Use of Propagators in the Hückel Model. VI. Magnetic Perturbation and Ring Current

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(Received September 6, 1984)

The electron propagator in the magnetic field is investigated under the Hückel approximation, and the electronic energy and the aromatic ring current are evaluated. The perturbation treatment for the ring current developed by McWeeny is easily reformulated in terms of propagator and then the physical features involved in this problem have been made considerably clearer.

The diamagnetic anisotropy of an aromatic hydrocarbon may be attributed to induced currents flowing round the aromatic rings. This picture first proposed by Pauling,[1] has been quantum mechanically formulated by London,[2] and extensively studied, *e.g.*, by Pople[3] or by McWeeny.[4] Recently this problem is investigated in connection with aromaticity by Aihara,[5] who uses a graph-theoretical formalism. In this paper we reformulate the above mentioned treatments in terms of propagator. The physical contents beyond the previous works will not be expected, but the general and compact analysis might be helpful in a deeper understanding of this problem.

Hückel Hamiltonian with Magnetic Field

In treating species in the magnetic field, we use the basis set:

$$\chi_s(\mathbf{r}) = \chi_s^0(\mathbf{r})e^{-iA_s\cdot r/\Phi},$$
$$\Phi = \hbar c/e, \tag{1}$$

where x_s^0 is the atomic orbital at s site in the absence of the magnetic field, A_s is the vector potential there and $\mathbf{r}$ is the position vector of electron. Meanwhile we manipulate in unit of $\Phi=1$ for simplicity, but if necessary we recover this constant. As usual the transfer integral β_{st} is approximately estimated as,

$$\begin{aligned}\beta_{st} &= \int d\mathbf{r}\chi_s^*H\chi_t \\ &= \int d\mathbf{r}e^{i(A_s-A_t)\cdot r}\chi_s^{0*}H\chi_t^0 \\ &\doteqdot e^{i(A_s-A_t)\cdot(R_s+R_t)/2}\int d\mathbf{r}\chi_s^{0*}H\chi_t^0 \\ &= \beta_{st}^0 e^{i\theta_{st}},\end{aligned} \tag{2}$$

where $\boldsymbol{R}_s$ is the position vector of the site s, and β_{st}^0 is the transfer integral in the absence of the magnetic field. In the Hückel approximation for the conjugated hydrocarbons, β_{st}^0's are constant, β only for the adjacent r and s. We proceed in unit of $\beta=1$ without confusion. In the above

$$\theta_{st} = \frac{1}{2}(\boldsymbol{A}_s-\boldsymbol{A}_t)\cdot(\boldsymbol{R}_s+\boldsymbol{R}_t) \tag{3}$$

from which it is apparent that

$$\theta_{st} = -\theta_{ts}. \tag{4}$$

A little more calculation of θ_{st} is useful for the later investigations. Remebering that

$$\boldsymbol{A}_s = -\frac{1}{2}H\boldsymbol{R}_s\times\boldsymbol{n}, \tag{5}$$

when the magnetic field, $\boldsymbol{H}=H\boldsymbol{n}$ is constant along the z axis (see Fig. 1), we obtain

$$\begin{aligned}\theta_{st} &= \frac{1}{2}(\boldsymbol{A}_s-\boldsymbol{A}_t)\cdot(\boldsymbol{R}_s+\boldsymbol{R}_t) \\ &= -\frac{1}{4}H[(\boldsymbol{R}_s-\boldsymbol{R}_t)\times\boldsymbol{n}]\cdot(\boldsymbol{R}_s+\boldsymbol{R}_t) \\ &= \frac{1}{2}H\boldsymbol{n}\cdot(\boldsymbol{R}_s+\boldsymbol{R}_t) \\ &= \boldsymbol{S}_{st}.\end{aligned} \tag{6}$$

Here S_{st} is the signed area of the triangle formed by the origin and the bond s—t, and counted positive if $s\rightarrow t$ is right handed about the normal $\boldsymbol{n}$.

Then we have the Hückel Hamiltonian with magnetic field as

$$H = \sum_s |s\rangle\alpha_s\langle s| + \sum_{st} e^{i\theta_{st}}\beta_{st}^0|s\rangle\langle t|, \tag{7}$$

and then with abbreviations:

$$\begin{aligned}\alpha_s &= \alpha = 0, \\ \beta_{st}^0 &= \beta = 1, \\ e^{i\theta_{st}} &= \omega_{st},\end{aligned} \tag{8}$$

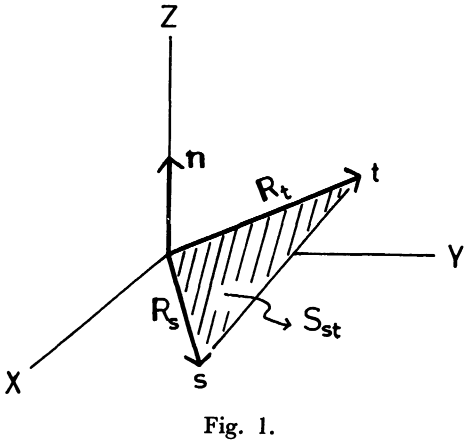


Fig. 1.

