Eur. Phys. J. B **54**, 11–17 (2006)
DOI: 10.1140/epjb/e2006-00430-4

The European Physical Journal B

Long-range correlation energies calculations for π electronic systems

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Received 1st June 2006 / Received in final form 25 September 2006

Abstract. A simple formula for correlation energy E_c of the π electron systems is obtained under an approximation for the electron-electron interactions. This formula is related directly to square of the bond order matrix and the nearest-neighbor Coulomb electron-electron interaction. The influence of the correlation energy on the band energy gap is discussed. The values of the correlation energy for polyacetylene (PA) are calculated and can be compared with those for PA obtained by other methods, including ab initio method.

PACS. 31.25.Qm Electron correlation calculations for polyatomic molecules – 71.45.Gm Exchange, correlation, dielectric and magnetic response functions, plasmons

1 Introduction

The electron correlations have been a very important issue in investigating the electronic structures of various electron systems. Especially the electron correlations have a strong influence on the bonding properties of atoms, semiconductor band gap [1]. However, it is well-known that it is very hard to completely solve a many electron system analytically using a single approximation because of the exchange and correlation problems. Hartree-Fock (HF) approximation deals with the exchange problem between the same spins among electrons but not resolve the correlation between the opposite spins among electrons [2,3]. The local density approximation (LDA) of Kohn and Sham [4] and later the density functional theory of Hohenberg and Kohn [5] made a contribution to the exchange-correlation energy, denoted by $E_{ex}[\rho(\vec{r})]$ using a complicated functional form. In the LDA, the ground state exchange energy E_x can be expressed an integral of the charge density. However, it is difficult to express the correlation energy E_c in an available form of integral of the charge density which is easy to calculate and only could be expressed as a numerical formula with the parameter r_s after a large number of works [6].

Besides the LDA, there are other methods which can be used to deal with the correlation effects of various electron systems such as metal and nonmetal atoms, small and big molecules, as well as conjugated polymers. They include unrestricted self-consistency field (SCF) Approximation [3], Configuration Interaction method(CI) [7], coupled-cluster method [8,9] that are applied to quantum chemistry and nuclear physics [10], Jastrow wavefunction method [11] that is used to describe correlations in homogeneous fermion systems like the electron gas or liquid He-III [12,13], the Projection Technique [14] for the strongly correlated systems, and the GW- approximation (the one-particle Green's function plus the screened Coulomb interactions) by Hedin [15]. For the conjugated polymers such as polyacetylene $(CH)_x$ (PA) or poly(p-phenylenevinylene) (PPV), the exchange-correlation energies has been calculated by the method of the ab initio with GW-approximation [16]. For the various metal and nonmetal atoms, the atomic Bethe-Goldstone equation under Hartree-Fock functions was used to calculate the electron correlation energies of the ground states [17]. For small or medium-size molecules(hydrocarbon molecules), a semi-empirical SCF scheme plus CNDO or INDO approximations was used to calculate inter-atomic correlations and intra-atomic correlations whose results could be compared with ab initio method [18].

For strongly correlated systems, the on-site Hubbard interaction U is much bigger than the nearest-neighbor Coulomb interaction v, so the contribution of the correlation energy are mainly from U. In the most conjugated polymers, the on-site Hubbard interaction U is not so bigger than the nearest-neighbor interaction v because of screening [19]. Thus both the on-site Hubbard interaction U and the long-range Coulomb interaction were considered in treating with the correlation energies of the conjugated polymers. In reference [20], authors studied the correlation energies of polyethylene $(CH_2)_x$(PE) using the local ansatz [20]. In reference [21], authors used

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the Gutzwiller ansatz as the variational ground state and studied correlation energy of polyacetylene (PA). First they used the Hubbard term plus SSH Hamiltonian to discuss the correlation energy and later added the nearest-neighbor interaction to get an effective on-site Coulomb interaction U_{eff} and discuss the correlation energy again. In reference [22], author used a variational method [23] to study the correlation of PA in the PPP model where both Hubbard term and the long-range Coulomb interaction were included. But author did not specifically deal with the correlation energy from the long-range Coulomb interaction which is important to the band energy gap in the conjugated polymers [24]. Although the importance of the correlation energy from the long-range Coulomb interaction has realized, there is still lack of special studies on the correlation energy mainly from the long-range Coulomb interaction. Therefore, study of the correlation effect due to the long-range Coulomb interaction of two adjacent π electrons in the conjugated polymers becomes significant.

The purpose of the present work is to study the correlation energy mainly from the long-range Coulomb interaction (the nearest-neighbor interaction in this study). The starting point in this paper is the exchange-correlation energy E_{ex}. Although the correlation energy may be expressed as $E_c = \int \epsilon_c n(\vec{r}) d\vec{r}$, ϵ_c is hard to know and hard to obtain. Thus, available approximations will be adopted in this study. Finally, a formula of the electron correlation energy due to the nearest-neighbor Coulomb interaction is obtained in an analytical form. Using this formula, it is simple to calculate the correlation energy of a π conjugated polymer and available to discuss the influence of the correlation energy on the band energy gap.

