Long-range correlation energies and off-diagonal interactions for the $\pi$ electronic systems

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Abstract

The long-range correlation energies and the off-diagonal interactions are studied and a general formula for correlation energy $E_c$ of the $\pi$ electron systems is given, which is beyond the nearest-neighbor electron-electron interactions and includes the off-diagonal interactions. It is found that the effects of the off-diagonal interactions $W$ and $X$ on the correlation energies are opposite, but the influence of $X$ on the correlation energies is much stronger than that of $W$ on the correlation energies, and the correlation energies decrease with increasing the screening effect.

Key Words: Correlation energies, long-range correlation, off-diagonal interactions, $\pi$ electron conjugated polymers

PACS. 31.25.Qm Electron correlation for polymeric molecules - 71.45.Gm Exchange, correlation, dielectric and magnetic response function, plasmons

1 Introduction

In the previous paper (Ref.[1]), the author deduced a simple expression for the long-range electronic correlation energies $E_c$ of the $\pi$ electronic systems where only the nearest-neighbor electron-electron interaction $v$ between two adjacent lattices are considered, and the formula was applied to the polymer polyacetylene (PA) and used to calculate the correlation energies and the calculating results are well consistent with those obtained by other theoretical calculations including $ab$ $initio$ method[2]. In order to obtain more general correlation energies formula which includes the more long-range Coulomb interactions (that is the diagonal interactions) and also the off-diagonal interactions, the correlation energy formula in the Ref.[1] should be revised.

As we all have known, besides the diagonal interactions, there are off-diagonal interactions in the $\pi$ conjugated polymers. The nearest-neighbor diagonal interactions are the on-site Coulomb interaction $U$ (Hubbard interaction) and the nearest-neighbor Coulomb interaction $v$. The nearest-neighbor off-diagonal interactions have $X$ and $W$, which are so-called, respectively, the bond-charge interaction and the bond-bond interaction[3]. There have been many studies about the roles of the off-diagonal interactions[4]-[8]. There are also the studies about the effects of the off-diagonal interactions on the excitonic binding energies in the $\pi$ conjugated polymers [9][10]. It was also known that the off-diagonal interactions have relationship with the screening from the $\pi$ electrons in the conjugated polymers[11]. At the different screening and different conditions, the effects of the off-diagonal interactions on the physical properties of the electron systems may have different influences. For instance, $X$ can be used to describe the possible superconducting states of the organic polymers or the non-$\pi$ electron systems[12], and $W$ is used to describe the ferromagnetism in the polymers[13]. Until now, these issues have not been studied and there is no detailed studies about the contribution to the correlation energies from the off-diagonal interactions. Thus the correlation energies from the off-diagonal interactions should be studied. So, it is necessary to deduce a formula of the correlation energies where the off-diagonal interactions have been included explicitly and in the same time the Coulomb interactions are not limited to the nearest-neighbor interaction $v$.

Therefore, in this study we mainly consider the general situation where both the long-range electron-electron interactions and the off-diagonal interactions are considered at the same time as well as the relation of the screening and the correlation energies.

2 Theoretical formation

As the procedure of deducting the desired formula is similar to that used in the Ref.[1], so here some of the deduction procedure are omitted and the detailed are mainly referred to the Ref.[1]. We directly start to our discussion from the following correlation energy (see the expression (10) in the Ref.[1])

$$E_c = \frac{1}{2} \sum_{\sigma \sigma'} \int d^3 r d^3 r' \rho_\sigma(\vec{r}) v(\vec{r} - \vec{r}') \rho_{\sigma'}(\vec{r}, \vec{r}') \equiv \frac{1}{2} (I - I_{HF}) \quad (1)$$

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where $v(\vec{r} - \vec{r'}) = \frac{e^2}{|\vec{r} - \vec{r'}|}$, the Coulomb interaction between two charges at $\vec{r}$ and $\vec{r'}$. In calculation of conjugated polymers, it is parameterized by the Ohno potential. Here $I$ equals

$$I \equiv \sum_{\sigma,\sigma'} \int d^3 r d^3 r' \rho_\sigma(\vec{r}) v(\vec{r} - \vec{r'}) \rho_{\sigma'}(\vec{r'}) \tilde{g}_{\sigma\sigma'}(\vec{r}, \vec{r'})$$

(2)

and

$$I_{HF} \equiv \sum_{\sigma,\sigma'} \int d^3 r d^3 r' \rho_\sigma(\vec{r}) v(\vec{r} - \vec{r'}) \rho_{\sigma'}(\vec{r'}) \tilde{g}_{\sigma\sigma'}^{HF}(\vec{r}, \vec{r'})$$