we can write, for example, for naphthalene, (see Fig. 4)

$$\begin{pmatrix} 0 & \omega_{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \omega_{1,10} \\ \omega_{21} & 0 & \omega_{23} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \omega_{32} & 0 & \omega_{34} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_{43} & 0 & \omega_{45} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \omega_{54} & 0 & \omega_{56} & 0 & 0 & 0 & \omega_{5,10} \\ 0 & 0 & 0 & 0 & \omega_{65} & 0 & \omega_{67} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \omega_{76} & 0 & \omega_{78} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \omega_{87} & 0 & \omega_{89} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \omega_{98} & 0 & \omega_{9,10} \\ \omega_{10,1} & 0 & 0 & 0 & \omega_{10,5} & 0 & 0 & 0 & \omega_{10,9} & 0 \end{pmatrix} \tag{9}$$

Propagators

The propagators corresponding to the Hamiltonian in Eq. 7 are built similarly as the case without magnetic field.[6]

(i) The Edge of the Linear Chain Propagator. For the linear chain with n sites as numbered in Fig. 2a we have

$$\begin{aligned} {}^nG_0 &= {}^1G_0 + {}^1G_0 v_{01} {}^nG_{1\langle 0\rangle} v_{10} {}^nG_0 \\ &= {}^1G_0 + {}^1G_0 v_{01} {}^{n-1}G_0 v_{10} {}^nG_0, \end{aligned} \tag{10}$$

where ${}^nG_r$ is the r—r matrix element of the matrix propagator for the n membered chain, and ${}^nG_{r\langle s\rangle}$ is one in the absence of the s site. Obviously

$${}^nG_0 = [({}^1G_0)^{-1} - v_{01} {}^{n-1}G_0 v_{10}]^{-1}. \tag{11}$$

Now we can understand that ${}^nG_0$ is independent of the magnetic field, because the phase factors of interaction terms arising from magnetic interactions cancel out with each other. Using abbreviations of Eq. 8 and changing variable as

$$z = 2\cos\theta, \tag{12}$$

we can obtain as before,[6]

$${}^nG_0 = \sin\theta / \sin(n+1)\theta, \tag{13}$$

(ii) The k-th Diagonal Element of the Linear Chain Propagator. In a similar way,

$${}^nG_k(\theta) = \frac{\sin(n-k)\theta \sin(k+1)\theta}{\sin(n+1)\theta \sin\theta}, \tag{14}$$

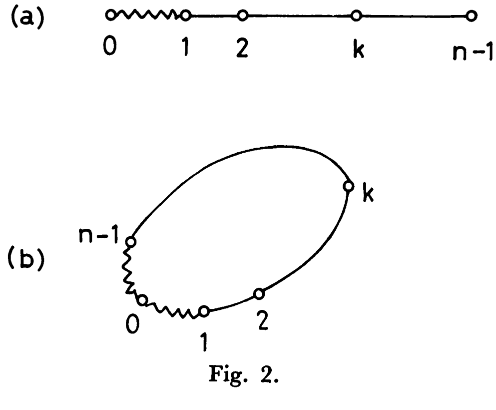


Fig. 2.

which also independent of the magnetic field.

(iii) The Off-diagonal Element of the Linear Chain Propagator. For simplicity, we deal with the three membered chain, a-b-c, and then obtain

$$\begin{aligned} {}^3G_{\mathrm{ac}} &= {}^3G_{\mathrm{a}} v_{\mathrm{ab}} {}^3G_{\mathrm{b}\langle \mathrm{a}\rangle} v_{\mathrm{bc}} {}^3G_{\mathrm{c}\langle \mathrm{b}\rangle} \\ &= \omega_{\mathrm{ab}}\omega_{\mathrm{bc}} {}^3G_{\mathrm{ac}}^{(\mathrm{non})}, \end{aligned} \tag{15}$$

where ${}^3G_{\mathrm{ac}}^{(\mathrm{non})}$ is the a—c matrix element of the 3-membered chain propagator in the absence of magnetic field. It is noted that in this case the propagator has a phase factor responsible to magnetic effect. In general,

$${}^nG_{k,k+l} = \omega_{k,k+1} \cdots \omega_{l-1,l} \frac{\sin(n-k-l)\theta \sin(k+1)\theta}{\sin(n+1)\theta \sin\theta}. \tag{16}$$

(iv) The Diagonal Element of the Ring Propagator. Observing Fig. 2b, we obtain

$$\begin{aligned} ({}^nR_0)^{-1} &= ({}^1G_0)^{-1} - v_{01} {}^nG_{1\langle 0\rangle} v_{10} - v_{0,n-1} {}^nG_{n-1\langle 0\rangle} v_{n-1,0} \\ &\quad - v_{01} {}^nG_{1,n-1\langle 0\rangle} v_{n-1,0} - v_{0,n-1} {}^nG_{n-1,1\langle 0\rangle} v_{n-1,0} \\ &= ({}^1G_0)^{-1} - 2 {}^{n-1}G_0 - \omega_{01}\omega_{12}\cdots\omega_{n-1,0} {}^{n-1}G_{0,n-2}^{(\mathrm{non})} \\ &\quad - \omega_{0,n-1}\omega_{n-1,n-2}\cdots\omega_{10} {}^{n-1}G_{n-2,0}^{(\mathrm{non})}, \end{aligned} \tag{17}$$

where propagators appearing in the right-hand side are all non-magnetic. Noting that $\omega_{rs} = \omega_{sr}^*$, we get

$$\begin{aligned} ({}^nR_0)^{-1} &= ({}^1G_0)^{-1} - 2 {}^{n-1}G_0 \\ &\quad - 2\cdot Re[\omega_{01}\omega_{12}\cdots\omega_{n-1,0}] {}^{n-1}G_{0,n-1}^{(\mathrm{non})} \\ &= 2\cos\theta - \frac{2\sin(n+1)\theta}{\sin\theta} - 2\cos HS \frac{\sin\theta}{\sin(n\theta)} \\ &= -\frac{4\sin\theta}{\sin n\theta} \sin(n\theta + HS/2)\cdot\sin(n\theta - HS/2). \end{aligned} \tag{18}$$