The arrangement of this paper is as follows. In Section 2, the expression of the pair-distribution function for the electronic systems by omitting wave function overlap integrals between two adjacent atomic sites is presented. In Section 3, an approximation for the electron-electron interaction integral is made and an analytical expression of the correlation energy for the conjugated polymers is obtained. In Section 4, the correlation energy calculation for one-dimensional polyacetylene (PA) chain under tight-bind approximation (SSH Hamiltonian plus electron-electron interactions), and results are presented, and in Section 5 is discussion with a summary.

2 Pair-distribution function for electron systems

The correlation effect between two electrons in a many-electron system may be described by a two-point density-density correlation function $\langle \hat{\rho}(\vec{r})\hat{\rho}(\vec{r'})\rangle$ at a given state $|\Phi\rangle$, where $\hat{\rho}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$, a density operator of the electron for a homogeneous or an inhomogeneous electron gas system, where the index i indicates the sequence number of electrons if the system is just electron gas or the position of the atomic sites if the system is a lattice system. To calculate the two-point density-density correlation function, one introduces the pair-distribution function which is defined as [25]

$$\left\langle \hat{\rho}\left(\vec{r}\right)\hat{\rho}\left(\vec{r'}\right)\right\rangle = g\left(\vec{r},\vec{r'}\right)\left\langle \hat{\rho}\left(\vec{r}\right)\right\rangle\left\langle \hat{\rho}\left(\vec{r'}\right)\right\rangle. \qquad (1)$$

In terms of the second quantized operators, $\hat{\rho}(\vec{r})$ can be represented by

$$\hat{\rho}\left(\vec{r}\right) = \sum_{i,j}^{N} \hat{\rho}_{ij}\phi_i^*\left(\vec{r}\right)\phi_j\left(\vec{r}\right) \qquad (2)$$

where $\hat{\rho}_{ij} = \sum_\sigma a_{i\sigma}^\dagger a_{j\sigma}$ and the indices i and j refer to the atomic sites in this study. $a_{i\sigma}^\dagger$ $(a_{j\sigma})$ is the electron creative (annihilation) operator with spin σ at the site i (j). $\phi_i(\vec{r})$ is the electron orbital wave function at the atomic site i and is normalized to one. Thus the two-point density-density correlation function may be expressed as

$$\left\langle \hat{\rho}\left(\vec{r}\right)\hat{\rho}\left(\vec{r'}\right)\right\rangle = \sum_{\sigma\sigma'}\sum_{ik(i\neq k)}^{N}\left\langle \hat{\rho}_{ii}^{\sigma}\hat{\rho}_{kk}^{\sigma'}\right\rangle\left|\phi_i\left(\vec{r}\right)\right|^2\left|\phi_k\left(\vec{r'}\right)\right|^2 + \sum_{\sigma\sigma'}\sum_{ij(i\neq j)}^{N}\sum_{kl(k\neq l)}^{N}\left\langle \hat{\rho}_{ij}^{\sigma}\hat{\rho}_{kl}^{\sigma'}\right\rangle\phi_i^*\left(\vec{r}\right)\phi_j\left(\vec{r}\right)\phi_k^*\left(\vec{r'}\right)\phi_l\left(\vec{r'}\right) \qquad (3)$$

and the density distribution function of the electrons is expressed as

$$\left\langle \hat{\rho}\left(\vec{r}\right)\right\rangle = \sum_{\sigma i}\left\langle \hat{\rho}_{ii}^{\sigma}\right\rangle\left|\phi_i(\vec{r})\right|^2 + \sum_{\sigma}\sum_{i\neq j}^{N}\left\langle \hat{\rho}_{ij}^{\sigma}\right\rangle\phi_i^*(\vec{r})\phi_j\left(\vec{r}\right). \qquad (4)$$

The second terms in (3) and (4) involves in the overlap integral effect between two electron wave functions lying at different atomic sites. As a first order approximation and without loss generality, the second terms in (3) and (4) could be omitted in this study. Therefore, the pair-distribution function $g(\vec{r},\vec{r'})$ from (1) becomes

$$g_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right) = \frac{\sum_{ik(i\neq k)}^{N}\left\langle \hat{\rho}_{ii}^{\sigma}\hat{\rho}_{kk}^{\sigma'}\right\rangle\left|\phi_i\left(\vec{r}\right)\right|^2\left|\phi_k\left(\vec{r'}\right)\right|^2}{\sum_{\sigma i}\left\langle \hat{\rho}_{ii}^{\sigma}\right\rangle\left|\phi_i\left(\vec{r}\right)\right|^2\sum_{\sigma k}\left\langle \hat{\rho}_{kk}^{\sigma}\right\rangle\left|\phi_k\left(\vec{r'}\right)\right|^2} \qquad (5)$$

with $g(\vec{r},\vec{r'}) = \sum_{\sigma\sigma'} g(\vec{r},\vec{r'})$ and $\rho_{ij}^{\sigma} = \langle a_{i\sigma}^\dagger a_{j\sigma}\rangle$. About the pair-distribution function $g(\vec{r},\vec{r'})$ there are different approximations. For example it can be cast into an analytic expression for the homogeneous gas [26].

3 The correlation energy

The so-called correlation is the correlation hole appearing around an electron moving in the medium. Remarkably the correlation in fact is due to the electron-electron interaction among electrons.

