energies of the molecular orbitals, ψ_i and ψ_j, respectively. Also,

$$< ii|jj > = \int dv(1)dv(2)\psi_i(1)\psi_i(1)\frac{1}{r_{12}}\psi_j(2)\psi_j(2) \tag{35}$$

and

$$< ij|ji > = \int dv(1)dv(2)\psi_i(1)\psi_j(1)\frac{1}{r_{12}}\psi_j(2)\psi_i(2), \tag{36}$$

are the so-called direct and exchange integrals, respectively. Note that the energy of the triplet state is lower by twice of the exchange integral than that of the corresponding singlet state.
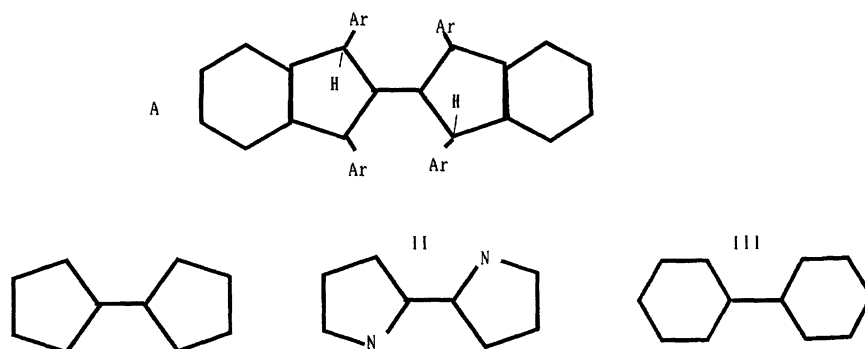
Fig. 1.

Therefore, if we want to treat the singlet–triplet separation, the electron–electron interaction must be taken into account explicitly in a proper approximation. Since the ground state of a molecule is usually the singlet, the excitation to the triplet state is spin-forbidden. However, we always have a small possibility to get the triplet state through the spin–orbit interaction.

In the π approximation, the bonding and anti-bonding orbitals of ethylene are written, respectively as

$$\psi_1 \sim (a+b)$$
$$\psi_2 \sim (a-b), \tag{37}$$

where a and b are the $2p\pi$ atomic orbitals. It is known that, in the ground state, the planar structure is stabilized by the double bond, while in the excited state, this molecule tends to twist around the central bond. For the twisted structure of 90 degrees, where two CH_2 planes are perpendicular to each other, the above two orbitals become non-bonding, so that $\epsilon_1 = \epsilon_2$ in Eqs. 32 and 33. However, due to the exchange integral, the triplet state is lower in energy[8] than the singlet state. At this point some comments should be added. A more elaborate calculation[9] insists that, in the perpendicular conformation, the single determinant as the state function is not adequate; in order to explain the intricate energy spectra, the σ states should be combined with the π states to carry out an extended configuration interaction. However, since we are now dealing with molecules very much larger than ethylene, we must be satisfied with a simple treatment in a prospect of physical intuition.

Let us briefly review the theory for chemical reactivity. The extra energy to the first order of the pertubation, v is written in Eqs. 9 and 32 as

$$\Delta E \sim \mathrm{Tr}\, qv \quad \text{(thermo-chemically)}, \tag{38}$$

and

$$\Delta E_f \sim \mathrm{Tr}\, q^{LH} v \quad \text{(photo-chemically)}, \tag{39}$$

where Tr is the trace operation, and q is the bond order matrix, while $q^{LH}(=q^L-q^H)$ is the diffrence between the partial bond order matrices, for the lowest vacant and the highest occupied orbitals. Here, the L and H orbitals are understood to be connected by the radiation field with frequency, ω. If ΔE or ΔE_f is negative, the reaction drived by v is likely.