Here S is the area of ring counted positive, if the path goes round as 0→1→2→…→n−1→0 in Fig. 2b.

(v) The Off-diagonal Element of the Ring Propagator. We devide ${}^nR_{ok}$ into two parts:

$${}^nR_{0k}^{(1)} + {}^nR_{0k}^{(2)}. \tag{19}$$

The former corresponds to the path with normal order, 0→1→2…→k, while the latter to the reverse path 0→n−1→…→k. Then we have

$$\begin{aligned} {}^nR_{0k}^{(1)} &= {}^nR_0 v_{01} {}^nG_{1k\langle 0\rangle} \\ &= {}^nR_0 {}^{n-1}G_{0,k-1}^{(\mathrm{non})} \omega_{01}\omega_{12}\cdots\omega_{k-1,k} \\ &= \frac{-\sin n\theta}{4\sin\theta\sin(n\theta+HS)/2\cdot\sin(n\theta-HS)/2} \\ &\quad \times \frac{\sin(n-k)\theta\sin\theta}{\sin n\theta\sin\theta}\omega_{01}\omega_{12}\cdots\omega_{k-1,k} \\ &= \frac{-\sin(n-k)\theta}{4\sin(n\theta+HS)/2\cdot\sin(n\theta-HS)/2}\cdot\omega_{01}\omega_{12}\cdots\omega_{k-1,k}, \end{aligned} \tag{20}$$

and similarly

$$\begin{aligned} {}^nR_{0k}^{(2)} &= \frac{-\sin k\theta}{4\sin\theta\sin(n\theta+HS)/2\cdot\sin(n\theta-HS)/2} \\ &\quad \times \omega_{k,k+1}^*\omega_{k+1,k+2}^*\cdots\omega_{n-2,n-1}^*\omega_{n-1,0}^*. \end{aligned} \tag{21}$$

Conclusively all the matrix elements of the ring propagator depend on magnetic field, while only the off-diagonal elements of the chain propagator does.

Energy

The total energies for various system will be calculated to estimate induced currents.

(i) Linear Chain with n *Sites and* n *Electrons.* The diagonal elements of this propagator in magnetic field are same as those of non magnetic case. Then the energy expression

$$E = \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}zz\boldsymbol{G}(z) \tag{22}$$

leads to the same result as for the non-magnetic case. Namely

$$\begin{aligned} E &= \sum_{k=0}^{n-1} \frac{-1}{\pi \mathrm{i}}\int \mathrm{d}\theta \frac{\sin(n-k)\theta \sin(k+1)\theta \cos\theta}{\sin(n+1)\theta} \\ &= 2\left[-1+\operatorname{cosec}\frac{\pi}{2(n+1)}\right]. \end{aligned} \tag{23}$$

In the above, integration is carried out along the so-called Coulson contour mapped through the relation (12).[6,8] Poles of the first line of Eq. 23 are

$$\theta_{\mathrm{r}} = \frac{\pi r}{n+1},\quad r = \pm 1, \pm 2, \pm 3, \cdots, \pm n. \tag{24}$$

Among them poles up to $|n/2|$ are doubly occupied, which are enclosed by the contour. The integration above is assumed to include the spin sum.

(ii) Mono-ring with n *Sites and* N *Electrons.* Using Eq. 22, we obtain

$$E = \frac{n}{4\pi \mathrm{i}}\int_c \mathrm{d}\theta \frac{\cos\theta \sin n\theta}{\sin(n\theta+HS/2)\cdot\sin(n\theta-HS/2)}. \tag{25}$$

Poles arising from the denominator are

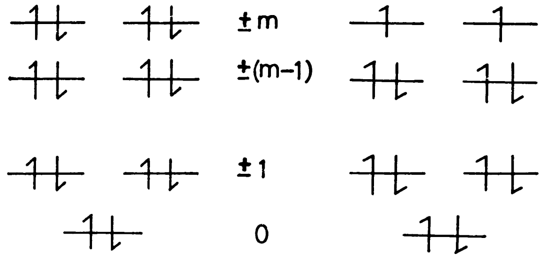
$$\begin{aligned} &\theta_r^+ = (2\pi r-HS)/n \text{ and } \theta_r^- = (2\pi r+HS)/n, \\ &\quad r = 0, \pm 1, \pm 2, \cdots, \pm(n/2-1), n/2 \end{aligned} \tag{26}$$

in which ones up to $\pm n/4$ are occupied. Then calculations are straightforward:

