Use of Propagators in the Hückel Model. II. Propagators in Terms of Trigonometrical Functions

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The propagators of the chain molecules with and without the bond alternation are expressed in terms of trigonometrical functions. These expressions are convenient to practical manipulations. For exercises, the total energy, charge density and bond order are calculated.

In the previous paper,[1] we have developed a propagator theory for the Hückel model or in the tight-binding approximation. Useful methods to obtain the propagators of general networks have been presented, and propagators have been finally expressed as polynomials in terms of the energy parameter z. This analytical form being convincing from the theoretical viewpoints, is not so convenient for various application. As has been done in the simple examples of I, the actual calculations always need the contour integrals around the poles. If we use the polynomial expressions for propagators, it is difficult for us to find poles except the simplest cases. Therefore we give the compact analytical forms to the propagators in terms of trigonometrical functions. Then we calculate the charge density, bond order and total energy of the systems under consideration. Mathematical tools are almost due to the Coulson's old paper,[2] which is not so far in spirit from the present modern treatment.

Propagators of Linear Chain Molecules with Equal Bond Distance

In this section, the propagator of the linear chain molecule with same atoms and with equal bond length is investigated. The transfer integral between the nearest sites is scaled to be unity and if necessary it will be recovered by the dimensional analysis. The linear chain molecule with n sites are numbered as Fig. 1. The propagator of this system has been given in I as

$$G_n(0)^{-1} = z - \cfrac{1}{z - \cfrac{1}{z - \cfrac{1}{z - \cfrac{1}{\vdots}}}} = z + \frac{-1}{z} + \frac{-1}{z} + \frac{-1}{z} + \cdots, \tag{1}$$

where $G_n(0)$ is the (0,0) matrix element of the Green's function operator of this chain.

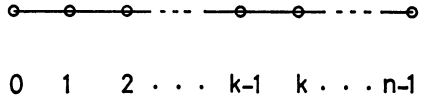

Fig. 1. Linear chain molecule.

The continued fraction more general than Eq. 1

$$S_n = b_0 + \frac{a_1}{b_1} + \frac{a_2}{b_2} + \cdots + \frac{a_{n-1}}{b_{n-1}} \tag{2}$$

is expressed as[3]

$$S_n = A_{n-1}/B_{n-1}. \tag{3}$$

Here A_k and B_k satisfy the recurrance formula

$$\begin{pmatrix} A_k \\ B_k \end{pmatrix} = \begin{pmatrix} A_{k-1} & A_{k-2} \\ B_{k-1} & B_{k-2} \end{pmatrix} \begin{pmatrix} b_k \\ a_k \end{pmatrix} \tag{4}$$

with

$$\begin{pmatrix} A_{-1} \\ A_0 \end{pmatrix} = \begin{pmatrix} 1 \\ b_0 \end{pmatrix}, \quad \begin{pmatrix} B_{-1} \\ B_0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{5}$$

In our case, b_k and a_k in Eq. 2 are simply

$$\begin{aligned} b_0 &= b_1 = b_2 = \cdots = z, \\ a_1 &= a_2 = a_3 = \cdots = -1, \end{aligned} \tag{6}$$

and then

$$\begin{aligned} A_k &= zA_{k-1} - A_{k-2}, \\ B_k &= zB_{k-1} - B_{k-2}, \end{aligned} \tag{7}$$

with the initial conditions

$$\begin{aligned} A_0 &= z, \quad A_1 = z^2 - 1, \\ B_0 &= 1, \quad B_1 = z. \end{aligned} \tag{8}$$

We have a theorem: If it holds that

$$S_k = bS_{k-1} + aS_{k-2}, \ (S_1 \text{ and } S_2 \text{ are given}) \tag{9}$$

the polynomial defined by

$$S(x) \equiv 1 + S_1x + S_2x^2 + \cdots \tag{10}$$

is calculated as

$$S(x) = \frac{1}{1-(bx+ax^2)}\{1+(S_1-b)x+(S_2-bS_1-a)x^2\}. \tag{11}$$

The proof is very easy and omitted.