In the local density approximation (LDA) the exchange-correlation energy E_{xc} can be described by the exchange-correlation hole in terms of the pair-distribution function $\widetilde{g}(\vec{r},\vec{r'})$ [27]. Here $\widetilde{g}(\vec{r},\vec{r'})$ includes the exchange-correlation information between two spatial points $\vec{r}$ and $\vec{r'}$, and it satisfies the sum rule by the exchange-correlation hole:

$$\int d^3\vec{r'}\rho\left(\vec{r'}\right)\left[\tilde{g}\left(\vec{r},\vec{r'}\right)-1\right]=-1 \tag{6}$$

where $\rho(\vec{r'})=\langle\Phi|\hat{\rho}(\vec{r'})|\Phi\rangle=\sum_{i,j}^{N}\langle\hat{\rho}_{ij}\rangle\phi_i^*(\vec{r'})\phi_j(\vec{r'})$.

Since the HF approximation has already contained the contribution from the exchange effect between two electrons with the same spins, the correlation energy may be obtained by subtracting the HF pair-distribution function $g^{HF}_{\sigma\sigma}(\vec{r},\vec{r'})$ from the exchange-correlation energy E_{xc} [25,28],

$$E_c=\frac{1}{2}\sum_{\sigma\sigma'}\int d^3rd^3r'\rho_\sigma\frac{e^2}{|\vec{r}-\vec{r'}|}\rho^c_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right) \tag{7}$$

where e is the charge (negative) of the electron, $\vec{r}$ and $\vec{r'}$ are the position vectors of two electrons and $\rho^c_{\sigma\sigma'}$ is the spin-dependent correlation hole and given by

$$\rho^c_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)=\rho_{\sigma'}\left(\vec{r'}\right)\left[\widetilde{g}_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)-\delta_{\sigma\sigma'}\widetilde{g}^{HF}_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)\right]. \tag{8}$$

where

$$\widetilde{g}_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)=\int_0^1 d\lambda g_{\sigma\sigma'}\left(\vec{r},\vec{r'};\lambda\right). \tag{9}$$

and $\widetilde{g}^{HF}_{\sigma\sigma'}(\vec{r},\vec{r'})$ is the pair-distribution function under the HF approximation and has the same relation as $\widetilde{g}_{\sigma\sigma'}(\vec{r},\vec{r'})$. Here λ means the charge e^2 in Coulomb interaction is replaced by λe^2 in the process of calculation.

The difference between the two pair-distribution functions $(\widetilde{g}-\widetilde{g}^{HF})$ has to do with the electron correlation. The expression (7) now can be regarded as an integral between the π electron at the position $\vec{r}$ and the charge cloud of the spin-dependent correlation hole around the position $\vec{r'}$ of the other π electron. Thus the expression (7) can be rewritten as

$$E_c=\frac{1}{2}\sum_{\sigma\sigma'}\int d^3rd^3r'\rho_\sigma\left(\vec{r}\right)v\left(\vec{r}-\vec{r'}\right)\rho^c_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right) \tag{10}$$

where $v(\vec{r}-\vec{r'})=\frac{e^2}{|\vec{r}-\vec{r'}|}$, the Coulomb interaction between two electrons at the positions $\vec{r}$ and $\vec{r'}$.

In order to complete the calculation of the integration of E_c, an approximation is needed to simplify the expression for E_c. In the study of polyacetylene (PA) oligomer, two-electron interaction integral was approximated by abstracting the Coulomb interaction $v(\vec{r}-\vec{r'})$ out of the integrand of the many-centered Coulomb integral, and the results showed that the approximation is reasonable [29]. According to that spirit, we may take $v(\vec{r}-\vec{r'})$ out of the integrand in (10). For simplicity, in this study only consider the nearest-neighbor electron-electron interaction between two adjacent carbon atom sites are considered, that is, $v(\vec{r}-\vec{r'})=\lambda v$, where λ is due to the replacement of the charge e^2 in the Coulomb interaction. In this way the expression for E_c may become

$$E_c\approx\frac{\lambda v}{2}\left[\sum_{\sigma\sigma'}\int d^3rd^3r'\rho_\sigma\left(\vec{r}\right)\rho_{\sigma'}\left(\vec{r'}\right)\widetilde{g}_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)\right.$$
$$\left.-\sum_{\sigma}\int d^3rd^3r'\rho_\sigma\left(\vec{r}\right)\rho_\sigma\left(\vec{r'}\right)\widetilde{g}^{HF}_{\sigma\sigma}\left(\vec{r},\vec{r'}\right)\right]. \tag{11}$$

Remarkably, it is not easy to calculate it without further approximation. According to the sum rule (6), we have

$$\sum_{\sigma\sigma'}\int d^3rd^3r'\rho_\sigma\left(\vec{r}\right)\rho_{\sigma'}\left(\vec{r'}\right)\widetilde{g}_{\sigma\sigma'}\left(\vec{r},\vec{r'}\right)$$
$$=\frac{1}{2}\sum_{\sigma\sigma'}\int d^3rd^3r'\rho_\sigma\left(\vec{r}\right)\rho_{\sigma'}\left(\vec{r'}\right)-\frac{1}{2}\sum_{\sigma}\int d^3r\rho_\sigma\left(\vec{r}\right). \tag{12}$$