(3)

Here the pair-distribution $\tilde{g}(\vec{r}, \vec{r'}) = \sum_{\sigma,\sigma'} \tilde{g}_{\sigma\sigma'}(\vec{r}, \vec{r'})$ satisfies the sum rule: $\int d^3 r' \rho(\vec{r'})[\tilde{g}(\vec{r}, \vec{r'}) - 1] = -1$. Using the relation $\rho_\sigma(\vec{r}) = \sum_i \rho_{\sigma i}^* \rho_i(\vec{r})$ and the sum rule, (2) reads

$$I = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j,k,l} \rho_{\sigma i}^* \rho_{\sigma k}^* \int d^3 r d^3 r' \phi_i(\vec{r}) \phi_j(\vec{r}) v(\vec{r} - \vec{r'}) \phi_k^*(\vec{r'}) \phi_l^*(\vec{r}) - \frac{1}{2} \sum_{\sigma} \sum_{i,j} \rho_{\sigma i}^* \int d^3 r \phi_i^*(\vec{r}) \phi_j(\vec{r})$$

(4)

The two-fold integration in the first term in (4) is a many-center integral which describes the Coulomb interaction between two $\pi$ electrons lying, respectively, at the positions $\vec{r}$ with spin $\sigma$ and $\vec{r'}$ with spin $\sigma'$; it is denoted generally as $V_{ij,kl}$. As for $V_{ij,kl}$, generally it is hard for us to analytically calculate this many-centered integral easily and simply. In the CNDO (complete neglect of differential overlap) approximation[14], $V_{ij,kl}$ reduces to the Coulomb integrals $V_{ii,kl}$ which is a two-center integral. In the situation of the conjugated polymers, $V_{ii,kl}$ is further parameterized into the Ohno potential, that is, $V_{ii,kl} \equiv V_{i,k} = U/\sqrt{1 + ((\vec{r}_i - \vec{r}_k)/\alpha_0)^2}$, where $U$ is the on-site electron-electron interaction[15]. If the overlap integrals are explicitly considered, the two-electron interaction integral $V_{ij,kl}$ in (4) may be approximated as $US_{ij} S_{kl}/\sqrt{1 + ((\vec{r}_ij - \vec{r}_kl)/\alpha_0)^2}$, where $S_{ij} = \int d^3 r \phi_i^*(\vec{r}) \phi_j(\vec{r})$ is the overlap integral, and $\vec{r}_{ij}$ means the position vector between the site $i$ and the site $j$[16]. When the overlap integrals are omitted, $S_{ij}$ becomes $\delta_{ij}$, and then $V_{ij,kl}$ goes back to the above expression $V_{ii,kl}$.

After rearrangement, we obtain

$$I = \frac{\lambda}{2} \sum_{\sigma,\sigma'} \sum_{i,k} V_{ii,kl} \rho_{\sigma i}^* \rho_{\sigma k}^* + \frac{\lambda}{2} \sum_{\sigma,\sigma'} \sum_{i,k} V_{ij,kl} \rho_{\sigma i}^* \rho_{\sigma k}^* + \frac{\lambda}{2} \sum_{\sigma,\sigma'} \sum_{i,j,k,l} V_{ij,kl} \rho_{\sigma i}^* \rho_{\sigma l}^*$$

$$+ \frac{\lambda}{2} \sum_{\sigma} \sum_{i} V_{ii} \rho_{\sigma i}^* + \frac{\lambda}{2} \sum_{\sigma} \sum_{i,j} J_{ij} \rho_{\sigma i}^*$$

(5)

where the parameter $\lambda$ has been introduced again by the replacement of $e^2$ by $\lambda e^2$ in $v(\vec{r} - \vec{r'})$. And $V_i$ and $J_{ij}$ are

$$V_i = - \int d^3 r \phi_i^*(\vec{r}) \phi_i(\vec{r}) = -e^2 \int d^3 r \frac{\phi_i^2(\vec{r})}{r}$$

(6)

$$J_{ij} = - \int d^3 r \phi_i^*(\vec{r}) v(\vec{r}) \phi_j(\vec{r})$$

(7)

Here the integral $V_i$ is the Coulomb interaction of a positive charge $(+e)$ at the position $\vec{r} = 0$ with the $\pi$ electron at the position $\vec{r}$ near the site $i$. This positive charge is in fact just the correlation hole moving together with the $\pi$ electron. The $\pi$ electron and the positive charge is at least a lattice distant apart. The integral $J_{ij}$ ($i \neq j$) is a two-center integral.

