Electron Correlation and Bond Alternation in Polymers

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The effect of electron correlation on bond alternation of polymers is clarified by calculation of the electron correlation function. Instead of the extended Hubbard model, we start from the full Coulomb interaction with any strength and range. In contrast to the other theories, our results disclose the following: (1) When the interaction range is short the bond alternation monotonically decreases with increasing strength. (2) Extension of the interaction range will increase bond alternation. (3) If the electron-lattice coupling is strong, bond alternation is suppressed by electron repulsion; but if it is weak the bond alternation is mainly caused by repulsion.

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Soliton theory has achieved success in the understanding of many peculiar properties of polymers. In the early version of this theory, only electron-lattice coupling was taken into account; the electron interaction was neglected.[1] But many experiments demonstrated the importance of the *e-e* interaction, such as the nonvanishing negative spin density on alternate carbon atoms,[2] the relative ordering between states ^1A_g and ^1B_u,[3] the optical absorption associated with neutral soliton,[4] etc.

In recent years many theories have been developed to deal with the electron repulsion; among them are the mean-field and perturbation theories,[5] the valence-bond method,[6] Monte Carlo simulation,[7] the renormalization-group method,[8] the Gutzwiller variational method,[9] and some others. Once the repulsion is involved, the theory becomes a complicated many-body problem; one of the unsolved problems is the effect of electron interaction on bond alternation. Although the above-mentioned theories have studied this problem, the matter is still uncertain since these theories have some defects. First, they start from the extended Hubbard model, but it is unsuitable for the polymers. In fact, in the Wannier representation, the Coulomb interaction $V(\mathbf{r}-\mathbf{r}')$ can be written as

$$H'=\sum\nolimits_{i,j,m,n} V_{i,j;m,n} c_{i,s}^{\dagger} c_{j,s'}^{\dagger} c_{m,s'} c_{n,s},$$

where

$$V_{i,j;m,n} = \int d^3r \int d^3r' \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}') V(\mathbf{r}-\mathbf{r}')\phi_m(\mathbf{r}')\phi_n(\mathbf{r}).$$

If we take only the diagonal terms $U \equiv V_{n,n;n,n}$ and $V_{n,m} \equiv V_{n,m;m,n}$, and neglect all off-diagonal terms, H' is reduced to an extended Hubbard model. As is well known, only for narrow bandwidth W are the diagonal terms dominant. However, in polymers, $W \simeq U \simeq 10$ eV, the off-diagonal terms have equal and even greater contributions compared with the diagonal terms. Thus, in order to get reliable results, one should use the full Coulomb interaction rather than the extended Hubbard model. Second, even within the extended Hubbard model, further approximations are used in practical calculations. Such approximations are reasonable only for weak repulsion or in small-size systems.

In order to eliminate these defects, we present a new method. First, instead of the extended Hubbard model, we start with the Coulomb interaction. Second, we calculate the electron correlation function from a full variational wave function without truncating it; then our method can deal with the electron interaction with any strength and any range.

If we suppose that the potential given to the ith electron at x_i by the lth atom on X_l is $V(x_i - X_l)$, then

$$H_0 = \sum\nolimits_i \left[-(\hbar^2/2m)\nabla_i^2 + \sum\nolimits_l V(x_i - X_l) \right]. \tag{1}$$

Because of the screening by the other chains and the polarization of σ electrons within the same chain, the electron interaction can be described as

$$H' = \sum_{i,j} v(i,j) = \sum_{i,j} \frac{U}{[1+(x_i-x_j)^2/a^2]^{1/2}} \exp\left[-\beta \frac{|x_i - x_j|}{a} \right], \tag{2}$$

where U and β denote the strength and the screening factor, and a is the lattice constant. Then the total Hamiltonian reads

$$H=H_0+H'+\tfrac{1}{2}K\textstyle\sum_l(X_{l+1}-X_l-a)^2, \qquad (3)$$

where the last term is the elastic energy.

According to Jastrow-Feenberg variational theory,[10] the wave function of the ground state for a system with repulsive interaction can be generally expressed as

$$\Psi(1,2,\ldots,N)=D[\varphi]\exp[u(1,2,\ldots,N)], \qquad (4)$$

where $D[\varphi]$ is the Slater determinant consisting of single-electron orbitals φ_μ. $u(1,2,\ldots,N)$ reflects electron correlation and can be determined by the variational principle. It can be decomposed as

$$u(1,2,\ldots,N)=(1/2!)\textstyle\sum_{i,j}u_{ij}+(1/3!)\sum_{i,j,k}u_{ijk}+\cdots,$$

where u_{ij}, u_{ijk}, ... are two-body, three-body, ... correlation factors. Since each cell has only one electron and the interaction is repulsive, the density is not high, and it is rare for three or more electrons to gather closely; then the two-body correlation u_{ij} is dominant, and multibody correlation can be neglected. Thus, the wave function (4) is reduced to

$$\Psi(1,2,\ldots,N)=D[\varphi]\exp[\tfrac{1}{2}\textstyle\sum_{i,j}u_{ij}]. \qquad (5)$$