Using (2) and (5), the expression of E_c reduces to

$$E_c=\frac{\lambda v}{2}\left[-\frac{1}{2}\sum_{i\sigma}\rho^\sigma_{ii}+\frac{1}{2}\sum_{ik,\sigma\sigma'}^{i\neq k}\rho^\sigma_{ii}\rho^{\sigma'}_{kk}\right.$$
$$\left.-\sum_{ik,\sigma}^{i\neq k}\langle\Phi_{HF}\left|\hat{\rho}^\sigma_{ii}\hat{\rho}^\sigma_{kk}\right|\Phi_{HF}\rangle\right]. \tag{13}$$

where $|\Phi_{HF}\rangle$ is the HF ground state. The third term in the above expression can be evaluated and it equals

$$\sum_\sigma\langle\Phi_{HF}|\hat{\rho}^\sigma_{ii}\hat{\rho}^\sigma_{kk}|\Phi_{HF}\rangle=\sum_\sigma\left[\rho^\sigma_{ii}\rho^\sigma_{kk}-(\rho^\sigma_{ik})^2\right]. \tag{14}$$

Here the symmetry that $\rho^\sigma_{ik}=\rho^\sigma_{ki}$ has been used. Finally the correlation energy obtained is

$$E_c=\frac{\lambda v}{2}\left[-\frac{1}{2}\sum_{i\sigma}\rho^\sigma_{ii}+\sum_{ik\sigma}^{i\neq k}(\rho^\sigma_{ik})^2\right]. \tag{15}$$

This expression (15) is the central result in this study. Because there are no constraints to the systems in the process of the deduction, this relation may be applied to the various π electron systems such as C_{60}, benzene rings, and carbon nanotubes, etc. The correlation energy per electron is $\epsilon_c=E_c/N$, N is the total numbers of the carbon atoms in a π electron system. For a half filled system, the number of atomic sites and the number of electrons are equal. This relation tells us that when the averages of the bond charge and the electron density at the site i are known, the correlation energy can be evaluated.

4 Calculation and results

For the π conjugated polymers, the Hamiltonian of the system is the SSH-type Hamiltonian $H_0(=\sum_{ij\sigma} t_{ij}(a_{i\sigma}^\dagger a_{j\sigma} + h.c.))$ plus the electron-electron interaction term,

$$H = H_0 + \frac{1}{2}\sum_{ij\sigma\sigma'} v\left(\vec{r} - \vec{r'}\right) a_{i\sigma}^\dagger a_{i\sigma} a_{j\sigma'}^\dagger a_{j\sigma'} \tag{16}$$

where $a_{i\sigma}^\dagger(a_{j\sigma})$ is the creation (annihilation) operator of an π electron at the site i (j) with spin σ. $v(\vec{r} - \vec{r'})$ is the electron-electron interaction, and $\vec{r}$ $(\vec{r'})$ means the position vector of an π electron at the site i (j). t_{ij} is the hopping term. For an bond-alternated chain, $t_{i,i+1} = t_0 + (-1)^i \delta t_0$ with t_0 being the hopping integral without dimerization and δt_0 being the magnitude of the dimerization due to Peierls transition.

For the one-dimensional π electron conjugated polymers with N carbon atoms such as the bond-alternated chain PA, in the bond order wave (BOW) phase, the average charge density at the site i $\rho_{ii}^\sigma = 1/2$, and the average of the bond charge density $\rho_{ik}^\sigma = \rho_{ki}^\sigma = \langle a_{i\sigma}^\dagger a_{k\sigma}\rangle$ (here $k = i+1$). Dropping the spin index because of $\rho_{ik}^\sigma = \rho_{ik}^{\bar\sigma} = \rho_{ik}$, we have $\rho_{ii+1} = \bar\rho + (-1)^i \delta\rho$. ρ_{ij}^σ is also called the bond-order matrix [25] (see Sect. 5 for its discussion.) Thus (15) yields

$$E_c = -N\frac{\lambda v}{2}\left[\frac{1}{2} - 2\left(\bar\rho^2 + (\delta\rho)^2\right)\right]. \tag{17}$$

where N is the carbon atom numbers in the system, and $\bar\rho$ and $\delta\rho$ are function of λ, denoted by $\bar\rho(\lambda)$ and $\delta\rho(\lambda)$. The correlation energy per π electron is then obtained by integration over the parameter λ from 0 to 1 [25],

$$\epsilon_c = -\frac{v}{2}\left\{\int_0^1 \frac{\lambda}{2} d\lambda - 2\int_0^1 \left[\lambda(\bar\rho(\lambda))^2 + \lambda(\delta\rho(\lambda))^2\right] d\lambda\right\}. \tag{18}$$

Here $\bar\rho(\lambda)$ and $\delta\rho(\lambda)$ are given by the first and second elliptic integrals [21,30]

$$\bar\rho(\lambda) = \frac{1}{\pi\left(1 - z(\lambda)^2\right)} \times \left[E\left(\sqrt{1 - z(\lambda)^2}\right) - z(\lambda)^2 K\left(\sqrt{1 - z(\lambda)^2}\right)\right] \tag{19}$$

$$\delta\rho(\lambda) = \frac{z(\lambda)}{\pi(1 - z(\lambda)^2)} \times \left[K\left(\sqrt{1 - z(\lambda)^2}\right) - E\left(\sqrt{1 - z(\lambda)^2}\right)\right] \tag{20}$$

where $z(\lambda) = \delta t/t$ and the parameters t and δt are determined by the relations $t = t_0 + \lambda v \bar\rho_0$ and $\delta t = \delta t_0 + \lambda v \delta\rho_0$, where $\bar\rho_0$ and $\delta\rho_0$ are the average charge density and the change of the charge density without the Coulomb interactions.