First of all, the double-bond character of the central bond of species (**I**, **II**, and **III**) must be investigated. This is usually done by writing the Kekulé structures for these. As is easily done, we can put the double lines for the central bonds of **I** and **II**. While, for **III** the Kekulé structure in which the central bond is double is hardly written; therefore, we say that the central bond of **III** is almost single. However, this consideration is not always correct. It is preferable to discuss this problem in terms of the π-bond order of the bond in question.

In the case of ethylene, the π-bond order of the C–C bond is 1, indicating that this bond is purely double, while that of ethane is 0, telling us that it is single. Other conjugate molecules distribute between these two,[10] for example, the bond order of the adjacent sites in benzene is 2/3. In the following, we list the bond orders of the central bonds of species, **I**, **II**, and **III**.

By observing the values of q we can infer whether the bond under consideration has the double-bond character or not. The value of q of **I**, 0.625 nearly equal that of benzene, then we can see this bond has the double bond character. While, those for **II** and **III** are about 0.370, indicatig that these bond are almost single. This conclusion is reasonable for **III**, but is unexpected for **II**, against the consideration using the Kekulé structure. The reasoning for this lies in the number of electrons. Since the nitrogene atoms of the five-member rings supply totally two electrons to the conjuagated system, the number of electrons suject to conjugation in **II** is the same as in **III**. We must remember that, in considering the chemical reactivity, the number of electrons is crucial, while the number of sites is not so much. In this respects, **II** resembles **III**.

We now turn to the twisting motion of the molecules under consideration. If they twist by an angle of θ, the resonance integral between the $2p\pi$ atomic orbitals of the central bond varies with the factor of $\cos\theta$, while the electron–electron interactions are almost independent of the geometry change. As the molecules twist, the value of the resonance integral with the minus sign becomes less and less in absolute value, so that the perturbation, v due to this motion must have the positive sign. By observing the values of the bond orders in Table 1 we can see that the extra energies for **I**, **II**, and **III** given by Eq. 38 are all positive. Therefore, three species are expected not to twist thermo-chemically in the ground

Table 1.   Bond Orders of the Central Bonds for **I**, **II**, and **III**

	q	q^{LH}
I	0.665	−0.156
II	0.370	0.246
III	0.369	0.261

state. On the other hand, the extra energy given by Eq. 39 is negative only for **I**. It is thus presumable that only this molecule can twist in the radiation field. We can understand that, on the same footing, species **II** and **III** are both optically stable. Here, we must stress again that it is not the shape of molecule, but the electron number that is fatal for the chemical reactivity.

The above speculations will be confirmed by a numerical calculation which requires us to take the electron–electron interaction into account. The simplest way to this end may be the Pariser–Parr–Pople approximation. The electron–electron interactions are estimated by the Nishimoto–Mataga parametrization,[11] which is a kind of classical approximation including the screening effect. Calculations are carried out for every species step by step at the twisted angles. The results are shown in Figs. 2a and 2b, which are for species **I** and **II**, respectively. The figure for **III** is omitted, since it is very similar to that for **II**. Here S_0, S_1, and T_1 denote the ground state, the singlet first excited state, and the triplet first excited state, respectively

As expected, only **I** which is the proto-type for **A**, displays a distinguished behavior to twist to the perpendicular structure which is most stable in the radiation field. The whole pattern of Fig. 2a looks very much similar to that of ethylene in the π approximation, which is not presented here. It is needless to say that although the numerals of the calculated result are at most semi-quantitative, the qualitative features of figures should be believable.

Finally, we return back to the original molecule, **A** (reddish purple one). Even if unpaired electrons are produced, the recombination of these will easily take place. Aromatic rings at both ends of the molecule effectively capture the unpaired electrons and help to make this molecule electrically stable.