$$\begin{aligned} E &= \sum_\sigma \sum_r (-)^r\left[\frac{\cos(2\pi r-HS)/n\cdot\sin(2\pi r-HS)}{\sin(\pi r-HS)}\right. \\ &\qquad \left.+\frac{\cos(2\pi r+HS)/n\cdot\sin(2\pi r+HS)}{\sin(\pi r+HS)}\right] \\ &= \sum_\sigma \sum_r \left(\cos\frac{2\pi r-HS}{n}+\cos\frac{2\pi r+HS}{n}\right) \\ &= 2\sum_\sigma \sum_r \frac{\cos 2\pi r}{n}\,\frac{\cos HS}{n}, \end{aligned} \tag{27}$$

where Σ_σ indicates the spin sum which is carefully taken in the present case. In order to obtain Eq. 27 we have a useful relation

$$\sum_{r=1}^{k} \cos rx = \cos\frac{(k+1)x}{2}\,\sin\frac{kx}{2}/\sin\frac{x}{2} \tag{28}$$



(a) N=4m+2 (b) N=4m

Fig. 3.

(a) The Closed System with N=4m+2 *Electrons:* In this case electrons occupy the levels as shown in Fig. 3a and then

$$\sum_\sigma \sum_{r=0}^{|m|} \cos\frac{2\pi r}{n} = 2\frac{\sin N\pi/2n}{\sin \pi/n}. \tag{29}$$

(b) The Open System with N=4m *Electrons:* Observing Fig. 3b, we get

$$\sum_\sigma \sum_{r=0}^{|m|} \cos\frac{2\pi r}{n} = 2\cos\frac{N\pi}{2n} + 2\frac{\sin(N-2)\pi/2}{\sin\pi/n} \tag{30}$$

Thus we have results; for the system with n sites and $4m+2$ electrons

$${}^nE_{4m+2} = 4\cos\frac{HS}{n}\cdot\frac{\sin N\pi/2n}{\sin\pi/n}, \tag{31}$$

and for the system with n sites ans $4m$ electrons

$${}^nE_{4m} = 4\cos\frac{HS}{n}\cdot\left(\cos\frac{N\pi}{2n}+\frac{\sin(N-2)\pi/2n}{\sin\pi/n}\right). \tag{32}$$

For special cases that number of sites is equal to that of electrons we have:

$${}^{4m+2}E_{4m+2} = 4\cos\frac{HS}{4m+2}\operatorname{cosec}\frac{\pi}{4m+2}, \tag{33}$$

$${}^{4m}E_{4m} = 4\cos\frac{HS}{4m}\cot\frac{\pi}{4m}. \tag{34}$$

Current

The ring current J is defined in terms of energy modified by magnetic field as follows.[7] The external field provokes an induced moment M opposing it and given by

$$M = -\frac{\delta E}{\delta H}, \tag{35}$$

or

$$M = \sum_k M_k = -\sum_k \frac{\delta E}{\delta f_k}\,\frac{\delta f_k}{\delta H}, \tag{36}$$

where

$$f_k = HS_k, \tag{37}$$

is the magnetic flux associated with the irreducible circuit (ring). Our hypothesis is that the partial moment M_k of the k-th ring arises from an induced current J_k circulating around the ring and such that

$$M_k = \frac{1}{c} J_k S_k. \tag{38}$$

Therefore the current J_k is given by (recovering constant Φ_0)

$$J_k = -\frac{c}{\Phi_0}\frac{\delta E}{\delta f_k}. \tag{39}$$

It is needless to say that there is no current in the linear chain.

We want to apply Eq. 39 to various mono-ring compounds. For species corresponding to Eqs. 31 and 32

$${}^{n}J_{4m+2} = \frac{4\beta c}{n\Phi_0}\sin\frac{HS}{n\Phi_0}\,\frac{\sin N\pi/2n}{\sin \pi/n}, \tag{40}$$

$${}^{n}J_{4m} = \frac{4\beta c}{n\Phi_0}\sin\frac{HS}{n\Phi_0}\left(\cos\frac{N\pi}{2n} + \frac{\sin (N-2)\pi/2n}{\sin \pi/n}\right). \tag{41}$$

The area in the aboves is expressed by the use of the bond length d and the number of sites n as

$$S = \frac{nd^2}{4}\cot\frac{\pi}{n}. \tag{42}$$

At this stage it is instructive to make an order estimate of magnetic parameter such that for benzene $SH/\Phi_0 \sim 10^{-9}H$ which is very small even for $H \sim 10^4$ gauss. Accordingly it is good approximation that

$${}^{4m+2}J_{4m+2} = 4\beta\left(\frac{1}{4m+2}\right)^2 \frac{cHS}{\Phi_0^2}\operatorname{cosec}\frac{\pi}{4m+2}, \tag{43}$$

$${}^{4m}J_{4m} = 4\beta\left(\frac{1}{4m}\right)^2 \frac{cHS}{\Phi_0^2}\cot\frac{\pi}{4m}. \tag{44}$$

Next we calculate ${}^5J_6$, ${}^6J_6$, and ${}^7J_6$ which correspond to $C_5H_5^-$, C_6H_6, and $C_7H_7^+$, respectively. In the same approximation to obtain the previous results, we have

$$\begin{aligned} {}^5J_6 &= A\frac{\sin 6\pi/10}{\sin \pi/5} \fallingdotseq 1.6A, \\ {}^6J_6 &= A\frac{\sin 6\pi/12}{\sin \pi/5} = 2A, \\ {}^7J_6 &= A\frac{\sin 6\pi/14}{\sin \pi/5} \fallingdotseq 2.2A, \end{aligned} \tag{45}$$

with

$$A = \beta\frac{c}{\Phi_0^2}\frac{Hd^2}{4\pi}. \tag{46}$$

Hence ring currents increase significantly as number of sites increase although number of electrons remain constant.