For the PA, $t_0 = 2.5$ eV and $\delta t_0 = 2\alpha u_0 = 0.269$ eV, where the electron-phonon coupling constant $\alpha = 4.1$ eV Å, and the dimerization $u_0 = 0.0328$ Å [24]. In calculation, the lang-range interaction v is 2.4 eV [24]. Table 1 lists the values for different λ under t_0, $\bar\rho_0$, δt_0, and $\delta\rho_0$ to calculate the average of the bond charge density $\bar\rho$ and its change $\delta\rho$ from the relations (19) and (20). Putting the resulting $\bar\rho$ and $\delta\rho$ into (18) and integrating over λ from 0 to 1, the correlation energy is then obtained. In Table 1 $I(\lambda) = (\bar\rho(\lambda))^2 + (\delta\rho(\lambda))^2$, and $I = 2\int_0^1 [\lambda(\bar\rho(\lambda))^2 + \lambda(\delta\rho(\lambda))^2] d\lambda$. Table 2 lists the values of the correlation energies for PE and PA for contributions from the on-site Coulomb interaction and the nearest-neighbor Coulomb interaction, and also lists the band energy gap E_g' in this study and that from reference [24]. Figure 1 shows the correlation energy vs. the dimerization δt_0.

To see the influence of the parameter λ on the the bond charge density and finally on the correlation energy, I calculate the $\bar\rho(\lambda)$ and $\delta\rho(\lambda)$ (see the lines from 2nd to 11th in Tab. 1). It is seen from Table 1 that the differences about the various quantities when $\lambda = 0$ and when $\lambda = 1$ are very small: $\bar\rho(0) - \bar\rho(1) = 0.0026$, $|\delta\rho(0) - \delta\rho(1)| = 0.0200$, $|I(0) - I(1)| = 0.0024$. In addition, the differences between I and $I(\lambda)$ are also small: $|I - I(0)| = 0.0017$ eV, $|I - I(1)| = 0.0007$ eV, and $|\epsilon_c - \epsilon_c(\lambda = 0)| = 0.0020$ eV, $|\epsilon_c - \epsilon_c(\lambda = 1)| = 0.0009$ eV.

The treatment of the pair-distribution function (9), $\tilde g(\vec{r}, \vec{r'}) = \int_0^1 d\lambda g(\vec{r}, \vec{r'}; \lambda)$ is as follows. In the formula (9), Coulomb interaction e^2 in the Coulomb interaction $v(\vec{r} - \vec{r'})$ is replaced by λe^2, λ changes from 0 to 1 [25]. When $v(\vec{r} - \vec{r'})$ appears and changes, the electron wave functions follows the changes. Then the electron density distribution $\rho(\vec{r})$ changes, and then ρ_{ij} changes, which may be expressed as $\bar\rho(\lambda)$ and $\delta\rho(\lambda)$ (see (19) and (20)). This can be seen through the relations $t = t_0 + \lambda v \bar\rho_0$ and $\delta t = \delta t_0 + \lambda v \delta\rho_0$. Therefore the calculation of $\tilde g(\vec{r}, \vec{r'})$ is realized actually through the calculation of $\rho(\vec{r})(\lambda)$. Table 1 shows the results of the correlation energies with integration about the parameter λ (see the first line in Tab. 1).

Note that the bond charge density ρ_{ij}^σ always is less than half and about 0.3 or so, therefore the second term is less than the first term in the formula (15) and the correlation energy is negative. The electron systems to which the formula is suitable is supposed to be π conjugated polymers with long chain (N is very large) with half filled band in the ground state. For a small molecule system such as H_2, etc., and those without π electrons, the formula is not suitable because the molecule like H_2 is covalent molecules where the charge density gathers between two atoms. Another reason is that the approximation (11) may bring a bigger error about the electron-electron interaction integral if it is applied to small molecules like H_2 etc. It is also not suitable to the hydrocarbon such as methane molecule that has no π electrons. In derivation of the formula, there is no the excited states to be dealt with.

Table 1. To see the influence of the parameter λ on the the bond charge density and finally on the correlation energy, the $\bar{\rho}(\lambda)$ and $\delta\rho(\lambda)$ are calculated (see the lines from 2nd to 11th in the Table). It is seen that the differences about the various quantities when $\lambda = 0$ and when $\lambda = 1$ are very small. $t_0 = 2.5$, $u_0 = 0.0328$, $\alpha = 4.1$ eV Å and $v = 2.4$ for PA. The unit is eV.