Observations have been made in the solid state of a molecular crystal. If an external magnetic field is put on, the bulk of biradicals may be, to some extent, magnetized as a whole. This is a phase transition to yield a new thermodynamic phase. We are not concerned with this problem, the general treatment being found in the text-books of solid state physics.[4]

Internal Rotation of Methyl Group in Toluene and Substituted Toluenes

Recently, detail observations and analyses have been made concerning the internal rotation of the methyl group in various species.[12—16] In the followings we are concerned with toluene[12] and o-, m-, and p-fluorotoluenes.[13] Experimental observations are: Except for o-fluorotoluene the rotation of the methyl groups are almost free in the ground state (S_0) and considerably hindered in the first excited state (S_1). How-
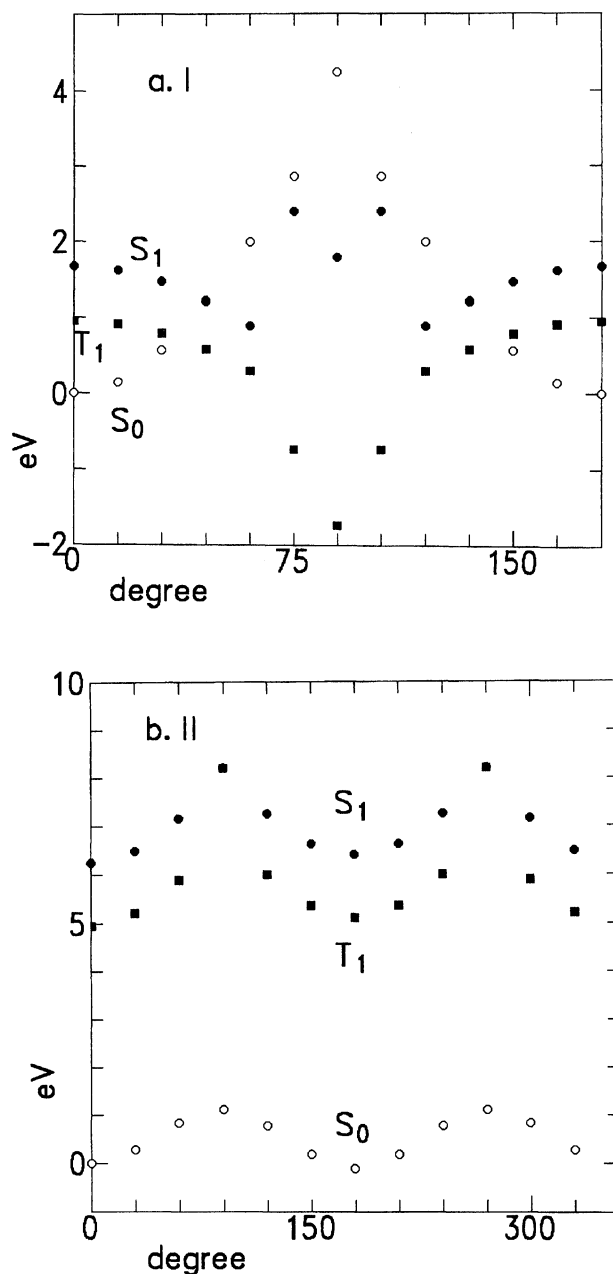

Fig. 2.   State energies vs. twist angles. S_0: ground, S_1: singlet excited, T_1: triplet excited.

ever, in the case of o-fluorotoluene, the outlook is entirely changed. For the rotation of the methyl group, there is a large potential barrier in the ground state, which is, however, greatly reduced in the first excited state. Simply speaking, the rotation of the methyl group is hindered in the ground state, and tends to be free in the excited state. It is also found that the most stable conformation of the methyl group in the ground state is most unstable in the first excited state. That is to say, the phase of the barrier is reversed.

The origin of the potential barrier for the internal rotation of the methyl group is so mischievous that various explanations should be admitted.[10] Here, we postulate a fundamental idea that the potential barrier is due to electrostatic interac-

tions, and that the charge deviations from the standard value responsible for this are caused by hyperconjugation. However, as will be seen in the following, the present treatment gives merely a qualitaive explanation for the observations.