Perturbation Treatment I

In the preceding section we have presented some examples in which propagators are obtained in a compact analytical form. Such a fortune can not be expected for more general or complicated systems. Hence a perturbation method will be preferable for the latter case. We are now going on as McWeeny has done.[4] In order to avoid the explicit use of the current density operator, we introduce a point dipole as a test body and evaluate the additional energy due to this effect and the effective magnetic field secondaly produced by the ring current. If a dipole moment $\boldsymbol{m}=m\boldsymbol{n}$ ($\boldsymbol{n}$ is the unit vector along z axis) is introduced at any point on the molecular plane, this point being chosen as origin, the vector potential at point r will be

$$A = -\frac{1}{2}H\boldsymbol{r}\times\boldsymbol{n} - m\frac{\boldsymbol{r}\times\boldsymbol{n}}{r^3}. \tag{47}$$

It is easily seen that Eq. 6 is replaced by

$$\begin{aligned} \theta_{st} &= S_{st}\left(H + \frac{m}{R_s^3} + \frac{m}{R_t^3}\right) \\ &= Ss_{st}\left(H + \frac{m}{\mathrm{d}^3}k_{st}\right), \end{aligned} \tag{48}$$

where areas are measured in unit of S, that of benzene ring, and distances are in unit of d, the C–C bond distance;

$$\begin{aligned} S_{st} &= Ss_{st}, \\ R_s &= r_s\mathrm{d}, \\ k_{st} &= \left(\frac{1}{r_s^3} + \frac{1}{r_t^3}\right). \end{aligned} \tag{49}$$

From the Hamiltonian in Eq. 7, we have a magnetic perturbation as

$$\begin{aligned} v &= \sum_{st}(e^{i\theta_{st}} - 1)|s\rangle\langle s| \\ &\fallingdotseq \sum_{st}\left(i\theta_{st} - \frac{1}{2}\theta_{st}^2\right)|s\rangle\langle s|. \end{aligned} \tag{50}$$

Here we have used the fact that $\theta_{st} \ll 1$, and note that v consists of the real and imaginary parts.

In general, if we wite the matrix element of v as

$$v_{rs} = v_{st}^0 + iv'_{st}, \tag{51}$$

the energy change up to the second order of v is,[8)]

$$\begin{aligned} \delta E = {} & 2\sum_{k<l} q_{kl}v_{kl}^0 \\ & + \sum_{k<l}\sum_{m<n}(v_{kl}^0\pi_{kl;mn}v_{mn}^0 + v'_{kl}\bar{\pi}_{kl;mn}v'_{mn}), \end{aligned} \tag{52}$$

where the bond order q_{rs} and the bond-bond polarizabilities $\pi_{kl;mn}$, $\bar{\pi}_{kl;mn}$ are given in terms of non-magnetic propagators as

$$q_{kl} = \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\,\boldsymbol{G}_{kl}^0(z) \tag{53}$$

$$\pi_{kl;mn}(\bar{\pi}_{kl;mn}) = \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(\boldsymbol{G}_{km}^0(z)\boldsymbol{G}_{nl}^0(z) \pm \boldsymbol{G}_{kn}^0(z)\boldsymbol{G}_{ml}^0(z)). \tag{54}$$

The above quantities are already been evaluated in analytic forms for simple species, linear chain and ring compounds.[8] However usual expressions in terms of LCAO coefficients are useful for more complicated molecules. It should be noted that if we use

$$G_{rs}(z) = \sum_i \frac{\langle r|i\rangle\langle i|s\rangle}{z-\varepsilon_i} \tag{55}$$

in Eqs. 53 and 54, we can easily obtain common expressions for them found in text-books.

$$q_{kl} = 2\sum_i^{\text{occ}} C_{ki}C_{li}^*, \tag{56}$$

$$\begin{aligned}\pi_{kl;mn}(\bar{\pi}_{kl;mn}) = 2\sum_i^{\text{occ}}\sum_j^{\text{un}} \frac{1}{\varepsilon_i-\varepsilon_j}(C_{ki}C_{mi}^*C_{lj}C_{mj}^* \pm C_{ki}C_{ni}^*C_{lj}C_{mj}^* \\ + C_{kj}C_{mj}^*C_{li}C_{mi}^* \pm C_{kj}C_{nj}^*C_{li}C_{mi}^*).\end{aligned} \tag{57}$$

Now the first order energy change $\delta E^{(1)}$ is

$$\begin{aligned}\delta E^{(1)} &= -\sum_{k<l} q_{kl}\theta_{kl}^2 \\ &= -\beta\left(\frac{S}{\Phi_0}\right)^2 \sum_{k<l} q_{kl}s_{kl}^2\left[H^2+2H\left(\frac{m}{\mathrm{d}^3}\right)\right. \\ &\qquad \left.\times k_{kl}+\left(\frac{m}{\mathrm{d}^3}\right)^2 k_{kl}^2\right].\end{aligned} \tag{58}$$