Applying this theorem to A_k and B_k, we can find

$$\begin{aligned} A(x) &= 1 + A_0x + A_1x^2 + \cdots = \sum_{n=0}^{\infty} A_{n-1}x^n \\ &= \frac{1}{1-zx+x^2} = \sum_{n=0}^{\infty} \frac{\sin(n+1)\theta}{\sin\theta} x^n, \end{aligned} \tag{12}$$

$$z = 2\cos\theta \tag{13}$$

and

$$\begin{aligned} B(x) &= 1 + B_1x + B_2x^2 + \cdots = \sum_{n=0}^{\infty} B_nx^n \\ &= \frac{1}{1-zx+x^2} = \sum_{n=0}^{\infty} \frac{\sin(n+1)\theta}{\sin\theta} x^n. \end{aligned} \tag{14}$$

From Eq. 12 and Eq. 14 we can obtain

$$\begin{aligned} A_{k-1} &= \sin(k+1)\theta/\sin\theta \\ B_{k-1} &= \sin k\theta/\sin\theta \end{aligned} \tag{15}$$

and

$$G_n^{-1}(0) = A_{n-1}/B_{n-1} = \sin(n+1)\theta/\sin n\theta. \tag{16}$$

It should be mentioned that the replacement of Eq. 13 is safely permitted, because any site of this chain is

connected only to two nearest neighbors, and the value of z does not exceed 2.

The next problem is to obtain any diagonal element of the propagator, $G_n(k)$. If we employ a method composing the propagator,[1] it yields that

$$G_n^{-1}(k) = G_{n-k}^{-1}(0) - G_k(0) \tag{17a}$$

$$= \frac{\sin(n+1)\theta \sin\theta}{\sin(n-k)\theta \sin(k+1)\theta}. \tag{17b}$$

The relation (17a) is nothing but the Dyson equation in the site representation.

The off-diagonal element of propagator, $G_n(k,k+l)$ is expressed as

$$\begin{aligned} G_n(k,k+l) &= G_n(k)G_n(k+1,[k]) \cdots G_n(k+l[k+l-1]) \\ &= G_n(k)G_{n-k-1}(0) \cdots G_{n-k-l}(0), \end{aligned} \tag{18}$$

where $G_n(p[q])$ is the p-th diagonal element, when the q-th site is omitted. Note that the transfer integral is scaled to be unity. Using Eq. 17b in Eq. 18, we can easily obtain

$$G_n(k,k+l) = \frac{\sin(n-k-l)\theta \sin(k+1)\theta}{\sin(n+1)\theta \sin\theta}. \tag{19}$$

We now turn to evaluation of the charge density, bond order and total energy.

The charge density at k-th site is written as

$$q_n(k) = \frac{1}{2\pi i}\int_C dz G_n(k;z), \tag{20}$$

where integration is carried out along the so-called Coulson contour shown in Fig. 2a. In evaluating Eq. 20, we want to use the expression (17b) for G_n. Then we have to examine how the contour and poles are mapped onto the θ-plane by the relation (13). Let

$$z = x + iy, \quad \theta = \varphi + i\psi, \tag{21}$$

so that

$$x + iy = 2(\cos\varphi \cosh\psi - i \sin\varphi \sinh\psi). \tag{22}$$

The results obtained are displayed by Fig. 2b. The corresponding positions on the contours between two are indicated by ①. How the poles are mapped is also explained in the figure caption in the case of the six members ring. We note first of all that while the contour turns round once in the z-plane, it goes round twice in the θ-plane, so that we need the additional multiplicative factor, 1/2. Second, every pole in the z-plane splits into two except ones of values $\theta=0$ and π. However we need not worry about this behavior since the pole strength at any pole correctly produces the result.

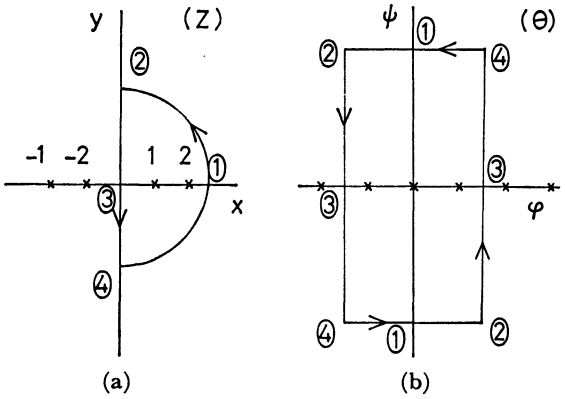

Fig. 2. (a) Contour in z-plane; Poles are those of the six member ring. (b) Contour in θ-plane; Poles are transfered as $2\to 0$; $1\to\pi/3$, $-\pi/3$; $-1\to 2\pi/3$, $-2\pi/3$; $-2\to\pi$.

