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Use of Propagators in the Hückel Model. V. Polarizabilities

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The ordinary perturbation theory is reformulated in terms of propagators. It is well known that, if the perturbing interaction has a single particle character, the additional energy up to the second order of the perturbation is expressed by bond orders and various polarizabilities. This is easily rewritten by use of propagators. In addition, under the tight-binding approximation, the propagators of linear and ring polyenes are expressed in simple analytical forms, which enable us to give also analytical expressions for bond orders and polarizabilities. A simple application is given to determine which is more stable, anthracene or phenanthrene.

The wave function plays a central role in the perturbation treatment of the quantum chemistry. The molecular orbital (MO) is usually constructed by the linear combination of atomic orbitals (LCAO). Since AO's are given as the basis set, the essential part of MO is LCAO coefficients. If any perturbing interaction is introduced, we begin with determining this effect on the wave function, and then obtain the first or second order correction to the physical quantity of interest in terms of LCAO coefficients.

It has been pointed out by Coulson and Longuet-Higgins[1] that the above mentioned procedure is not always necessary, but once the Hamiltonian matrix is given, any physical quantity is directly obtained by manipulating the corresponding determinant, not *via* wave functions. Let the Hückel determinant be

$$D(z) = \begin{vmatrix} \alpha_1-z & \beta_{12} & \beta_{13} & \cdot & \cdot & \cdot \\ \beta_{21} & \alpha_2-z & \beta_{23} & \cdot & \cdot & \cdot \\ \beta_{31} & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & & & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \alpha_n-z \end{vmatrix}, \tag{1}$$

then we have the total enery of the system,

$$E = \frac{1}{2\pi i}\int_c dz \frac{\partial}{\partial z} \log D(z), \tag{2}$$

or the bond order q_{rs} between atomic sites r and s,

$$q_{rs} = (-)^{r+s+1}\frac{1}{2\pi i}\int_c dz \frac{D_{rs}(z)}{D(z)}, \tag{3}$$

where D_{rs} is the r,s cofactor of D, and the integration is done along the so-called Coulson contour in Fig. 1a, which encloses the poles corresponding to the occupied levels. For simplicity, here and hereafter we assume the occupied levels have two electrons with up and down spins, and the spin summation is included in the integration.

The above expressions are nothing but ones by using propagators, *e.g.*, the integrand of Eq. 3 is the r,s matrix element of the matrix propagator, as will be clarified in the followings. In this sence, the work of Coulson and Longuet-Higgins is not old in spirit. In the present work the elementary perturbation theory is reformulated in terms of propagators. Procedures look abstract, but are much simpler than usual ones. For the simplest systems as linear and ring polyenes, we have already obtained analytical expressions of propagators,[2] which enable us to express bond orders and various polarizabilities also in analytical form.

Perturbation Theory

The Hamiltonian of the system in question is given in matrix form, $\boldsymbol{H}$ which satisfies the eigenvalue equation,

$$\boldsymbol{H}|i\rangle = \varepsilon|i\rangle, \tag{4}$$

where we assume that $|i\rangle$ is a single-particle state, and forms a complete set;

$$\sum_i |i\rangle\langle i| = 1. \tag{5}$$

Let us introduce the Green's operator,

$$G = \frac{1}{z-\boldsymbol{H}} \tag{6a}$$

$$= \sum_i \frac{|i\rangle\langle i|}{z-\varepsilon_i}, \tag{6b}$$

of which matrix element with respect to atomic sites r,s is

$$G_{rs}(z) = \sum_i \frac{\langle r|i\rangle\langle i|s\rangle}{z-\varepsilon_i}. \tag{7}$$