With the eigenfunctions of H_0 as the orbitals φ_μ, the total energy will be

$$\begin{aligned}E&=\langle\Psi|H|\Psi\rangle/\langle\Psi/\Psi\rangle\\&=\sum_{\text{occ}}\epsilon_\mu+\frac{1}{2}\int d1\int d2[P(1)-n_0]v(1,2)[P(2)-n_0]+\frac{1}{2}\int d1\int d2P(1)P(2)v(1,2)[g(1,2)-1]\\&\quad+\tfrac{1}{2}K\textstyle\sum_l(X_{l+1}-X_l-a)^2+\dfrac{\hbar^2}{8m}\displaystyle\int d1\int d2P(1,2)(\nabla_1u_{12})^2\\&\quad+\frac{\hbar^2}{8m}\int d1\int d2\int d3P(1,2,3)(\nabla_1u_{12})\cdot(\nabla_1u_{13}),\end{aligned} \qquad (6)$$

where $g(1,2)=P(1,2)/P(1)P(2)$ is the electron correlation function and $P(1,2,\ldots,n)$ is the n-body distribution function. The variational problem can be solved by the scheme of correlated basis functions.[11] First introduce a parameter ξ before the factor u_{ij} in Eq. (5); in this way, $P(1,2,\ldots,n|\xi)$ will depend on ξ. Differentiating $P(1,\ldots,n|\xi)$ with respect to ξ, and then integrating over it, we can get combined integral equations for $P(1)$ and $P(1,2)$ as

$$\begin{aligned}P(1|\xi)=P(1|0)\exp\Bigg\{&\int_0^\xi d\xi'\int d2\,u_{12}P(1,2|\xi')/P(1|\xi')\\&+\frac{1}{2}\int_0^\xi d\xi'\int d2\int d3\,u_{23}[P(1,2,3|\xi')/P(1|\xi')-P(2,3|\xi')]\Bigg\},\end{aligned} \qquad (7)$$

$$\begin{aligned}P(1,2|\xi)=P(1,2|0)\exp\Bigg\{&\xi u_{12}+\int_0^\xi d\xi'\int d3(u_{12}+u_{23})P(1,2,3|\xi')/P(1,2|\xi')\\&+\frac{1}{2}\int_0^\xi d\xi'\int d3\int d4\,u_{34}[P(1,2,3,4|\xi')-P(1,2|\xi')P(3,4|\xi')]/P(1,2|\xi')\Bigg\},\end{aligned} \qquad (8)$$

As we have explained previously the multibody correlations are much less important than the two-body correlation in our case, so that the convolution approximation can be used to express the three- and four-body distribution functions $P(1,2,3)$ and $P(1,2,3,4)$, which appear in the right-hand side of Eqs. (7) and (8), in terms of the correlation function $g(1,2)$ and its convolution integrals. The explicit formulas for the convolution approximation have been illustrated by the diagrams shown in Fig. 4 of Wu and Chien.[12] In this way Eqs. (7) and (8) have become closed combined equations for the density distribution $P(1)$ and the correlation function $g(1,2)$. Thus $P(1)$ and $g(1,2)$ can be solved numerically from Eqs. (7) and (8) by iteration. Figure 1 gives $g(1,2)$ for a particular case. Substituting $P(1)$ and $g(1,2)$ into Eq. (6), we can get the total energy, which is a functional of u_{ij}. In order to facilitate the variational procedure, let us analyze the behavior of u_{ij} first. The wave function (5) shows that $\exp(\frac{1}{2}u_{ij})$ is essentially the two-body wave function of electrons i and j with the repulsive interaction $v(i,j)$; then WKB indicates

$$u_{ij}=-\eta v(i,j)^\gamma,$$

where η and γ are the variational parameters determined by the minimization of the total energy. The numerical result shows that γ is nearly 0.5, which agrees with the inference from WKB.