z_0	$\bar{\rho}_0$	$\delta\rho_0$	λ	z	$\bar{\rho}(\lambda)$	$\delta\rho(\lambda)$	$I(\lambda)$	I	ϵ_c
0.1076	0.3144	0.0903						0.1087	–0.1696
0.1076	0.3144	0.0903	0	0.1076	0.3144	0.0903	0.1070		–0.1716
			0.1	0.1129	0.3141	0.0930	0.1073		–0.1713
			0.2	0.1178	0.3138	0.0956	0.1076		–0.1709
			0.3	0.1225	0.3135	0.0979	0.1079		–0.1706
			0.4	0.1269	0.3132	0.1001	0.1081		–0.1703
			0.5	0.1311	0.3130	0.1021	0.1084		–0.1700
			0.6	0.1351	0.3127	0.1039	0.1086		–0.1697
			0.7	0.1389	0.3125	0.1057	0.1088		–0.1694
			0.8	0.1425	0.3122	0.1073	0.1090		–0.1692
			0.9	0.1460	0.3120	0.1089	0.1092		–0.1690
			1.0	0.1492	0.3118	0.1103	0.1094		–0.1687

Table 2. Correlation energies ϵ_c from $n_i n_j$ and $n_{i\uparrow} n_{i\downarrow}$ for PA and PE. Here $\epsilon_c(V)$ means contribution from the nearest-neighbor Coulomb interaction, $\epsilon_c(U)$ means contribution from the on-site Hubbard interaction, and $\epsilon_c(U+V)$means contribution from both the on-site Hubbard interaction and the nearest-neighbor Coulomb interaction. $E'_g(= E_g + \epsilon_c)$ and E''_g are the band energy gap. The unit is eV.

Systems	PE	PA
E'_g		1.7832*
E''_g		1.8 [d]
ϵ_c(V)	–0.1725[a]	–0.1696*
ϵ_c(V)		–0.1567[b]
ϵ_c(V)		–0.0100[c]
ϵ_c(U)	–0.5760[a]	
ϵ_c(U)		–0.6319[b]
ϵ_c(U)		–0.6208[c]
ϵ_c(U+V)	–0.75[a]	
ϵ_c(U+V)		–0.7885[b]
ϵ_c(U+V)		–0.6308[c]

[a] Refers to the reference [20]; [b] refers to the reference [21]; [c] refers to the reference [22]; [d] refers to the reference [24]; * refers to the present study.

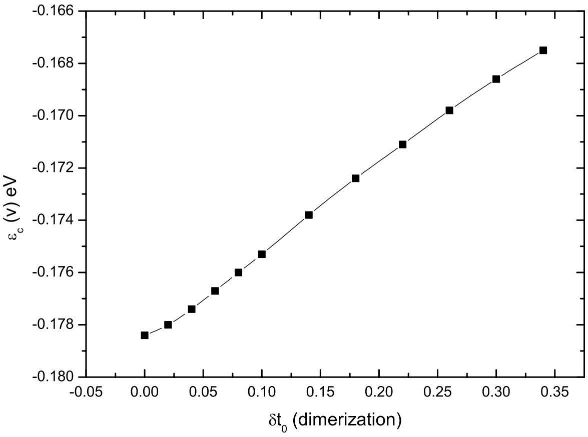

Fig. 1. ϵ_c changes with increasing dimerization δt_0 (=$2\alpha u_0$) under $v = 2.4$ eV according to the formula (18). Here v in $\epsilon_c(v)$ means the nearest-neighbor Coulomb interaction.

5 Discussion

In the process of derivation for the formula, there are two approximations to be used. One is the tight-bind approximation where the pair-distribution function $g(\vec{r}, \vec{r'})$ only involves diagonal elements ρ_{ii} of charge density. Other is that the electron-electron interaction $v(\vec{r} - \vec{r'})$ is drawn out of the integrand of the integral expression for E_c (see (11)), which was proved to be available in calculating the excitation of the conjugated polymer oligomer [29]. In this way, the correlation energy expression obtained is directly related to the diagonal site charge density $\rho^{\sigma}_{ii} = \langle a^{\dagger}_{i\sigma} a_{i\sigma} \rangle$ and square of the bond charge density $\rho^{\sigma}_{ik} = \langle a^{\dagger}_{i\sigma} a_{k\sigma} \rangle$ $(i \neq k)$ that can be calculated directly from the elliptic integrals (19) and (20). This is different from the variational methods [20–22], and also from the density matrix renormalization group (DMRG) [31]. Due to the overlap of the wave functions between two adjacent atomic sites, there exists some of charge distribution between two adjacent sites, and this part of the charge is called as "bond charge density" or "bond order matrix" ρ^{σ}_{ik} in discussing the π conjugated polymers. In the bond alternative chain such as PA, the bond charge will have fluctuation along the chain. In the single bond (that is, the longer bond), the bond charge is decreased due to the diminish of the overlap, while in the double bond (that is, the shorter bond), the bond charge is increased due to the more overlap. So we have that $\rho_{ii+1} = \bar{\rho} + (-1)^i \delta\rho$, where $\delta\rho$ means the charge fluctuation and $\bar{\rho}$ means the average of the bond charge [25,30].

If the second terms in (3) and (4) are kept, that means, the overlap effect is considered remarkably, then the pair-distribution function $g(\vec{r}, \vec{r'})$ will have both the diagonal terms ρ_{ii} and the off-diagonal terms ρ_{ij} of the charge density. In this case, the electron charge density ρ_{ii} on the sites will be less than half and the bond charge density ρ_{ij} $(i \neq j)$ will be enhanced a little. It may be predictable that when the overlap effects of the π electron waves are considered, the correlation energies will become smaller. Moreover, when the overlap integrals are considered, we may discuss the contributions of the correlation energy from the off-diagonal electron-electron interactions [30].