If we integrate this along the Coulson contour, we obtain immediately

$$\begin{aligned} q_{rs} &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z G_{rs}(z) \\ &= 2\sum_i^{\mathrm{occ}} \langle r|i\rangle\langle i|s\rangle \\ &= 2\sum_i^{\mathrm{occ}} C_{ri}C_{si}^{*}, \end{aligned} \tag{8}$$

where the factor 2 is due to the spin sum, and in the final expression we have used LCAO coefficients. We can understand here q_{rs} is the so-called bond order. Next we consider the integral which gives the total energy,

$$\begin{aligned} E &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}zz\boldsymbol{G}(z) \\ &= \sum_s \sum_i \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}zz\frac{\langle s|i\rangle\langle i|s\rangle}{z-\varepsilon_i} \\ &= 2\sum_i^{\mathrm{occ}} \varepsilon_i, \end{aligned} \tag{9}$$

where the factor 2 is due to the spin sum and we have also assumed that the set $\{|s\rangle\}$ is complete:

$$\sum_s |s\rangle\langle s| = 1. \tag{10}$$

Now we turn to the perturbation treatments. Almost all of them have already been done,[3] and then concentrate ourselves to connect with the conventional theory. The total Hamiltonian is devided into two parts:

$$\boldsymbol{H} = \boldsymbol{H}^0 + \boldsymbol{v}, \tag{11}$$

and $\boldsymbol{v}$ is assumed to be much smaller than $\boldsymbol{H}^0$ and further the propagator $\boldsymbol{G}^0$ for $\boldsymbol{H}^0$ is known. The perturbation expansion of G is as follows:

$$\boldsymbol{G} = \boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \cdots. \tag{12}$$

If we take the effect of $\boldsymbol{v}$ into account up to the first order and integrate the r,s matrix elements of both sides along the Coulson contour, we obtain

$$\frac{1}{2\pi \mathrm{i}}\int_c G_{rs}\mathrm{d}z = \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}zG_{rs}^0 + \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\sum_{tu} G_{rt}^0 v_{tu} G_{us}^0. \tag{13}$$

Then we have a small change of the bond order q_{rs} caused by a specified v_{tu}

$$\begin{aligned} \delta q_{rs} &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(G_{rs} - G_{rs}^0) \\ &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(G_{rt}^0 v_{tu} G_{us}^0 + G_{ru}^0 v_{ut} G_{ts}^0). \end{aligned} \tag{14}$$

If v_{tu} is real, namely, $v_{tu}=v_{ut}$, it follows that

$$\begin{aligned} \frac{\delta q_{rs}}{\delta v_{tu}} &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(G_{rt}^0 G_{us}^0 + G_{ru}^0 G_{ts}^0) \\ &= \pi_{rs;tu}, \end{aligned} \tag{15}$$

where we rewrite v_{tu} as δv_{tu}, stressing it be small. This is the bond-bond polarizability defined by Coulson. Other simpler polarizabilities are obtained as special ones of the above.

When v_{tu} is pure imaginary, say $v_{ut}=-v_{tu}$, we get

$$\bar{\pi}_{rs;tu} = \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(G_{rt}^0 G_{us}^0 - G_{ru}^0 G_{ts}^0). \tag{16}$$

This is employed by McWeeny in analysis of the ring current of aromatic compounds.[6] It is mentioned that using a explicit form of G_{rs}^0 in Eq. 7, we can easily derive the common expression of $\pi_{rs;tu}$ in terms of LCAO coefficients.

Next placing Eq. 12 in the first line of Eq. 9 we have

$$E = \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}zz(\boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \cdots)$$

so that, up to the second order with respect to $\boldsymbol{v}$,

$$\begin{aligned} \delta E &= E - E^0 \\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c (\mathrm{d}zz(\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0) \\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\left(\boldsymbol{G}^0\boldsymbol{v} + \frac{1}{2}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\right), \end{aligned} \tag{17}$$

where the last result is obtained as follows: Remembering that $\boldsymbol{G}^0=(z-\boldsymbol{H}^0)^{-1}$, we integrate by parts and use the permutation invariability inside Tr.[4] In general $\boldsymbol{v}$ being complex:

$$v_{rs} = v_{rs}^0 + iv'_{rs}, \quad v_{sr} = v_{rs}^0 - iv'_{rs}, \tag{18}$$

and then using Eqs. 8 and 15, we obtain

$$\delta E = 2\sum_{(rs)} v_{rs}^0 q_{rs} + \sum_{(rs)}\sum_{(tu)} (v_{rs}^0 \pi_{rs;tu} v_{tu}^0 + v'_{rs}\bar{\pi}_{rs;tu} v'_{tu}) \tag{19}$$

where (rs) means that the summation is carried out with respect to the bond (r,s), or under the restriction, $r<s$.