Hyperconjugation.   The group orbitals for H_3 in the methyl radical are constructed of three hydrogene 1s orbitals, a, b, and c:

$$A = \frac{1}{\sqrt{6}}(2a - b - c),$$

$$B = \frac{1}{\sqrt{2}}(b - c),$$ (40)

$$C = \frac{1}{\sqrt{3}}(a + b + c),$$

where C is a σ-type orbital, while A and B are π-type orbitals, which are conjugate with other π orbitals of the system. In the above the overlap integrals between the atomic orbitals are neglected. Throughout the present investigation this approximation is used; we also employ the Hückel approximation, since we need not account for the electron–electron interaction explicitly. Even if a better approximation be used, improvements in the molecular orbitals are not so significant for the present purpose.

In Fig. 3, three hydrogens are shown by apices of a triangle perpendicular to the benzene plane. The benzene plane is the xy plane, and the y-axis is the rotation axis of the methyl group. We assume that, at the beginning, the hydrogene a is just on the xy plane, and the methyl group begin to rotate through an angle of θ. Then, a pseudo π-orbital (along the z axis) becomes

$$\pi = B\cos\theta + A\sin\theta \equiv \chi_1,$$ (41)

and another π-type orbital orthogonal to the above is

$$\bar{\pi} = -B\sin\theta + A\cos\theta.$$ (42)

Let us construct the π-molecular orbitals, ψ_i by linear combination of the atomic orbitals, as

$$\psi_i = \sum_r \chi_r C_{ri}.$$ (43)

The numbering for the atomic sites is given in Fig. 4.

The matrix elements of the Hückel Hamiltonian are as follows:[17] The coulomb integral of the benzene carbon is put
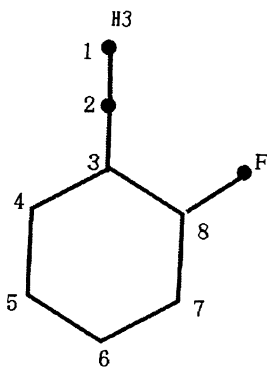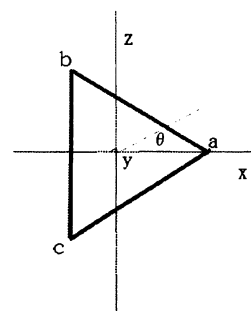

Fig. 3.

Fig. 4.

as the standard in the energy scale, and others are measured from this (in the $|\beta|$ unit of benzene); that for the methyl carbon is $\alpha_2 = 0.1$, for the pseudo π orbital of the methyl group, $\alpha_1 = 0.4$, and for the fluorine atom, $\alpha_F = -3.0$. As for the resonance integrals, those for carbon–carbon in benzene are $\beta_{rs} = -1$, and for others, $\beta_{23} = -0.8$, $\beta_{12} = -3.0$, and $\beta_{CF} = -0.6$.

Once this eigen-value problem is solved, the square of C_{ri} is the lebel i contribution to the charge density at the r site. In the case of the methyl group, this is shared by three methyl hydrogens. As to speak the a hydrogen, $<a|i>$ is the probability amplitude of finding the i-th electron at the a site, and the similar contributions of electrons in χ_2 and C orbitals should be taken into account. Then the π electron density at site a, ρ_a is

$$\rho_a = \sum_i^{occ} <a|i>^2 + <a|\bar{\pi}_2>^2 + <a|C>^2,$$ (44)

where the summation includes the spin sum. The term $<a|C>^2$ gives 1/3, while other two show the θ dependence. Thus we obtain, omitting the constant factor:

$$\rho_a = \rho_H \frac{2}{3}\sin^2\theta,$$

$$\rho_b = \rho_H(\frac{1}{6}\sin^2\theta + \frac{1}{2}\cos^2\theta - \frac{1}{2\sqrt{3}}\sin 2\theta),$$ (45)

$$\rho_c = \rho_H(\frac{1}{6}\cos^2\theta + \frac{1}{2}\sin^2\theta + \frac{1}{2\sqrt{3}}\sin 2\theta),$$

where ρ_H is, for the ground state,

$$\rho_H = \sum_i^{occ} <1|i>^2 - 1,$$ (46)

and for the excited states, the electron densities for levels in question. At a glance these expressions are a little curious becasus ρ_a, ρ_b, and ρ_c are not equal, but give a θ dependence. However, if we take average with respect to θ (assumng free rotation) over one period, these becomes identical (=1/3).