Using Eq. 17b and Eq. 20, we obtain

$$q_n(k) = \frac{-1}{2\pi i}\int_C d\theta \frac{\sin(n-k)\theta \sin(k+1)\theta}{\sin(n+1)\theta}, \tag{23}$$

where poles are

$$\theta_r = \pi r/(n+1), \quad r = \pm 1, \pm 2, \cdots, \pm n. \tag{24}$$

Hereafter we confine ourselves to the simplest case of the so-called half-filled band, *i.e.*, the levels with $|n| \leq n/2$ being occupied. The contour integral in Eq. 23 yields (the spin factor, 2 is included)

$$\begin{aligned} q_n(k) &= -2\sum_{r=-n/2}^{n/2} \frac{\sin(n-k)\theta_r \sin(k+1)\theta_r}{(n+1)\cos(n+1)\theta_r} \\ &= \frac{n}{n+1} - \frac{2}{n+1}\sum_{r=1}^{n/2}(-1)^r \cos\left(\frac{n-2k-1}{n+1}\right)\pi r \\ &= 1. \end{aligned} \tag{25}$$

Here we have used the relation

$$\begin{aligned} &\sum_{r=1}^{k}(-1)^{r-1}\cos xr \\ &= \frac{1}{2} + (-1)^r \cos\frac{(k+1)}{2}x/2\cos\frac{x}{2} \end{aligned} \tag{26}$$

and see that in the second term of Eq. 25, the terms except with $r=1$ vanish. Note that $q_n(k)$ is independent of k.

The bond order, $q_n(k,k+1)$ is given by Eq. 19 as

$$\begin{aligned} q_n(k,k+l) &= \frac{1}{2\pi i}\int_C dz G_n(k,k+l;z) \\ &= \frac{-1}{2\pi i}\int_C d\theta \frac{\sin(k+1)\theta \sin(n-k-l)\theta}{\sin(n+1)\theta}. \end{aligned} \tag{27}$$

In the similar way but a little tedious calculations lead to

$$\begin{aligned} q_n(k,k+l) = \frac{1}{n+1}\Bigg\{&\frac{\sin l\pi/2}{\sin l\pi/2(n+1)} \\ &- \frac{\sin(2k+l+2)\pi/2}{\sin(2k+l+2)\pi/2(n+1)}\Bigg\}. \end{aligned} \tag{28a}$$

If we here put

$$k = S - 1, \quad k + l = t - 1,$$

the above becomes

$$\begin{aligned} q_n(s-1,t-1) = \frac{1}{n+1}\Bigg\{&\frac{\sin(t-s)\pi/2}{\sin(t-s)\pi/2(n+1)} \\ &- \frac{\sin(t+s)\pi/2}{\sin(t+s)\pi/2(n+1)}\Bigg\} \end{aligned} \tag{28b}$$

as usual. From this expression, we can clearly conclude that $q_n(s-l, t-l)$ vanishes for the cases that $(t-s)$ is even, *i.e.*, between the starred atoms, or between the unstarred atoms.

The total energy of the present system, E is

$$E_n = \mathrm{Tr}\frac{1}{2\pi i}\int_C dz\, z\mathbf{G}_n(z) \tag{29}$$

$$= \sum_{k=0}^{n-1}\frac{-1}{\pi i}\int_C d\theta \frac{\cos\theta \sin(n-k)\theta \sin(k+1)\theta}{\sin(n+1)\theta}$$

$$= 4\sum_{r=1}^{n/2}\cos\theta_r$$

$$= 2\sum_{r=1}^{n/2} z(\theta_r). \tag{30}$$

In obtaining this result, we have made the k-summation at the beginning, using the relations,

$$\sum_{k=1}^{n}\sin xk = \sin\frac{(n+1)x}{2}\sin\frac{nx}{2}\Big/\sin\frac{x}{2}$$

$$\sum_{k=1}^{n}\cos xk = \cos\frac{(n+1)x}{2}\sin\frac{nx}{2}\Big/\sin\frac{x}{2}. \tag{31}$$