It can be seen from the definitions of them that off-diagonal interactions refer to the overlaps of two $\pi$ wave functions lying at two different sites[9]. Thus they are actually very small compared with the diagonal interactions $V_{ii,kl}$[17]. Thus, in ordinary theoretical studies, only the diagonal interactions $V_{ii,kl}$ are kept and the off-diagonal interactions are not considered. So only the interactions $V_{ii,kl}$ in the first term of (5) are kept in the physical study of low-dimensional $\pi$ electron systems, just like that in the CDNO approximation. Similarly, the integral $J_{ik}$ also refers to the overlap between two $\pi$ electronic wave functions respectively lying at two different lattice sites and is a very small quantity compared with $V_{ii,kl}$, then it can be omitted in some actual theoretical calculations. It can be kept in theoretical calculations where more accuracy is required.

By these considerations, (5) reduces into the form

$$I \equiv \frac{\lambda}{2} \sum_{\sigma,\sigma'} \sum_{i,k} V_{ii,kl} \rho_{\sigma i}^* \rho_{\sigma k}^* + \frac{\lambda}{2} \sum_{\sigma} \sum_{i} V_{ii} \rho_{\sigma i}^*$$

(8)

Now we calculate $I_{HF}$. Because the procedure of calculating $I_{HF}$ is given in the Ref.[1], here is not given out and readers can be referred to that paper. Finally we have

$$I_{HF} = \lambda \sum_{\sigma, i,k} (\rho_{\sigma i}^* \rho_{\sigma k}^* - \rho_{\sigma i}^* \rho_{\sigma k}^*)$$

(9)
Inserting (8) and (9) into (1), the expression of $E_c$ is obtained

$$
E_c = \frac{\lambda}{2} \left\{ -\frac{1}{2} \sum_{\sigma \sigma'} |V_{\sigma \sigma'}|^2 \rho_{\sigma \sigma'}^2 + \frac{1}{2} \sum_{\sigma \sigma'} \sum_{i \neq k} V_{i,k} (\rho_{\sigma \sigma'}^2)^2 \right\}
$$

(10)

This is a more general formula for the electronic correlation energy. The correlation energy can be acquired using this formula when the averages of the diagonal charge density $\rho_{\sigma \sigma}^2$ and the off-diagonal charge density $\rho_{\sigma \sigma'}^2 (i \neq k)$ between the sites $i$ and $k$ and also $V_{i,k} (i \neq k)$ are known. When all $|V_{\sigma \sigma'}|$ is assumed to take the nearest-neighbor Coulomb interaction $v$ and $V_{i,k} = V_{i,k} = v$ with $k = i + 1$, the above formula (10) reduces to Eq.(15) obtained in the Ref.[1] which is a special case of this formula.

When all kinds of electron-electron interactions are kept, the correlation energy formula is given by

$$
E_c' = \frac{\lambda}{2} \left\{ \frac{1}{2} \sum_{\sigma} |V_{\sigma \sigma}| \rho_{\sigma \sigma}^2 + \frac{1}{2} \sum_{\sigma \sigma'} \sum_{i \neq k} V_{i,k} \rho_{\sigma \sigma'} \rho_{\sigma \sigma'}^2 \right\}
$$

\[+ \frac{1}{2} \sum_{\sigma \sigma'} \sum_{i \neq k}(X_{i,k} \rho_{\sigma \sigma} \rho_{\sigma \sigma}^2) + \frac{1}{2} \sum_{\sigma \sigma'} \sum_{i \neq j} W_{i,j,k} \rho_{\sigma \sigma} \rho_{\sigma \sigma}^2 + \frac{1}{2} \sum_{\sigma \sigma'} \sum_{i \neq j} J_{i,j,k} \rho_{\sigma \sigma}^2 \]

(11)

where $X_{i,k} \equiv V_{i,k} (k \neq i)$, $W_{i,j,k} \equiv V_{i,j,k} (i \neq j, k \neq i)$. Here the off-diagonal interaction $X_{i,k}$ is called the bond-site interaction, the off-diagonal interaction $W_{i,j,k}$ is called the bond-bond interaction. This is general form of the correlation energy which includes all kinds of the electron-electron interactions (the diagonal and the off-diagonal interactions).