However when the molecule is in the radiation field, the effective charge densities directly associated with the photochemical phenomena are given by the diagonal part of Eq. 30,

$$\rho_H = C_{1L}^2 - C_{1H}^2,$$ (47)

which is not the charge density of the excited configuration.

Potential Barrier for the Internal Rotation of the Methyl Group.   The potential barrier for the internal rotation of

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the methyl group is obtained by

$$P(\theta) = \sum_{r>s} \rho_r \rho_s / R_{rs}, \tag{48}$$

where R_{rs} is the internuclear distance between sites r and s. Here, r refers to the methyl hydrogene atoms are s to others (not on the rotation axis, y). The dependence on the rotation angle, θ arises from the former. Their θ-dependent positions are:

$$x_r = l\cos \theta_r, \quad z_r = l\sin \theta_r, \tag{49}$$

where $l=\overline{Oa}$ in Fig. 3, and

$$\theta_r = \theta, \ \theta + 2\pi/3, \ \theta + 4\pi/3, \ \text{for } a, b, \text{and } c, \text{respectivly.} \tag{50}$$

Analysis.   In the following, the analysis is made for toluene and fluorotoluenes; however, for the latter, o-fluorotoluene is mainly investigated, since the *para*-substitution does not change the symmetry of toluene and the *meta*-substitution, as is well known, has little effect on the π levels of the pre-substituted species. Thus, for these two species, we cannot expect a very great change. Therefore, the analysis for the latter two is merely supplemental.

Since the rotation of the methyl group in toluene is very subtle, the pure theoretical analysis of this problem seems to be beyond the accuracy of the current technique of computational quantum chemistry. For such a reason we would rather begin by treating o-fluorotoluene.

o-Fluorotoluene.   This molecule shows distinct characteristics from those of toluene. The fluorine atom, substituting at the o-position, has two π electrons taking part in conjugation. Further, the conjugation between the π orbitals of fluorine and the methyl group is considered to be a newly arising perturbation. Whether the internal rotation of the

methyl group tends to be free or hindered may be considered as an effect of this conjugation.

First of all, we keep in mind that this perturbation, v_{1F} has the negative sign. For the standard conformation of the H_3 group, the extra due to this perturbation are given by (see Eqs. 38 and 39)

$$\Delta E = v_{1F}q_{1F} \quad \text{(for the ground state)}$$

and

$$\Delta E_f = v_{1F}q_{1F}^{LH} \quad \text{(for the excited state).}$$

From Table 2 we can see that $q_{1F}=0.019$ and $q_{1F}^{LH}=-0.204$. Thus, the extra energy of the ground state is negative, while that of the excited state (exactly speaking, for the system in the radiation field) is positive, from which we infer that the ground state becomes more stable and the excited state unstable. Namely, the rotation of the methyl radical tends to be hindered in the ground state and be free in the presence of the radiation field.

Detail informations are given from the feature of the potential barrier. For the ground state, the charge density at each site in the ground-state configuration is used to obtain an agreement that is not so bad compared with the observation (see Table 3 and Fig. 5a).