Propagator of Ring Molecule with Equal Bond Distance

We shall obtain the propagator of the ring molecule shown in Fig. 3. For simplicity, the number of atoms, n is assumed to be $4m+2$, $m=1,2,\cdots$ Employing the method[1] to build up the ring propagator from the chain propagator, we get

$$\begin{aligned} R_n^{-1}(0) &= G_1^{-1}(0) - G_n(1[0]) - G_n(1,n[0]) \\ &\quad - G_n(n[0]) - G_n(n,1[0]) \\ &= G_1^{-1}(0) - 2G_{n-1}(0) - 2G_{n-1}(0,n-2) \\ &= \frac{\sin 2\theta}{\sin\theta} - 2\left\{\frac{\sin(n-1)\theta}{\sin n\theta} + \frac{\sin\theta}{\sin n\theta}\right\} \\ &= -\frac{2\sin(n\theta/2)\sin\theta}{\cos(n\theta/2)}. \end{aligned} \tag{32}$$

The poles of R_n are

$$\theta_r = \frac{2\pi r}{n},\ r = 0,\ \pm 1,\ \cdots,\ \pm\left(\frac{n}{2}-1\right),\ \frac{n}{2} \tag{33}$$

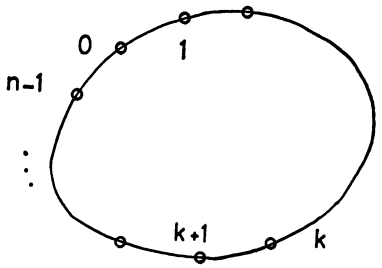

Fig. 3. Ring molecule.

Now we calculate the charge density, bond order and total energy for the case of the half-filled band. The charge density at any site is given by

$$\begin{aligned} q_n^R(0) &= \frac{1}{2\pi i}\int_C dz\, R_n(0;z) \\ &= \frac{1}{4\pi i}\int_C d\theta\,\frac{\cos(n\theta/2)}{\sin(n\theta/2)}. \end{aligned} \tag{34}$$

The integration along the contour shown in Fig. 2b is easily carried out as

$$q_n^R(0) = \frac{2}{n}\sum_{\text{Poles}} 1 = 1, \tag{35}$$

where the fact has been used that the number of poles corresponding occupied levels, *i.e.*$|\theta_r|<\pi/2$ is $n/2$. The spin summation is also done.

In order to estimate the bond order, $q_n(0,k)$, we need the off-diagonal element of the ring propagator, which is

$$\begin{aligned} R_n(0,k) &= R_n(0)R_n(1,k[0]) + R_n(0)R_n(n-1,k[0]) \\ &= R_n(0)G_{n-1}(0,k) + R_n(0)G_{n-1}(0,n-k-1), \end{aligned} \tag{36}$$

where the first and second terms correspond to the clockwise and anticlockwise propagations in Fig. 3, respectively. Using Eq. 32 and Eq. 19 in Eq. 36, we get

$$R_n(0,k) = \frac{-1}{4\sin^2\dfrac{n\theta}{2}\sin\theta}\{\sin(n-k)\theta + \sin k\theta\}. \tag{37}$$

Thus a little tedious but straightforward calculations yield

$$\begin{aligned} q_n^R(0,k) &= \frac{1}{4\pi i}\int_C d\theta\,\frac{1}{2\sin^2\dfrac{n\theta}{2}}\{\sin(n-k)\theta + \sin k\theta\} \\ &= \frac{2}{n^2}\{(n-k)+k\}\frac{\sin k\pi/2}{\sin k\pi/n} \\ &= \frac{2}{n}\frac{\sin k\pi/2}{\sin k\pi/n}, \end{aligned} \tag{38}$$

where, in the second line, the first and second terms are contributions from the clockwise and anticlockwise pathes, respectively. The final result clearly shows that in the alternant hydrocarbons the bond order vanishes between the starred atoms or between the unstarred atoms, *i.e.*, k is even. In the case of $k=1$,

$$q_n^R(0,1) = \frac{2}{n}\operatorname{cosec}\frac{\pi}{n}. \tag{39}$$

The total energy is given as

$$\begin{aligned} E &= \mathrm{Tr}\,\frac{1}{2\pi i}\int_C dz\, z\mathbf{R}_n(z) \\ &= n\frac{1}{4\pi i}\int_C d\theta\,\frac{\cos\theta\sin n\theta}{\sin^2(n\theta/2)} \\ &= 4\operatorname{cosec}\frac{\pi}{n}. \end{aligned} \tag{40}$$

Linear Chains with Bond Alternation

Linear polyenes actually show the bond alternation. If we consider phenomena concerning with linear polyene, it is natural to start with systems with the bond alternation. In this sense, it seems instructive to investigate the propagators for these molecules. Those which we are now considering are shown in Fig. 4.