It is seen from Table 2 that for an infinite polymer PE, the correlation energy was obtained and was $\epsilon_c(U+V) = -0.75$ eV [20]. According to reference [20], 77% the correlation energy comes from the contribution of the operator $n_{i\uparrow}n_{i\downarrow}$. Thus the remaining 23% of the correlation energy comes from the contribution of the long-range Coulomb interaction V_{ij} $(i \neq j)$ or equivalently from the contribution of the operator $n_i n_j$ $(i \neq j)$. From this, we may have $\epsilon_c(V) = 0.23 \times (-0.75) = -0.1725$ eV. The present correlation energy ($\epsilon_c(V)$) comes from the contribution of the nearest-neighbor Coulomb interaction ($v = 2.4$ eV) between two π electrons and is -0.1696 eV. In reference [21], the long-range interaction V (here $V = V_{i,i+1} = v$) was included within an "effective on-site Coulomb interaction U_{eff}" after using some approximation, and the correlation energy $\epsilon_c(U+V)$ both including the on-site Hubbard interaction U and the long-range Coulomb interaction V and $\epsilon_c(U)$ were obtained for PA, then the correlation energy $\epsilon_c(V)$ from the contribution of the long-range Coulomb interaction V may be obtained from the difference between $\epsilon_c(U+V)$ and $\epsilon_c(U)$ and it yielded -0.1567 eV with $t_0 = 2.9$ eV. This value is smaller than the result of the present study. Reference [22] used the local approach [32] to calculate the correlation energies. However, the difference between $\epsilon_c(U+V)$ and $\epsilon_c(U)$ was very small and $\epsilon_c(V) = -0.0100$ eV with $t_0 = 2.5$ eV in reference [22], and this result seems so small.

It is also seen from Table 2 that the present result of the correlation energy $\epsilon_c(V)$ for PA is little smaller than that for PE. Both PE and PA includes sp^3 hybridization. In the calculation of the correlation energy for PE [20], except π electrons between two nearest-neighbor carbon atoms, factors from the different π bonds were also taken in numerical computation, so the more correlation effects were included in $\epsilon_c(U+V)$ for PE. In addition, the present result $\epsilon_c(V) = -0.1696$ eV is little larger compared with $\epsilon_c(V) = -0.1567$ eV from reference [21]. This may be caused by the approximation where the overlap effect between two adjacent π electronic wave functions is omitted. When the overlap effect is considered in calculation, the bond charge density will be larger and the site charge density will be less than half, then the result will become smaller.

It is seen from (18) that the correlation energy is an even function of dimerization. The trend of the curve in Figure 1 is kind of quadratic but not complete because there are also the dimerization parameter z in the denominators in the formula. This point can be seen by the following way. Because $z \ll 1$, if we replace z in the denominator in the formula by $z_0(=\delta t_0/t_0)$, then the correlation energy ϵ_c is approximately proportional to $-0.125v + \frac{Av}{2\pi^2} + \frac{Bv}{2\pi^2}z^2$, where A and B are the integral constants. At present, there is no similar curve to compare. We may compare the curve in Figure 1 with those in references [22] and [24]. Because the correlation energy (18) do not contain the contribution form the on-site Hubbard interaction U, the curve in Figure 1 is not completely like those in Figure 2 in reference [22] and those in Figure 1 in reference [24] where both U and the long-range interaction were included. Nevertheless, it could be found here that the curve in Figure 1 still have some similar trend with them when the dimerization value is bigger. Though the curve in Figure 2 in reference [24] was about the ground state energy vs. the dimerization, the curve also reflects some information about the correlation energy vs the dimerization because the ground state energy contains the correlation energy contribution in reference [24].

It is all known that when screening is weak or normal in the π electronic conjugated polymers, the electron-electron interaction increases the dimerization and band energy gap [30]. That is, v increases δt_0 and E_g. In equilibrium state and rigid background, the band energy gap E_g of PA is given by $4\delta t = 4(\delta t_0 + v\delta\rho_0)$. Under the electron-electron interaction v, the average bond charge density $\bar{\rho}_0$ decreases slightly with increasing δt_0 and the fluctuation of the bond charge density $\delta\rho_0$ increases with increasing δt_0. The decrease of $\bar{\rho}_0$ causes the bandwidth (see $t = t_0 + v\bar{\rho}_0$) to diminish, and the increase of $\delta\rho_0$ make E_g increase and at the same time cause ϵ_c (see (18)) to decrease. Then it can be seen from these that v and $\delta\rho_0$ are two opposite factors to the correlation energy: v is in favor of the correlation energy but $\delta\rho_0$ is a disadvantage to the correlation energy in this study. That is to say, on the one hand, v makes δt_0 and accordingly $\delta\rho_0$ increase and then the band energy gap E_g increase, on the other hand, the fluctuation $\delta\rho_0$ will cause the correlation energy ϵ_c to decrease. As a result, these two opposite influence makes E_g decrease from $E_g = 4\delta t$ to $E'_g = E_g + \epsilon_c$. When $\delta t_0 = 0.269$ eV and the corresponding bond charge density $\delta\rho_0 = 0.0903$, we have $E_g = 1.9429$ eV and $\epsilon_c = -0.1696$ eV. Therefore the band energy gap E'_g containing the nearest-neighbor Coulomb interaction correlation effect becomes 1.7832 eV. This value of the band energy gap is close to E''_g (1.8 eV) obtained by ab initio computation by author in reference [24] where the screened interaction was used. These are in qualitative agreement with experiment. In addition, E'_g increase with increasing dimerization because the correlation energy ϵ_c decreases with dimerization, which is consistent with relation of the band gap and the dimerization.