The second order energy of which magnitude is same order to the first order one arises from the imaginary part of v, and then we obtain

$$\begin{aligned}\delta E^{(2)} &= \sum_{k<l}\sum_{m<n} \theta_{kl}\pi_{kl;mn}\theta_{mn} \\ &= \beta^2\left(\frac{S}{\Phi_0}\right)^2 \sum_{k<l}\sum_{m<n} \bar{\pi}_{kl;mn}s_{kl}s_{mn}\left[H^2+\frac{mH}{\mathrm{d}^3}(k_{kl}+k_{mn})\right. \\ &\qquad \left.+\left(\frac{m}{\mathrm{d}^3}\right)^2 k_{kl}k_{mn}\right].\end{aligned} \tag{59}$$

The linear terms with respect to the test dipole m is needed to evaluate the effective field secondaly produced:

$$\begin{aligned}\delta E_{maq}(=-mH') &= \delta E_{maq}^{(1)} + \delta E_{maq}^{(2)} \\ &= -2\beta\left(\frac{S}{\Phi_0}\right)^2 \frac{mH}{\mathrm{d}^3}(\sigma_1+\sigma_2),\end{aligned} \tag{60}$$

where σ_1 and σ_2 are dimensionless shielding constants:

$$\sigma_1 = \sum_{k<l} q_{kl}s_{kl}^2 k_{kl}, \tag{61}$$

$$\sigma_2 = \sum_{k<l}\sum_{m<n} \beta\bar{\pi}_{kl;mn}s_{kl}s_{mn}\cdot\frac{1}{2}(k_{kl}+k_{mn}). \tag{62}$$

Thus we have completely reproduced the result obtained by McWeeny (see Eqs. (4,2) and (4,3) of Ref. 4).

Perturbation Treatment II

If we start with the transformed Hamiltonian given by McWeeny,[4] the procedure is much more simplified. McWeeny transformation is as follows: Introducing a new basis set,

$$\langle\bar{\chi}_{\mathrm{a}}, \bar{\chi}_{\mathrm{b}}, \bar{\chi}_{\mathrm{c}}, \cdots| = \langle\chi_{\mathrm{a}}, \chi_{\mathrm{b}}, \chi_{\mathrm{c}}, \cdots|U \tag{63}$$

where U is a diagonal matrix,

$$U = \mathrm{diag.}(1, \omega_{12}^*, \omega_{12}^*\omega_{23}^*, \cdots, \omega_{12}^*\omega_{23}^*\cdots\omega_{i-1,i}^*, \cdots). \tag{64}$$

Then we have a transformed Hamiltonian, $\tilde{H}=U^{+}HU$, or in details

$$\tilde{H}_{ij} = U_{ii}^* H_{ij} U_{jj}. \tag{65}$$

Remembering that $\omega_{ij}=\omega_{ji}^*$ and $|\omega_{ij}|=1$, we can see that H of naphthalene given in Eq. 9 is transformed to such that with all the near-diagonal ω's replaced by 1, say

$$\tilde{\omega}_{34} = \omega_{12}\omega_{23}\omega_{34}\omega_{12}^*\omega_{23}^*\omega_{34}^* = 1, \tag{66}$$

and

$$\tilde{\omega}_{10,1} = \omega_{12}\omega_{23}\cdots\omega_{9,10}\omega_{10,1} = e^{i\theta_{10\to 1}}, \tag{67}$$

$$\begin{aligned}\tilde{\omega}_{10,5} &= \omega_{12}\omega_{23}\cdots\omega_{9,10}\omega_{10,5}\omega_{12}^*\omega_{23}^*\cdots\omega_{45}^* \\ &= \omega_{56}\omega_{67}\cdots\omega_{9,10}\omega_{10,5} = e^{i\theta_{10\to 5}}.\end{aligned} \tag{68}$$

Thus we have

$$\begin{aligned}\tilde{H} &= \begin{pmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & a \\ 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & b \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 \\ a^* & \cdot & \cdot & \cdot & b^* & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} \\ &= \begin{pmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} \\ &+ \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \bar{a} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \bar{b} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \bar{a}^* & \cdot & \cdot & \cdot & \bar{b}^* & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}\end{aligned} \tag{69}$$

where

$$a = \omega_{1,10},\quad b=\omega_{5,10},\quad \overline{a}=1-a,\quad \overline{b}=1-b \tag{70}$$

The transformed Hamiltonian is thus written as

$$H = H_0 + v, \tag{71}$$

however, v has non-vanishing matrix elements only at bonds which complete circuits. In the case of naphthalene, if we draw the path seen in Fig. 4a, the bonds, 10→1 and 10→5 complete the naphthalene and benzene rings, respectively. The arrow showing enclosing direction suggests the sign of the ring area (see Eqs. 67 and 68).

The energy change due to magnetic interaction is

$$\begin{aligned}\delta E &= \mathrm{Tr}\frac{1}{2\pi\mathrm{i}}\int_c \mathrm{d}z z(\boldsymbol{G}(z)-\boldsymbol{G}^0(z))\\ &= \mathrm{Tr}\frac{1}{2\pi\mathrm{i}}\int_c \mathrm{d}z z(\tilde{\boldsymbol{G}}(z)-\boldsymbol{G}^0(z)).\end{aligned} \tag{72}$$

In the above it is legitimate to replace $\boldsymbol{G}$ by $\tilde{\boldsymbol{G}}$ inside Tr.