As for the excited state, exactly speaking for the species in the radiation field, discussions are required. In treating the photochemical reactivity in the radiation field, it has been stated that q^{LH}, or the difference between the partial bond order of the lowest vacant and that of the highest occupied levels, plays a central part. However, since the excited state has a rather long lifetime compaired to the period of the vibrational or rotational motion, it is usually considered that the electron in the methyl group equally sees not only q^{LH} (of

Table 2. Bond Orders

	o-Fluorotoluene	m-Fluorotoluene	p-Fluorotoluene	Toluene
q_{1F}	0.019	0.002	-0.014	
q_{1F}^{LH}	-0.204	0.017	0.027	
q_{14}	-0.118	-0.118	-0.118	-0.118
q_{14}^{LH}	0.058	0.085	0.04	0.202

Table 3. Barrier Heights for the Internal Rotation of the Methyl Group (Unit cm^{-1})

	S_0	S_1	Note	Rotation angle (degree)
o-Fluorotoluene	-17.0	3.3	$q_M=0.$	60
	$(-123.)$	(6.8)	$q_B=0.$	
m-Fluorotoluene	-2.53	-10.1	$q_M=0.$	60
	(-16.9)	$(-124.)$	$q_B=0.$	
p-Fluorotoluene	-0.021	-0.062	$q_M=0.$	30
	(-4.8)	(-33.7)	$q_B=0.$	
Toluene	-4.3	-8.7	$q_M=-0.2$	30
	$(-10.)$	$(-25.)$	$q_B=-0.2$	

S_0, the ground state; S_1, the first excited state. The upper values theoretical, and the lower (in parentheses) the observed. The positive sign designates the barrier height, and the negative sign the barrier depth. q_M and q_B are parameters which indicate the polarizations of the methyl hydrogen and the benzene hydrogen, respectively, in the σ state; for example, the negative sign means an excess of positive charge.
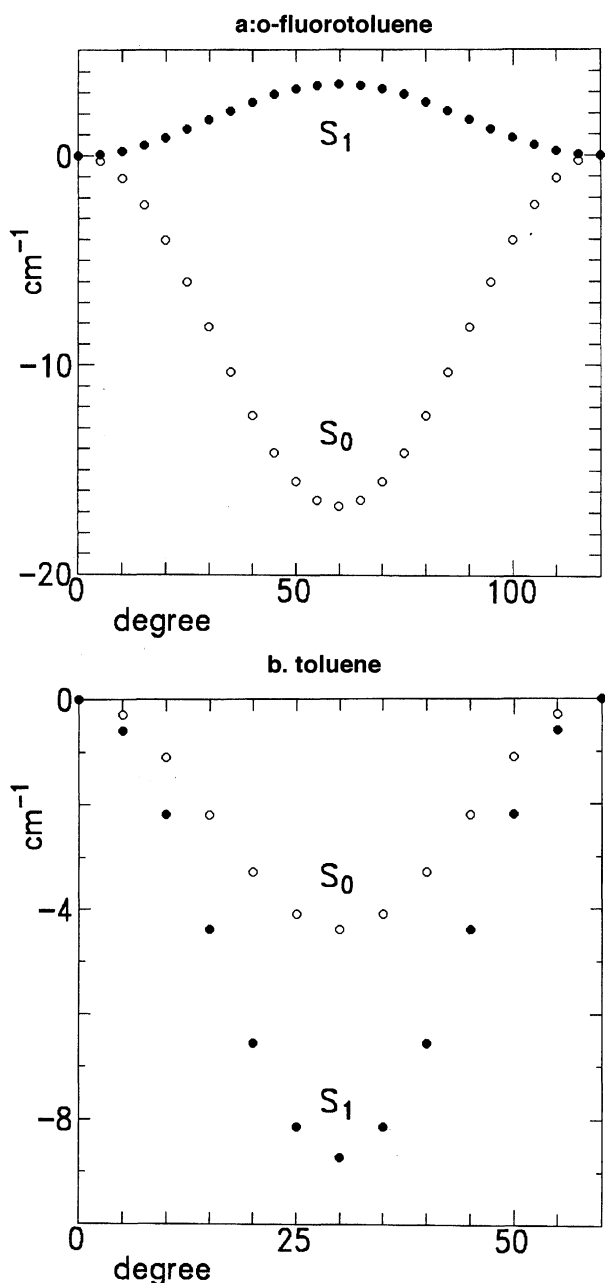
a:o-fluorotoluene

b. toluene

Fig. 5. Barrier for the methyl rotation.