To my knowledge, there is no similar expressions for the correlation energy only from the nearest-neighbor Coulomb interaction that exists in a simple form at present. In the next study, the more electron-electron interaction terms in the long-range Coulomb interaction will be considered. In addition, although the DMRG is a strong tool to deal with the correlation problems in a many-particle electron system, it is basically a complicated numerical calculation method but not is an analytical expression.

In summary, under the approximation (11) and the tight-bind approximation, a formula (15) of the correlation energy for the long-range (nearest-neighbor) Coulomb interaction v for the conjugated polymers is obtained with the rigid backbone background. Although it is simple, it is direct and effective and easily operational in comparison with other highly involved numerical computation methods including DMRG. The computational result for the correlation energy for PA is available compared to those for PA and PE in different methods [20,21]. The band energy gap E'_g containing the correlation effect is close to that by ab initio method containing the screening interaction [24]. Since the process of derivation is general, the correlation energies of other π conjugated polymers (such as PPV) or carbon atomic systems with π electrons (such as C_{60} and carbon nanotubes) can also be calculated using this formula which are under way.

References

1. W. Borrmann, P. Fulde, Phys. Rev. B **35**, 9569 (1987)
2. D.R. Hatree, Proc. Cambridge Philos. Soc. **24**, 89 (1928)
3. V. Fock, Z. Phys. **61**, 126 (1930)
4. W. Kohn, L.J. Sham, Phys. Rev. A **140**, 1133 (1965)
5. P. Hohenberg, W. Kohn, Phys. Rev. B **136**, 864 (1964)
6. G.D. Mahan, K.R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum Press, New York 1990)
7. S.F. Boys, Proc. R. Soc. London A **200**, 542 (1950)
8. J. Cizek, Adv. Chem. Phys. **14**, 35 (1969)
9. H. Kümmel, K.H. Lührmann, J.G. Zabolitzky, Phys. Lett. C **36**, 1 (1978)
10. F. Coester, H. Kümmel, Nucl. Phys. **17**, 477 (1960)
11. R. Jastrow, Phys. Rev. **98**, 1479 (1955)
12. J.G. Zabolitzky, in *Advances in Nuclear Physics*, Vol. 12, edited by W. Negele, E. Vogt (Plenum, New York, 1981)
13. V.R. Pandharipande, R.B. Wiringa, Rev. Mod. Phys. **51**, 821 (1979)
14. H. Mori, Prog. Theor. Phys. **33**, 423 (1965); R. Zwanzig, in *Lecture in Theoretcial Physics*, Vol. 3 (Interscience, New York, 1961)
15. L. Hedin, Phys. Rev. A **139**, 796 (1965)
16. M. Rohling, S.G. Louie, Phys. Rev. Lett. **82**, 1959 (1999)
17. R.K. Nesbet, Phys. Rev. **175**, 51 (1967); R.K. Nesbet, Phys. Rev. **175**, 2 (1968); R.K. Nesbet, Phys. Rev. A **3**, 87 (1971)
18. G. Stollhoff, P. Vasilopoulos, J. Chem. Phys. **84**, 2744 (1986)
19. X. Sun, Z. Shuai, K. Naxu, D.L. Lin, T.F. George, Phys. Rev. B **44**, 11024 (1991)
20. G. König, G. Tollhoff, J. Chem. Phys. **91**, 2993 (1989)
21. D. Baeriswyl, K. Maki, Phys. Rev. B **31**, 6633 (1985)
22. P. Horsch, Phys. Rev. B **24**, 7351 (1981)
23. G. Stollhoff, P. Fulde, J. Chem. Phys. **73**, 4548 (1980); P. Horsch, P. Fulde, Z. Phys. B **36**, 23 (1979)
24. G. König, G. Stollhoff, Phys. Rev. Lett. **65**, 1239 (1990)
25. P. Fulde, *Electron Correlations in Molecules and Solids* (Springer-Verlag, Berlin, 1993)
26. O. Gunnarsson, R.O. Jones, J. Chem. Phys. **72**, 5357 (1980)
27. O. Gunnarsson, B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976); D.C. Langreth, J.P. Perdew, Solid State Common. **17**, 1425 (1975)
28. H. Stoll, C.M.E. Pavlidou, H. Preuss, Theor. Chim. Acta **49**, 143 (1978)
29. H. Zhao, S. Yokojima, X. Sun, G.H. Chen (unpublished); also see: WanZhen Liang Satoshi Yokojima, GuanHuan Chen, J. Chem. Phys. **110**, 1844 (1999)
30. Hua Zhao, Rong-tong Fu, Xin Sun, Zhi-lin Zhang, Phys. Rev. B **56**, 12268 (1997)
31. S.R. White, Phys. Rev. Lett. **69**, 2863 (1990)
32. G. Stollhoff, P. Fulde, Z. Phys. B **26**, 251 (1977)