The propagator $\tilde{\boldsymbol{G}}$ is given, by virtue of Eq. 71, as

$$\begin{aligned}\tilde{\boldsymbol{G}} &= \frac{1}{z-\boldsymbol{H}} = \frac{1}{z-\boldsymbol{H}_0-\boldsymbol{v}}\\ &= \frac{1}{z-\boldsymbol{H}_0} + \frac{1}{z-\boldsymbol{H}_0}\boldsymbol{v}\frac{1}{z-\boldsymbol{H}_0}\\ &\quad + \frac{1}{z-\boldsymbol{H}_0}\boldsymbol{v}\frac{1}{z-\boldsymbol{H}_0}\boldsymbol{v}\frac{1}{z-\boldsymbol{H}_0} + \cdots\\ &= \boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0 + \cdots\end{aligned} \tag{73}$$

Substituting this into Eq. 71 we can easily obtain, as has been done in the previous section, as

$$\begin{aligned}\delta E &= \mathrm{Tr}\frac{1}{2\pi\mathrm{i}}\int_c \mathrm{d}z\left(\boldsymbol{G}^0\boldsymbol{v}+\frac{1}{2}\boldsymbol{G}^0\boldsymbol{v}\boldsymbol{G}^0\boldsymbol{v}\right)\\ &= 2\sum_{m>n} q_{mn}v^0_{mn} + \sum_{m>n}\sum_{k>l} v'_{mn}\overline{\pi}_{mn;kl}v'_{kl},\end{aligned} \tag{74}$$

where v^0_{mn} and v'_{mn} are respectively the real and imaginary parts of v_{mn}, which is precisely

$$v_{mn} \doteqdot \beta\left(i\theta_{m\to n}-\frac{1}{2}\theta^2_{m\to n}\right), \tag{75}$$

with

$$\theta_{m\to n} = \frac{S}{\Phi_0}\left(s_{m\to n}H+\frac{m}{\mathrm{d}^3}\kappa_{m\to n}\right) \tag{76a}$$

and

$$\begin{aligned}s_{m\to n} &= s_{n,n+1} + s_{n+1,n+2} + \cdots s_{m-1,m} + s_{mn},\\ \kappa_{m\to n} &= s_{n,n+1}k_{n,n+1} + s_{n+1,n+2}k_{n+1,n+2} + \cdots\\ &\quad + s_{mn}k_{mn}.\end{aligned} \tag{76b}$$

Namely, $s_{m\to n}$ is the area surrounded by the circle which goes round $n\to n+1\to\cdots\to m\to n$, and $\kappa_{m\to n}$ is understood similarly.

Using aboves in Eq. 74, we obtain

$$\delta E^{(1)} = -\beta\left(\frac{S}{\Phi_0}\right)^2\sum_{m>n} q_{mn}\left(Hs_{m\to n}+\frac{m}{\mathrm{d}^3}\kappa_{m\to n}\right)^2, \tag{77}$$

$$\begin{aligned}\delta E^{(2)} &= \beta^2\left(\frac{S}{\Phi_0}\right)^2\sum_{m>n}\sum_{k>l}\overline{\pi}_{mn;kl}\left(HS_{m\to n}+\frac{m}{\mathrm{d}^3}\kappa_{m\to n}\right)\\ &\quad \times\left(Hs_{k\to l}+\frac{m}{\mathrm{d}^3}\kappa_{k\to l}\right).\end{aligned} \tag{78}$$

The linear terms with respect to m in Eqs. 77 and 78 yield

$$\begin{aligned}\delta E &= (-mH') = \delta E^{(1)}_{\mathrm{mag}} + \delta E^{(2)}_{\mathrm{mag}}\\ &= -2\beta\left(\frac{S}{\Phi_0}\right)^2\frac{m}{\mathrm{d}^3}(\sigma_1+\sigma_2),\end{aligned} \tag{79}$$

where

$$\sigma_1 = \sum_{m,n} q_{mn}s_{m\to n}\kappa_{m\to n},$$

$$\sigma_2 = \sum_{m>n}\sum_{k>l}\beta\overline{\pi}_{mn;kl}\frac{1}{2}(s_{m\to n}\kappa_{k\to l}+s_{k\to l}\kappa_{m\to n}). \tag{80}$$

In this treatment the summation is restricted to the bonds which complete circuits. Also note that $\overline{\pi}_{mn;kl}$ is given in unit of $1/\beta$. Eq. 79 gives the same result with that of the previous section, but with more transparent physical image.

Illustrative Examples

A few examples will be presented in order to faciliate understanding of the preceding treatment.

(1) Benzene. This is the case of one ring, and calculation becomes trivially simple. Go round the ring along the positive direction and the circuite is completed by the bond 6→1, then we have; $s_{6\to1}=1$ and $\kappa_{61}=s_{12}k_{12}+s_{23}k_{23}+\cdots+s_{61}k_{61}$. Thus $\sigma_1=2/3\cdot\kappa_{1\to6}$ and $\sigma_2=-5/9\cdot\kappa_{1\to6}$. The secondary induced field at the test dipole is written as

$$H' = 2\beta\left(\frac{S}{\Phi_0}\right)^2\frac{H}{\mathrm{d}^3}\frac{1}{9}\kappa_{6\to1}. \tag{81}$$

Further discussion is refered to Ref. 4.