The propagator of the chain molecule and chain radical are denoted G_{2n} and F_{2n+1}, respectively, where

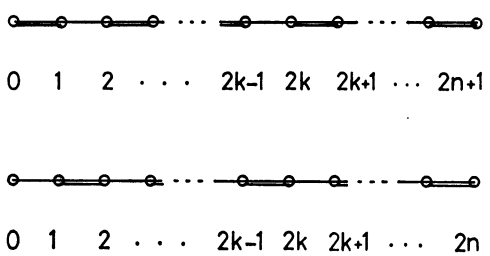

Fig. 4. Chain molecule $C_{2n}H_{2n+2}$ and chain radical $C_{2n+1}H_{2n+3}$.

indices give the number of the carbon atoms. The resonance integrals corresponding to the double and single bonds are written as β^* and β.

As has been done in Eq. 1, $G_{2n}(0)$ is given as

$$G_{2n}^{-1}(0) = z - \cfrac{\beta^{*2}}{z - \cfrac{\beta^2}{z - \cfrac{\beta^{*2}}{\ddots}}}$$

$$= z + \frac{-\beta^{*2}}{z} + \frac{-\beta^2}{z} + \cdots . \tag{41}$$

If we divide both sides by $\sqrt{\beta\beta^*}$, it yields that

$$\bar{G}_{2n}^{-1}(0) = \bar{z} + \frac{-\gamma}{\bar{z}} + \frac{-\gamma^{-1}}{\bar{z}} + \cdots , \tag{42}$$

where

$$\gamma = \beta^*/\beta , \tag{43}$$

and

$$\bar{G}_{2n} = G_{2n}/\sqrt{\beta\beta^*}, \quad \bar{z} = z/\sqrt{\beta\beta^*}. \tag{44}$$

Hereafter the dimensionless $\bar{G}_{2n}$ and $\bar{z}$ are rewritten as G_{2n} and z. Namely, instead of Eq. 42

$$G_{2n}^{-1}(0) = z + \frac{-\gamma}{z} + \frac{-\gamma^{-1}}{z} + \cdots . \tag{45}$$

Similarly, for the radical

$$F_{2n+1}^{-1}(0) = z + \frac{-\gamma^{-1}}{z} + \frac{-\gamma}{z} + \cdots . \tag{46}$$

If we write $G_k^{-1}(0)$ and $F_k^{-1}(0)$ as

$$G_k^{-1}(0) = \frac{A_{k-1}^*}{B_{k-1}^*}, \quad F_{k+1}^{-1}(0) = \frac{A_k}{B_k}. \tag{47}$$

The same treatments as has been done from Eq. 2 to Eq. 7 yield,

$$\begin{aligned}
&A_0^* = z \\
&A_1^* = z^2 - \gamma \\
&A_2^* = z^3 - z(\gamma+\gamma^{-1}) \\
&A_3^* = z^4 - z^2(2\gamma+\gamma^{-1}) + \gamma^2 \\
&A_4^* = z^5 - 2z^3(\gamma+\gamma^{-1}) + z(\gamma^2+1+\gamma^{-2}) \\
&A_5^* = z^6 - z^4(3\gamma+\gamma^{-1}) + z^2(3\gamma^2+\gamma^{-2}) - \gamma^3 \qquad (48a) \\
&\vdots \\
&B_0^* = 1 \\
&B_1^* = z \\
&B_2^* = z^2 - \gamma^{-1} \\
&B_3^* = z^3 - z(\gamma+\gamma^{-1}) \\
&B_4^* = z^4 - z^2(\gamma+2\gamma^{-1}) + \gamma^{-2} \\
&B_5^* = z^5 - 2z^3(\gamma+\gamma^{-1}) + z(\gamma^2+1+\gamma^{-2}) \qquad (48b) \\
&\vdots
\end{aligned}$$