Analytical Expression for Bond Order and Polarizability

In the Hückel approximation, the propagators of linear and ring polyenes are obtained in analytical forms.[2] The r,s matrix element of the chain propagator is given as, in unit of β

$$G^0_{rt} = \frac{\sin(r+1)\theta\sin(n-s)\theta}{\sin(n+1)\theta\sin\theta}, \tag{20}$$

where the linear chain with n atomic sites is numbered as Fig. 2, and we omit the index indicating the chain length n without confusion, and further

$$z = 2\cos\theta. \tag{21}$$

This variable transformation maps the Coulson contour in Fig. 1a to that in Fig. 1b.

For the ring polyene shown in Fig. 3, we have (β=1)

$$R^0_{0k} = \frac{-1}{4\sin^2(n\theta/2)\sin\theta}(\sin(n-k)\theta+\sin k\theta). \quad (k\geqq 0) \tag{22}$$

This propagator consists of two parts: The first term in the bracket represents the effect arised from the ordinary propagation, $0\to 1\to 2\to\cdots\to k$, while the second term the reverse propagation.

The bond order of them are already given:[2] For the linear chain

$$q^L_{r+1,s+1} = \frac{1}{n+1}\left[\frac{\sin(s-r)\pi/2}{\sin(s-r)\pi/2(n+1)} - \frac{\sin(s+r)\pi/2}{\sin(s+r)\pi/2(n+1)}\right], \tag{23}$$

and for the ring

$$q^R_{0k} = \frac{2}{n^2}[(n-k)+k]\frac{\sin k\pi}{\sin k\pi/n}. \tag{24}$$

In the latter, the first term in the square bracket is due to the ordinary propagation, while the second due to the reverse propagation. Such interpretation is one of the remarkable results of propagator analysis and gives a profound understanding of chemical reactivity and stability.[4,5,7] We can observe that at the limit, $k\to 0$, either $q^L_{r,r+k}$ and q^R_{0k} tend to 1 (Coulson-Rushbrooke theorem), and other properties of the bond order are to be derived from these expressions.

Now we begin to evaluate polarizabilities. For the linear chain the most general one is

$$\pi^L_{rs;tu} = \frac{1}{2\pi i}\int_c dz(G^0_{rt}G^0_{us}+G^0_{ru}G^0_{ts}). \tag{25}$$

We know a symmetrical property, $G^0_{rs}=G^0_{sr}$, but we have to stress that the analytical expression (20) is avairable, for G^0_{rt} only if $t\geqq r$. Therefore the calculation carried out under the condition that $t\geqq r$, $s\geqq u$, $u\geqq r$, and $s\geqq t$, which corresponds to the case shown in Fig. 2a. Substituting Eq. 20 into Eq. 25, we have

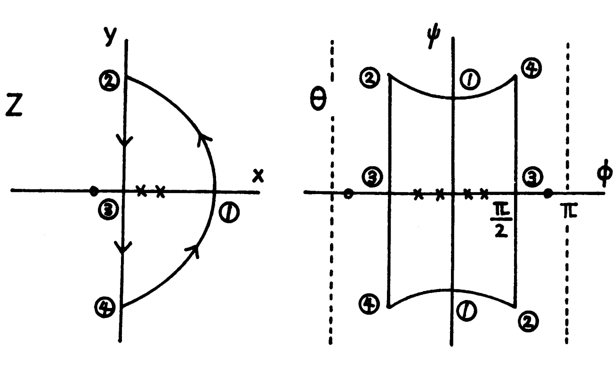
$$\begin{aligned}\pi^{L(a)}_{rs;tu} = \frac{1}{2}\frac{1}{2\pi i}\int_c d\theta(-2\sin\theta)\cdot\frac{1}{\sin^2\theta\sin^2(n+1)\theta}\\ \times[\sin(r+1)\theta\sin(n-t)\theta\sin(u+1)\theta\sin(n-s)\theta\\ +\sin(r+1)\theta\sin(n-u)\theta\sin(t+1)\theta\sin(n-s)\theta].\end{aligned} \tag{26}$$