which diagonal elements), but also others in the excited configuration. However, if we proceed along this understanding, the procedure completely fails to reproduce the observed results. The results for the excited states in Table 3 and Fig. 5 are those obtained merely by the use of q^{LH} in the right-hand side of Eq. 46. The calculated values are around one tenth of the observed ones. However, if we arange the polarization parameters, q_M and q_B as will be done for toluene, agreements with the observation are easily attained.

The molecule in the radiation field always absorbs and emitts photons, and oscillates rapidly between the ground and excited configurations with the excitation frequency. Thus, the molecule in the radiation field should be considered as an oscillating system rather than that specified by the excitation

configuration. In this respect the present unusual treatment happens to be adequate.

Toluene.   We now turn to toluene. The rotation of the methyl group in toluene was observed by Breen et al.[12] An interesting feature is as follows: the methyl group rotates almost freely either in the cases with and without the radiation field; however, it rotates more freely in the ground state than in the excited state. The potential barriers in both cases have the same shape or the same phase. These features show a sharp contrast to the barrier shape of o-fluorotoluene. Furthermore, the barrier heights are very small: the value in the ground state is 10 and 25 cm^{-1} in the excited state (as shown in Table 3).

If we try the chemical-reactivity approach as was done for o-fluorotoluene to the present case, the role of v_{1F} in the former is replaced by v_{14} and v_{18} in the present case. If we consider these long distant transfer integrals as perturbations (of which signs are negative) and combine them with the appropriate bond orders, the above mentioned trends of the rotational motion of the methyl group is qualitatively explained: The negative value of q_{14}, -0.118 makes ΔE positive, which means that the standard conformation becomes unstable; namely the rotation trends to be free. In the case of the radiation field, the situation is reversed. However, this consideration seems to be ridiculous, because the long-range bond order is acceptable while the long range transfer integral be hardly significant. The agreement with the observation may be accidental.

Numerical calculations have been made just as in the case of fluoro-substituted toluenes, and the obtained values are almost the same as those for p-fluorotoluene which are too small, say about 1/100-times the observed values. If we try to obtain values close to the observed ones, adjustable parameters, $q_M=-0.2$ and $q_B=-0.2$ are necessary as shown in Table 3, where the negative sign indicates the electron deficiencies at the methyl hydrogen and the benzene hydrogene, respectively. The result is also shown in Fig. 5b. The values of these parameters look too large, since the measurements of the dipole moments of hydrocarbons tell the values of around -0.1. This artificial parametrization suggests that the origin of the potential barrier for the methyl rotation in toluene (also in others) lies mainly in the polarization of the σ electronic structure of the molecular skelton. However, we may insist that the interesting behaviors of the methyl rotation observed in the ground and excited states of the above species are certainly switched on by the π-electron excitation.

Concluding Remarks

In spite of this so simple treatment, the obtained results are fairly fruitful. We have reproduced the observed results pretty well. The basic idea lies in Eq. 31 and the comments presented there. It is astonishing and still suspicious for the author himself that even for the rotation of the methyl group in toluene and substituted toluenes, this idea might be applicable for obtaining calculated results which agree with the observations.

Suppose that a big ab-initio calculation could be carried

out upon the present problems. Our pilot calculation which is completed in a second by a table machine suggests that the ground-state phenomena, or thermo-chemical reactivities will be well reproduced. However, for the problems in the radiation field, a huge machine time would be wasted as long as one takes into account the excitation configuration as usual. The author has an opinion that the theory does not necessarily reproduce the observed values, but presents a story capable of explaining the observation.

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