### 3 Estimation of correlation energies

For the situation where only the nearest-neighbor interactions are considered, the above (11) can be simplified. For the one-dimensional $\pi$ electron conjugated polymers with $N$ carbon atoms such as the bond-alternated chain polyacetylene (PA), in the bond order wave (BOW) phase, the average charge density $\rho_{\sigma \sigma}^2 = 1/2$, the bond charge density (also called the bond-order matrix) $\rho_{\sigma \sigma}^2 = \rho_{\sigma \sigma} + (-1)^\delta \rho$. Thus we have the correlation energy formula from (11)

$$
E_{c''} = \frac{\lambda N v}{2} \left\{ -\frac{v}{2} + 2(v + W)(\bar{\rho}^2 + (\delta \rho)^2) + (X + J)\bar{\rho} \right\}
$$

(12)

where $v \gg |X| > W > 0, v \gg |J|$, and $X < 0, J < 0$. Note (12) is suitable to an even number conjugated polymer chain with single bond and double bond. For a odd number conjugated polymer, there is a more term appearing in (12): $-4(v + W)\bar{\rho} \delta \rho$ and $-(X + J)\delta \rho$.

The values of $v, W$ and $X$ have been already estimated before for PA, which are shown in Table 1, and the value of $J$ is not known. However, we may estimated the value of $J$ through a rational comparison between $X$ and $J$. According to the definitions of the integrals of $X(<0)$ and $J(<0)$ in the nearest-neighbor situation, $X$ is $\int d^3r d^3r' \phi_i^*(\vec{r}) \phi_i^*(\vec{r}') \times v(\vec{r} - \vec{r}') \phi_i(\vec{r}) \phi_i(\vec{r'})$, and $|J|$ is about $\int d^3r \phi_i^*(\vec{r}) v(\vec{r}) \phi_i(\vec{r})$, where $v(\vec{r} - \vec{r}')$ is the Coulomb interaction between two electronic charges, then it may be estimated that the maximum of $|X|$ is about $2a^2/\alpha \int d^3r \phi_i^*(\vec{r}) \phi_i(\vec{r})$, and the maximum of $|J|$ is about $2a^2/\alpha \int d^3r \phi_i^*(\vec{r}) \phi_i(\vec{r})$, where $a$ is the lattice constant and the wave functions $\phi_i(\vec{r})$ is normalized. So the values of $|X|$ and $|J|$ are approximately comparable with each other, that is, $|X| \sim |J|$. Therefore the correlation energy formula for the nearest-neighbor interactions reads

$$
E_{c''} = \frac{\lambda N v}{2} \left\{ -\frac{v}{2} + 2(v + W)(\bar{\rho}^2 + (\delta \rho)^2) + 2X\bar{\rho} \right\}
$$

(13)

According to this formula we may estimate the correlation energies under different off-diagonal interactions. In ab initio numerical computations for many-electronic systems of atoms, molecules and solid state, the values of correlation energies are mixed in exchange-correlation energies $E_{xc}$ instead of a separate quantity, and moreover the off-diagonal interactions can not be calculated concretely. Those are shortcomings of the ab initio numerical calculations. Through the formula here we may clearly see the effect of the off-diagonal interactions on the correlation energies and may discuss the physical properties such as the band structure and electronic structure as well as other physical properties related to elemental excitations. The results of the calculations are shown in Table 2.
Table 2: The correlation energies $\epsilon_c(= E'''/N, N$ is number of the $\pi$ electrons in a conjugated polymer chain) at different screening $\beta$ and different off-diagonal interactions $X$ and $W$ when $U = 6$ eV. The unit is eV.

| $\beta$ | $X = 0$ | $X \neq 0$,
|---------|---------|---------|---------|---------|
| $W = 0$ | $-0.1673$ | $-0.1894$ | $-0.1648$ | $-0.1869$ |
| $W \neq 0$ | $-0.0472$ | $-0.0659$ | $-0.0437$ | $-0.0623$ |
| $X = 0$ | $-0.03$ | $-0.0597$ | $-0.0242$ | $-0.0539$ |
| $X \neq 0$ | $-0.0215$ | $-0.0578$ | $-0.0145$ | $-0.0509$ |

4 Discussion and summary

The integral $V_i$ is an integral of a positive charge (Correlation hole) at the origin with all other electrons in the whole system. Although the form of the integral $V_i$ is simple but its calculation still is not direct, and the approximate calculation about it is available for some special systems. The simplest is that $V_i$ takes the nearest-neighbor interaction $v$. The more complicated calculation is left in the later study and here we do not discuss its computation. Similarly direct computation of the integral $J$ is not considered here and is left in the later study. The site charge density $\rho_{ii}^c$ (that is, the diagonal elements of charge density) and the bond charge density $\rho_{ik}^c (i \neq k)$ (that is, the off-diagonal parts of charge density) can be calculated directly from the elliptic integrals for a rigid conjugated polymers[9], and also can be drawn from the results of numerical computation including \textit{ab initio} computations.