In the above interchanging γ and γ^{-1}, we can obtain the similar expressions for A_k and B_k,

$$\begin{aligned}
A_k &= A_k^*(\gamma \leftrightarrow \gamma^{-1}) \\
B_k &= B_k^*(\gamma \leftrightarrow \gamma^{-1}).
\end{aligned} \tag{49}$$

Also we can observe

$$\begin{aligned}
A_k &= B_{k+1}^* \\
B_k &= A_{k-1}^*.
\end{aligned} \tag{50}$$

From relations, Eqs. 48 and 49, we can immediately obtain the recurrance formulae:

$$\begin{aligned}
A_k^* &= zA_{k-1} - \gamma A_{k-2}^* \\
A_k &= zA_{k-1}^* - \gamma^{-1}A_{k-2}
\end{aligned} \tag{51}$$

and

$$\begin{aligned}
B_k^* &= zB_{k-1} - \gamma^{-1}B_{k-2}^* \\
B_k &= zB_{k-1}^* - \gamma B_{k-2}.
\end{aligned} \tag{52}$$

If we eliminate A in Eq. 51, we obtain

$$A_k^* + A_{k-2}^*(\gamma+\gamma^{-1}-z^2) + A_{k-4}^* = 0. \tag{53}$$

Entirely same relations hold for A_k, B_k^*, and B_k.

Now we can use the theorem given by Eq. 9 and Eq. 11. Let

$$A^*(x) = 1 + A_1^*x + A_2^*x^2 + \cdots + A_{2n-1}^*x^n + \cdots \tag{54}$$

and put

$$b = z^2 - \gamma - \gamma^{-1}, \quad a = -1 \tag{55}$$

in Eq. 9, it yields that

$$A^*(x) = \frac{1 + \gamma^{-1}x}{1 - (z^2-\gamma-\gamma^{-1})\,x + x^2}. \tag{56}$$

Here we put

$$z^2 = \gamma + \gamma^{-1} + 2\cos\theta \tag{57}$$

and obtain

$$\begin{aligned}
A^*(x) &= \sum_{n=0}^{\infty} \frac{\sin(n+1)\theta}{\sin\theta}\, x^n\,(1+\gamma^{-1}x) \\
&= \sum_{n=0}^{\infty} \left\{ \frac{\sin(n+1)\theta}{\sin\theta} + \gamma^{-1}\frac{\sin n\theta}{\sin\theta} \right\} x^n.
\end{aligned} \tag{58}$$

Combining this and Eq. 54, we get

$$A_{2n-1}^* = \left\{ \frac{\sin(n+1)\theta}{\sin\theta} + \gamma^{-1}\frac{\sin n\theta}{\sin\theta} \right\}. \tag{59a}$$

Similar analysis for B_{2n-1}^* enables us to get

$$B_{2n-1}^* = z\,\frac{\sin n\theta}{\sin\theta}. \tag{59b}$$

Remembering relations in Eq. 50, we obtain

$$A_{2n} = B_{2n+1}^* = z\frac{\sin(n+1)\theta}{\sin\theta}, \tag{60a}$$

$$B_{2n} = A_{2n-1}^* = \frac{\sin(n+1)\theta}{\sin\theta} + \gamma^{-1}\frac{\sin n\theta}{\sin\theta}. \tag{60b}$$

Consequently, the propagators of systems shown in Fig. 4 are

$$G_{2n}^{-1}(0) = \{\sin(n+1)\theta + \gamma^{-1}\sin n\theta\}/z\sin n\theta, \tag{61}$$

$$F_{2n+1}^{-1}(0) = z\sin(n+1)\theta/\{\sin(n+1)\theta + \gamma^{-1}\sin n\theta\}. \tag{62}$$

It is noted that once $G_{2n}^{-1}(0)$ is given, we can immediately obtain $F_{2n+1}^{-1}(0)$ by the following relation

$$F_{2n+1}^{-1}(0) = F_1^{-1}(0) - \gamma^{-1}G_{2n}(0), \tag{63}$$

and *vice versa*. Note that $F_1^{-1}(0) = z$.