Some comments should be added. The factor, 1/2 is needed due to the fact the contour in θ plane goes round the origin twice while the contour in z plane does once. As to poles, θ=0 is not the pole (as mentioned in the second paper of Ref. 1), and real poles are

$$\theta_\mu = \frac{\pi\mu}{n+1}, \quad \mu = \pm 1, \pm 2, \cdots, \pm n. \tag{27}$$

If we assume for simplicity that n is even and every site offers an electron, the levels are doubly occupied from the bottom to the $\pm n/2$ and the result is as follows:

$$\begin{aligned}\pi^{L(a)}_{rs;tu} = \frac{-4}{(n+1)^2}\sum_{\mu=1}^{n/2}\frac{1}{\sin\theta_\mu}\\ \{\sin(r+1)\theta_\mu\sin(n-t)\theta_\mu\sin(u+1)\theta_\mu\sin(n-s)\theta_\mu\\ [(r+1)\cot(r+1)\theta_\mu+(n-t)\cot(n-t)\theta_\mu\\ +(u+1)\cot(u+1)\theta_\mu+(n-s)\cot(n-s)\theta_\mu-\cot\theta_\mu]\\ +\sin(r+1)\theta_\mu\sin(n-u)\theta_\mu\sin(t+1)\theta_\mu\sin(n-s)\theta_\mu\\ [(r+1)\cot(r+1)\theta_\mu+(n-u)\cot(n-u)\theta_\mu\\ +(t+1)\cot(t+1)\theta_\mu+(n-s)\cot(n-s)\theta_\mu\\ -\cot\theta_\mu]\},\end{aligned} \tag{28}$$



(a) (b)

Fig. 1.

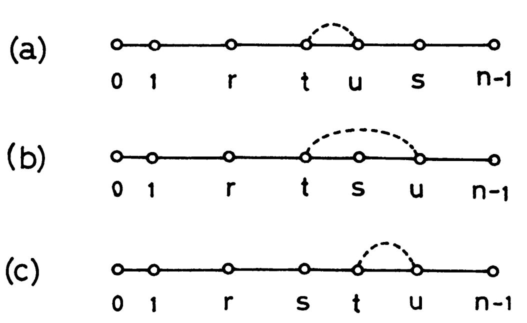


Fig. 2.

where the spin sum has been done. We can observe that the above result is valid for the exchange, $(r,s)\leftrightarrow(t,u)$.

There are other relations between pairs, (r,s) and (t,u) keeping $s>r$ and $u>t$, as shown in Figs. 2b and 2c. In the case of Fig. 2b, G^0_{us} in Eq. 25 should be read G^0_{su}, and then in order to obtain $\pi^{L(b)}_{rs;tu}$ we have to exchange u and s in the first square bracket of Eq. 28. In the case of Fig. 2c, $\pi^{L(c)}_{rs;tu}$ is obtained by exchanging not only u and s in the first term of the square bracket in Eq. 26 but also t and s in the second term. This makes two terms in Eq. 28 identical, and we denote the result for further investigations.

$$\begin{aligned}\pi^{L(c)}_{rs;tu} = {} & \frac{-8}{(n+1)^2}\sum_{\mu=1}^{n/2}\frac{1}{\sin\theta_\mu}\\ & \{\sin(r+1)\theta_\mu \sin(n-t)\theta_\mu \sin(s+1)\theta_\mu \sin(n-u)\theta_\mu\\ & [(r+1)\cot(r+1)\theta_\mu+(n-t)\cot(n-t)\theta_\mu\\ & +(s+1)\cot(s+1)\theta_\mu+(n-u)\cot(n-u)\theta_\mu\\ & -\cot\theta_\mu]\}. \end{aligned} \tag{29}$$

Other simpler polarizabilities will be obtained by the following procedures. One of self-polarizabilities, $\pi^L_{rs;tu}$ is obtained by putting $r=t$ and $s=u$, keeping $r,t<s,u$, therefore $\pi^{L(a)}_{rs;tu}$ or $\pi^{L(b)}_{rs;tu}$ should be used as a starting one, say,

$$\pi^L_{rs;rs} = (r=t,\ s=u \text{ in } \pi^{L(a)}_{rs;tu} \text{ or } \pi^{L(b)}_{rs;tu}). \tag{30}$$