(2) Naphthalene. It should be instructive to calculate in two alternative ways based on Fig. 4a and 4b. One of the purposes of the present example is that, as has been done intuitively, the whole effect of the (naphthalene) ring current is attributed to those of individual, constituent benzene rings.

(a) Bonds 10→5 and 10→1 together complete a positive circuite with $s_{10\to5}=1$ and $s_{10\to1}=2$. $\kappa_{10\to5}$ is occuring

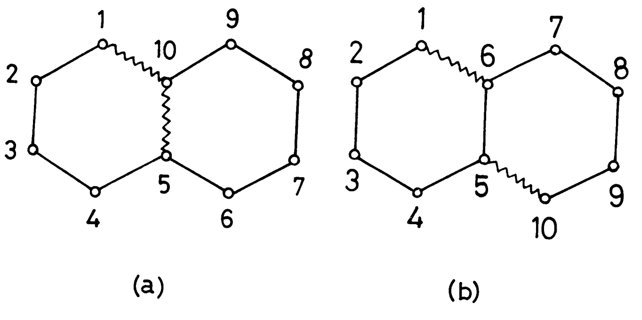


Fig. 4.

in the right hand side benzene ring, named R (while the left hand ring is called L). Then, if we write $\kappa_{10\rightarrow5}=\kappa_R$, it should be that $\kappa_{10\rightarrow1}=\kappa_R+\kappa_L$. Thus we obtain

$$\begin{aligned}\sigma_1 &= q_{1,10}(\kappa_R+\kappa_L) + q_{5,10}\kappa_L \\ &= 1.1094\kappa_R + 1.16277\kappa_L \end{aligned} \tag{82}$$

$$\begin{aligned}\sigma_2 &= -\ [\overline{\pi}_{5,10;5,10}\kappa_L+2\overline{\pi}_{1,10;1,10}(\kappa_R+\kappa_L) \\ &\quad +\overline{\pi}_{5,10;1,10}(\kappa_R+3\kappa_L)] \\ &= -\ 0.9880\kappa_{\mathrm{R}} - 1.5063\kappa_L, \end{aligned} \tag{83}$$

where $\overline{\pi}$'s are in unit β. It should be stressed that as shown in Fig. 4, if we begin with drawing a path numbered there, circuits concerning with magnetic interaction are identically determined. In this respective, we call these circuits irreducible ones.

(b) The bonds 6→1 and 10→5 complete, respectively, the positive and negative circuits with $s_{6\rightarrow1}=1$ and $s_{10\rightarrow5}=-1$. Therefore noting that $\kappa_{6\rightarrow1}=\kappa_R$ and $\kappa_{10\rightarrow5}=-\kappa_{\mathrm{L}}$, we obtain

$$\begin{aligned}\sigma_1 &= q_{16}(\kappa_R+\kappa_L) \\ &= 0.5547(\kappa_R+\kappa_L), \end{aligned} \tag{84}$$

and

$$\begin{aligned}\sigma_2 &= \overline{\pi}_{1,6;1,6}\kappa_R + \overline{\pi}_{5,10;5,10}\kappa_L + \kappa_{1,6;5,10}(\kappa_R+\kappa_L) \\ &= -\ 0.4333(\kappa_R+\kappa_L), \end{aligned} \tag{85}$$

by the use of $\overline{\pi}_{1,6;1,6}=\overline{\pi}_{5,10;5,10}=-0.4660$ and $\pi_{1,6;5,10}=-0.0327$.

The both calculations (a) and (b) result in the same value,

$$\sigma_1 + \sigma_2 = 0.1214(\kappa_R+\kappa_L), \tag{86}$$

which tells us the invariant character, independent of choice of the original path. Finally we note that $-\kappa_{\mathrm{p}}\rightarrow1/r^3$ at large distance and each ring behaves like an induced dipole.

Conclusion

As has been seen in the previous sections, the propagator theory works well and easily reproduces the current results. One may say that it yields nothing new beyond traditional methods, but we insist that, by this way, the analysis is very much simplified, physical processes involved are made clearer, and the method itself is considerably general, even for the complicated phenomena.

References

1) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).
2) F. London, *J. Phys. Radium*, **8**, 397 (1936).
3) J. A. Pople, *Mol. Phys.*, **1**, 175 (1958).
4) R. McWeeny, *Mol. Phys.*, **1**, 311 (1958).
5) J. Aihara, *J. Am. Chem. Soc.*, **101**, 5913 (1979); 103, 5704 (1981).
6) S. Aono and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **53**, 3418 (1980); S. Aono, T. Ohmae, and K. Nishikawa, *Bull. Chem. Soc. Jpn.*, **54**, 1645 (1981); K. Nishikawa, M. Yamamoto, and S. Aono, *J. Chem. Phys.*, **78**, 5031 (1983).
7) L. Salem, The Molecular Orbital Theory of Conjugated System, p 189 (Benjamin, 1966).
8) S. Aono and K. Nishikawa, previous paper.