Some Properties of Linear Chains with Bond Alternation

Since we have written the propagators of linear chains with bond alternation in the previous section, we now move to get some physical properties by use of them. The poles of propagators give the single particle energies: for example in the case of the chain with $2n$ members the relation

$$\sin(n+1)\theta_r + \gamma^{-1}\sin\theta_r = 0, \tag{64}$$

determines the single particle energies. The roots of Eq. 64 cannot be obtained easily, but if γ is not so far from unity, the solution has been approximately

obtained as[2,4]

$$\theta_r = \frac{2\pi r}{2n+1} - \frac{1}{2n+1}(1-\gamma^{-1}) + \tan\frac{\pi r}{2n+1}, \quad r=1,2,\cdots,2n, \quad (65)$$

where the first term stands for the case with equal bond distance, and the second for the correction in this case.

For further steps, we need the expressions of $G_{2n}(2k)$, $G_{2n}(2k+1)$, $F_{2n+1}(2k)$ and $F_{2n+1}(2k-1)$. For example, $G_{2n}(2k)$ is given as (see Fig. 4)

$$G_{2n}^{-1}(2k) = G_{2(n-k)}^{-1}(0) - \gamma^{-1} G_{2k}(0). \quad (66)$$

From this and similar equations for others, we obtain

$$G_{2n}^{-1}(2k) = \frac{\sin\theta\{\sin(n+1)\theta+\gamma^{-1}\sin n\theta\}}{z\sin(n-k)\theta\{\sin(k+1)\theta+\gamma^{-1}\sin k\theta\}}, \quad (67a)$$

$$G_{2n}^{-1}(2k-1) = \frac{\sin\theta\{\sin(n+1)\theta+\gamma^{-1}\sin n\theta\}}{z\sin k\theta\{\sin(n-k+1)\theta+\gamma^{-1}\sin(n-k)\theta\}}, \quad (67b)$$

$$F_{2n+1}^{-1}(2k) = \frac{z\sin(n+1)\theta\sin\theta}{\{\sin(k+1)\theta+\gamma\sin k\theta\}\{\sin(n-k+1)\theta+\gamma^{-1}\sin(n-k)\theta\}}, \quad (68a)$$

$$F_{2n+1}^{-1}(2k-1) = \frac{\sin(n+1)\theta\sin\theta}{z\sin(n-k+1)\theta\sin k\theta}, \quad (68b)$$

where $z=z(\theta)$ is shown in Eq. 57.

The Total Energy of the 2n *Chain.* This is given by

$$E_{2n} = \mathrm{Tr}\frac{1}{2\pi i}\int_C dz\, zG_{2n}(z) = 2\sum_{k=1}^{n-1}\frac{-1}{4\pi i}\int_C d\theta\frac{z\sin(n-k)\theta\{\sin(k+1)\theta+\gamma^{-1}\sin k\theta\}}{\sin(n+1)\theta+\gamma^{-1}\sin n\theta}. \quad (69)$$

The integration contour in this case is the same as Fig. 2b, if the two points $\pi/2$ and $-\pi/2$ are replaced by π and $-\pi$, respectively. Also note that the integration in Eq. 69 includes the spin sum. The summation with respect to k is made and then followed by the contour integration:

$$E_{2n} = 2\sum_{r=-n}^{n}\frac{z(\theta_r)\left[\frac{n}{2}\{\cos(n+1)\theta_r+\gamma^{-1}\cos n\theta_r\}-\frac{1}{2}\frac{\sin n\theta_r}{\sin\theta_r}\{1+\gamma^{-1}\cos\theta_r\}\right]}{(n+1)\cos(n+1)\theta_r+\gamma^{-1}\cos n\theta_r}. \quad (70)$$

Then using the relation (64), we can get

$$E_{2n} = \sum_{r=-n}^{n} z(\theta_r) = 2\sum_{r=1}^{n} z(\theta_r), \quad (71)$$

namely, we find the usual description that the levels with $r=1\sim n$ are doubly occupied. For numerical estimation, Eq. 65 should be invoked.

In the case of the $2n$ chain, we have been unable to give the simple and compact expressions for the poles of the propagator, which enable us difficult to carry out the contour integration. Therefore in the following we confine ourselves to treat the $2n+1$ chain, or radicals.