Similar considerations lead to the followings:

$$\begin{aligned}\pi^{L(a)}_{r;tu} &= (r=s \text{ in } \pi^{L(a)}_{rs;tu}) \text{ for } r \text{ inside } t-s,\\ \pi^{L(c)}_{r;tu} &= (r=s \text{ in } \pi^{L(a)}_{rs;tu}) \text{ for } r \text{ outside } t-s,\\ \pi^{L(a)}_{rs;t} &= \frac{1}{2}(t=u \text{ in } \pi^{L(a)}_{rs;tu}) \text{ for } t \text{ inside } r-s,\\ \pi^{L(a)}_{rs;t} &= \frac{1}{2}(t=u \text{ in } \pi^{L(c)}_{rs;tu}) \text{ for } t \text{ outside } r-s,\\ \pi^{L}_{r;t} &= \frac{1}{2}(r=s,\ t=s \text{ in } \pi^{L(c)}_{rs;tu}). \end{aligned} \tag{31}$$

The last one is given explicitly as

$$\begin{aligned}\pi^L_{r;t} = {} & \frac{-8}{(n+1)^2}\sum_{\mu=1}^{n/2}\frac{1}{\sin\theta_\mu}\sin^2(r+1)\theta_\mu \sin^2(n-t)\theta_\mu\\ & [(r+1)\cot(r+1)\theta_\mu+(n-t)\cot(n-t)\theta_\mu\\ & -\cot\theta_\mu] \end{aligned} \tag{32}$$

which precisely coincides the result obtained by Coulson and Longuet-Higgins.[1] When $r=0$, the denominator cancels out one of the numerators, so that the summation can be carried out to get the result:

$$\begin{aligned}\pi^L_{0;t} = {} & \frac{1}{2(n+1)^2}[(-)^t(2n-2t+1)\operatorname{cosec}(2t+3)\pi/2(n+1)\\ & +(-)^t(2n-2t+1)\operatorname{cosec}(2t+1)\pi/2(n+1)\\ & -2\operatorname{cosec}\pi/2(n+1)], \end{aligned} \tag{33}$$

which has been also obtained by the above-mentioned investigations.

Since $\bar{\pi}^L_{rs;tu}$ is expressed as

$$\bar{\pi}^L_{rs;tu} = \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(G^0_{rt}G^0_{us}-G^0_{ru}G^0_{ts}), \tag{34}$$

the (a) and (b) types have non-vanishing values and the second half of Eq. 26 or 28 changes sign, but the (c) type not.

We turn to the case of ring polyenes with n sites which are numbered as shown in Fig. 3a. Using the ring propagators of Eq. 22 in Eq. 25, we have

$$\begin{aligned}\pi^{R(a)}_{rs;tu} &= \frac{-1}{4}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}\theta(R^0_{rt}R^0_{us}+R^0_{ru}R^0_{ts})\\ &= \frac{-1}{4}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}\theta\frac{1}{\sin^2(n\theta/2)\sin\theta}(\cos\overline{tr}\theta\cos\overline{su}\theta\\ &\quad +\cos\overline{ur}\theta\cos\overline{st}\theta), \end{aligned} \tag{35}$$

where, for example

$$\overline{tr} = n/2 - (t-r), \tag{36}$$

and the first and second terms of the second line are originated from the first and second terms of the first line, respectively. We present the result for each term separately, for convenience of the later investigation. Here we have poles:

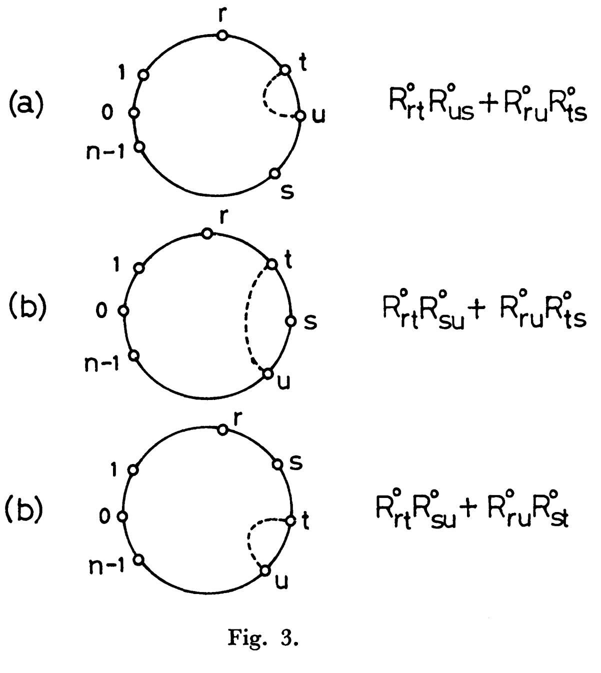


Fig. 3.

$$\theta_\mu = \frac{2\pi\mu}{n}, \quad \mu=0, \pm 1, \pm 2, \cdots, n/2, \tag{37}$$

and the levels from 0 to $\pm n/4$ are doubly occupied. Unlike the case of the linear chain, $\theta=0$ is a real pole. The result are:

The first term of Eq. 35

$$\begin{aligned} &= \frac{-1}{6} - \frac{1}{n^2}\left(\frac{1}{3} - \overline{tr}^2 - \overline{su}^2\right) \\ &+ \frac{4}{n^2}\sum_{\mu=1}^{[n/4]} \frac{1}{\sin\theta_\mu}\cos\overline{tr}\theta_\mu \cos\overline{su}\theta_\mu \\ &\times (\cot\theta_\mu + \overline{tr}\tan\overline{tr}\theta_\mu + \overline{su}\tan\overline{su}\theta_\mu), \end{aligned} \tag{38a}$$

and

The second term of Eq. 35

$$\begin{aligned} &= \frac{-1}{6} - \frac{1}{n^2}\left(\frac{1}{3} - \overline{ur}^2 - \overline{st}^2\right) \\ &+ \frac{4}{n^2}\sum_{\mu=1}^{[n/4]} \frac{1}{\sin\theta_\mu}\cos\overline{ur}\theta_\mu \cos\overline{st}\theta_\mu \\ &\times (\cot\theta_\mu + \overline{ur}\tan\overline{ur}\theta_\mu + \overline{st}\tan\overline{st}\theta_\mu). \end{aligned} \tag{38b}$$

In the above the terms without summation arise from the pole, $\theta_u=0$, and others from poles, $\theta_u \neq 0$, and further $[n/4]$ is the Gauss notation, which means the maximum integer at most $n/4$. It is needless to say

$$\pi^{R(a)}_{rs;tu} = \text{Eq. 38a} + \text{Eq. 38b}. \tag{39}$$

For the cases shown in Fig. 3b and 3c, entirely the same treatments that have been done in the case of the linear chain hold. Namely

$$\begin{aligned} \pi^{R(b)}_{rs;tu} &= [s \leftrightarrow u \text{ in the first term of Eq. 39}] \\ \pi^{R(c)}_{rs;tu} &= [s \leftrightarrow u \text{ in the first term and } t \leftrightarrow s \\ &\quad \text{in the second term of Eq. 39}]. \end{aligned} \tag{40}$$

but in $\pi^{R(c)}_{rs;tu}$ it does not happen that two terms are accidentally coincident as in $\pi^{L(c)}_{rs;tu}$. Further the relations as mentioned in Eqs. 30 and 31 also hold in this case.

It is rather striking that $\pi^{R}_{rs;tu}$ has a constant term, but it will be canceled out by a part of suceeding terms, as n tends to infinity.

The polarizability due to the imaginary perturbation, $\overline{\pi}^{R(a)}_{rs;tu}$ is simply obtained by changing the sign in Eq. 39:

$$\pi^{R(a)}_{rs;tu} = \text{Eq. 38a} - \text{Eq. 38b} \tag{41}$$

and for others the same relations hold.

Illustrative Example

As an example of previous treatments we consider which is more stable, anthracene (I) and phenanthrene (II). In each compound, the atomic sites are numbered as in Fig. 4. Namely, if we consider the ring polyene with fourteen sites as an unperturbed system, anthracene has additional bonds, (0,9) and (2,7), while phenanthrene has bonds, (0,9) and (1,6).