It is all known that the values of the off-diagonal interactions are related to the screening values[3]. Table 1 lists the values of the diagonal interaction $v$ and the off-diagonal interactions $X$ and $W$ according to the computing results of the Ref.[3]. According to the Ref.[3], the order of the diagonal and the off-diagonal interactions are $v > |X| > W$. All interactions (the diagonal and the off-diagonal interactions ) are related to the on-site Hubbard interaction which was discussed in the Ref.[9].

When $U$ is given, the values of $v$, $W$, and $X$ are determined. In our calculation, $U = 6$. It is seen from the Table 1 that at the normal screening case ($\beta \sim 1$) and the middle screening case ($\beta \sim 3$), $W$ is much smaller than $X$, and $X$ is much smaller than $v$. Only with increasing the screening up to the case $\beta \geq 5$, both $W$ and $X$ become stronger, they even go over the value of $v$. Anyway, at the normal screening and the middle screening, the off-diagonal interactions $W$ and $X$ may be regarded as a perturbation relative to $v$. Interesting is that the off-diagonal interaction $X$ is negative, which may be thought to be related to the possibility of the superconductivity of the conjugated polymers[12].

It is seen from our calculating results shown in Table 2 that when the screening $\beta$ increases from normal to strong, the correlation energies diminish from large to small whatever with the off-diagonal interactions ($X, W$) and without the off-diagonal interaction ($X, W$). It is seen from Table 2 that the off-diagonal interaction $X$ increases the correlation energies at most and the off-diagonal interaction $W$ decreases the correlation energies compared with those without considering the off-diagonal interactions $X$ or $W$. When both $X$ and $W$ are considered in calculations, the correlation energies increase compared with those without considering both $X$ and $W$. It has been known that the bond-site interaction $X$ was used to discuss the superconductivity of the polymers[12][17]. Here the $X$ is shown to have contribution to the correlation energy, which may imply important significance of the long-range correlation to the superconductivity of the polymers.

It has been known that under fixed $U$, the exciton binding energy decreases with increasing the screening $\beta$[9]. Here under fixed $U$, the correlation energies decrease with increasing the screening $\beta$. About the screening $\beta$, the bond density correlation of the $\pi$ electrons, the off-diagonal interactions, the exciton bonding energy, and their relations has been detailed in the Ref.[9]. $\beta$ is a cutoff parameter of the Coulomb interaction. The larger the $\beta$, the weaker the Coulomb interaction. Thus the factor $\beta$ reflects a kind of effect on the $\pi$ electrons in the conjugated polymers. But the larger the $\beta$, the changes of the relative values among $v, W$, and $X$, see Table 1. This shows the significance of the screening $\beta$: the larger $\beta$, the stronger the bond density correlations. Notice here that we should not confuse the correlation energy with the bond density correlation. Therefore, we see that with increasing the screening $\beta (\geq 3)$, the off-diagonal interaction $X$ increases much, the exciton binding energy decreases, the bond density correlation increases, and the correlation energies also increase. It is found from the Table 2 that the correlation energies decrease rapidly with increasing the screening when $\beta$ is from 1 to 7 when without considering the off-diagonal interactions $W$ and $X$. But when considering only $X$ or considering both $X$ and $W$, the change of the correlation energies with increasing screening ($\beta \geq 3$) is not so big, this is because when the screening $\beta$ increases the off-diagonal interaction $X$ also increases very much.

In summary, in this paper the general formula of the correlation energies has been deduced with the off-diagonal interactions $X$ and $W$ by the first time. The effect of the off-diagonal interactions $X$ and $W$ on the correlation energies are discussed. It is found that the effects of the off-diagonal interactions $W$ and $X$ on the correlation energies are opposite. Given the screening $\beta$, the off-diagonal interaction $X$ increase the correlation energies and the off-diagonal interaction $W$ decreases the correlation energies. But the influence of $X$ on the correlation energies is much larger than that of $W$ on the correlation energies, and the correlation energies decrease with increasing the screening factor $\beta$.

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