*The Charge Density at the (*2k−1*)-th Site of the* 2n+1 *Chain.* This is given simply by

$$q_{2n+1}(2k-1) = \frac{1}{2\pi i}\int_C dz\, F_{2n+1}(2k-1;z) = \frac{-1}{4\pi i}\int_C d\theta\frac{\sin(n-k+1)\theta\sin k\theta}{\sin(n+1)\theta}, \quad (72)$$

where poles are

$$\theta_r = \pi r/(n+1), \quad (73)$$

and those with $r=\pm1,\pm2,\cdots,\pm n$ are doubly occupied and $r=\pm(n+1)$ are singly occupied. In the course of the contour integration, we can observe that the contribution from the terms with $r=\pm(n+1)$ vanishes, and that from others exactly gives

$$q_{2n+1}(2k-1) = 1, \quad (74)$$

which is independent of k. Here we have also used the relation (26).

It is naturally expected to be

$$q_{2n+1}(2k) = 1, \quad (75)$$

but the proof seems tedious because of the rather complicated expression of Eq. 68a, and the z^2 term which appears in the denominator of the contour integrand. Briefly speaking, our proof is as follows: we separate the numerator into two parts, the first with z^2 as a common factor and the second not. We can show the contribution from the second to the integration vanishes. Concerning the first, the integration is carried out as well as in the case of $q_{2n+1}(2k-1)$, and yields the result (75). We expect a simpler proof.

The Bond Orders of the 2n+1 *Chain.* We investigate the bond order between the sites $2k-1$ and $2k$, which concerns with the double bond as indicated in Fig. 4. This is given by

$$q_{2n+1}(2k-1,2k) = \frac{1}{2\pi i}\int_C dz\, F_{2n+1}(2k-1,2k;z), \quad (76)$$

in which

$$F_{2n+1}(2k-1,2k) = F_{2n+1}(2k)\gamma^{-1/2}G_{2(n-k)}(0) = \frac{\sin k\theta\{\gamma^{1/2}\sin(n-k+1)\theta+\gamma^{-1/2}\sin(n-k)\theta\}}{\sin\theta\sin(n+1)\theta}. \quad (77)$$

Accordingly it follows that

$$q_{2n+1}(2k-1,2k) = \frac{-1}{4\pi i}\int_C\frac{d\theta}{z(\theta)}\frac{\sin k\theta\{\gamma^{1/2}\sin(n-k+1)\theta+\gamma^{-1/2}\sin(n-k)\theta\}}{\sin(n+1)\theta}. \quad (78)$$

Since the term, $z(\theta)$ is regular at the poles,

$$\theta_r=\pi r/(n+1), r=1,2,\cdots,(n+1). \quad (79)$$

The integration is easily carried out to yield,

$$q_{2n+1}(2k-1,2k) = \frac{2}{n+1}\sum_{r=1}^{n}\frac{\sin k\theta_r}{z(\theta_r)}\{\gamma^{1/2}\sin\theta_r+\gamma^{-1/2}\sin(k+1)\theta_r\}. \quad (80)$$

The similar result is also obtained for $q_{2n+1}(2k,2k+1)$ which concerns with the single bond:

$$q_{2n+1}(2k,2k+1) = \frac{2}{n+1}\sum_{r=1}^{n}\frac{\sin(k+1)\theta_r}{z(\theta_r)}\{\gamma^{1/2}\sin k\theta_r+\gamma^{-1/2}\sin(k+1)\theta_r\}. \quad (81)$$

In deriving these, we ignore the cut arisings from $z(\theta)=0$. If one worrys about this, the partial integration with respect to z should be done at the beginning. This

procedure moves $z(\theta)$ from the denominator to the numerator. Then tedious but straightforward calculations leads to the same results. For the case of $\gamma=1$, namely, with the equal bond length, it is simple task to get

$$q_{2n+1}(r, r+1) = \frac{1}{n+1}\left\{\cot\frac{\pi}{2n+2} + (-1)^{r-1}\cot\frac{(2r+1)\pi}{2n+2}\right\} \quad (85)^{5)}$$

from Eq. 80 or Eq. 81.

Concluding Remarks

We have presented some expressions for propagators of the chain molecules in the Hückel approximations. One may say that in deriving the physical quantity, *e.g.*, the charge density, the usual quantum chemical method is much simpler. However we can expect that in the future application, the propagator approach enables us to treat many problems in a quite general aspects and provide powerful devices to quantum chemical problems.

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