Considering that these bond formations are perturbation, we can estimate each stabilization energy. We begin with evaluating the first order energies:

$$\Delta E^{(1)}_{\mathrm{I}} = 2v(q^R_{09} + q^R_{27}), \tag{42a}$$

$$\Delta E^{(1)}_{\mathrm{II}} = 2v(q^R_{09} + q^R_{16}), \tag{42b}$$

where we put $v_{rs}=v_{sr}=v$. In the case of ring, the value of bond order depends only on the distance between sites along the ring perimeter, so that $q^R_{27}=q^R_{16}$ Therefore we can find no difference in the first order energies between I and II.

The second order energy is written in general as

$$\Delta E^{(2)} = \sum_{(rs)}\sum_{(tu)} v_{rs}\pi_{rs;tu}v_{tu}, \tag{43}$$

where the summations are carried out with repect to the bonds (r,s) and (t,u). Hence it follows that

$$\Delta E^{(2)}_{\mathrm{I}} = v^2(\pi^R_{09;09} + \pi^R_{27;27} + 2\pi^R_{09;27}), \tag{44a}$$

$$\Delta E^{(2)}_{\mathrm{II}} = v^2(\pi^R_{09;09} + \pi^R_{16;16} + 2\pi^R_{09;16}). \tag{44b}$$

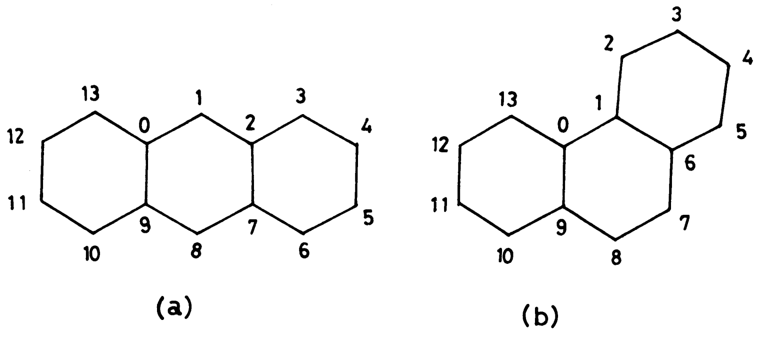


Fig. 4.

Thus we have a energy difference between I and II in the second order terms:

$$\begin{aligned}\Delta E &= \Delta E_{\mathrm{I}}^{(2)} - \Delta E_{\mathrm{II}}^{(2)} \\ &= 2v^2(\pi^{R}_{09;27} - \pi^{R}_{09;16}) \\ &= 2v^2(-0.00632/\beta - 0.08539/\beta) \\ &= -0.1834\beta, \end{aligned} \tag{45}$$

where in the final expression, β is recovered (note that polarizabilities are given in unit of β^{-1}), and we put $v=\beta$. Since β is negative, the result has a positive value. Therefore we can conclude that phenanthrene is more stable than anthracene.

Concluding Remarks

As long as the perturbing interaction is of a single particle character, the present treatment using propagator is quite general. Up to the second order of the perturbation, the additional energy and other physical quantities such as the diamagnetic susceptibility are expressed with bond orders and polarizabilities. The calculated results are solely depend upon, to what extent the zero-order propagators are already given.

As an advantage of our method, procedures are carried out without use of wave functions, so that we are able to analyze the problem under consideration in a compact and elegant way, and sometimes to insight the essential features of the subject. Some examples have been shown already in the analysis of chemical reactivities and stabilities.[4,7] For the simplest species such as linear or ring polyenes, the propagators are obtained in analytical forms. These are quite useful for qualitative and quantitative investigations of various chemical problems.

However we do not deny usefulness of the wave function. If we investigate too complicated species to take linear or ring polyene as an unperturbed system, the propagator of the starting substance is hardly obtained in an analytical way. Even in this case it is preferable that, at the stage of the general treatment, the problem is handled by the use of propagators, and then at the final calculating stage, the wave functions as accurate as possible should be used.

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