For any potential $V(x-X_l)$ the orbitals φ_μ can be obtained by solving the one-electron problem of Eq. (1). In order to make the calculation more transparent, we take $V(x-X_l)$ as a square well centered at X_l with the height

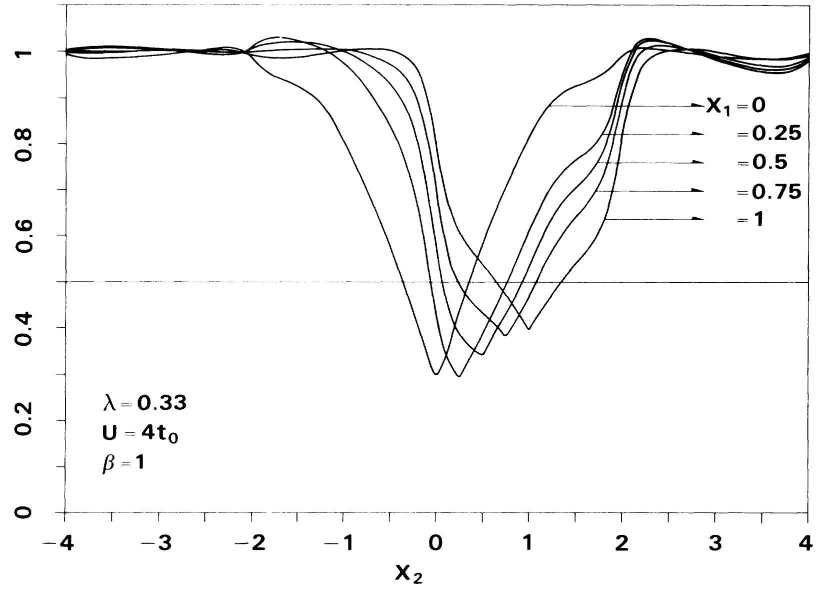

FIG. 1. The correlation function $g(x_1, x_2 - x_1)$; the unit of x is a.

$V_0 = 40$ eV and the width $b = 0.6$ Å. We also take $a = 1.22$ Å; then the bandwidth $W = 4t_0 = 14.92$ eV, and the electron-lattice-interaction coefficient is $\alpha = dt(a)/da = 9.65$ eV/Å. Three different elastic constants $K = 48.88$, 55.76, and 68.43 eV/Å^2 have been taken. They correspond to electron-lattice coupling constants $\lambda = 2\alpha^2/\pi t_0 K = 0.33$, 0.29, and 0.23.

In the case of a half-filled band, the instability makes

$$X_n = a[n + (-1)^n u],$$

where u is the amplitude of the bond alternation in units of a; u is determined by the minimization of the energy of the system. Our main concern is the dependence of u on the strength U and the range a/β of the electron repulsion for different coupling λ. The numerical results are shown in Figs. 2 and 3. From these results we can get the following conclusions:

(1) It is seen in Fig. 2 that when $\beta > 1.5$ the curve $u(U)$ declines monotonically. It indicates that, for a repulsion with short range, the bond alternation will decrease with increasing strength. However, the extended Hubbard model always gives an initial increase of bond alternation.[5-9] Apparently this contrast comes from the off-diagonal part of the Coulomb repulsion.[13] (2) Figure 2 also shows that when β decreases, the curve $u(U)$ rises. This indicates that extension of the repulsion range will increase bond alternation. (3) Figure 3 shows that when λ increases, the decay of the curve $u(U)$ becomes quick-

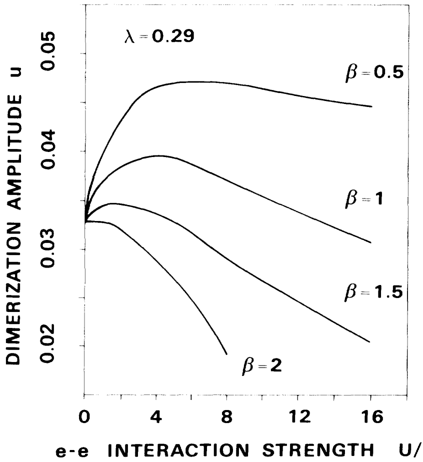

FIG. 2. The dependence of u on U for different β.

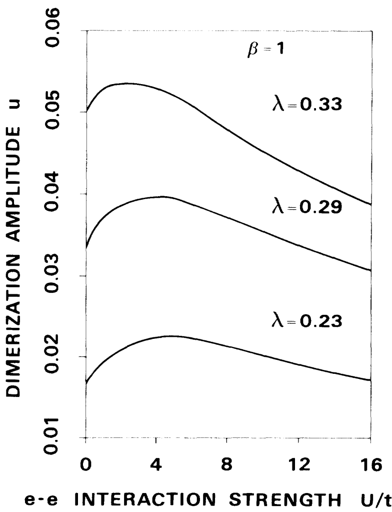

FIG. 3. The dependence of u on U for different λ.

er and the enhancement becomes weaker. It indicates that, in the system with stronger electron-lattice coupling, repulsion will suppress bond alternation rather than enhance it; but, in the system with weak λ and a wide repulsion range, bond alternation is mainly produced by the repulsion rather than the electron-lattice interaction.

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[1] W. Su, J. Schrieffer, and A. Heeger, Phys. Rev. B **22**, 2099 (1980).

[2] H. Thomann *et al.*, Phys. Rev. Lett. **50**, 533 (1983).

[3] B. Hudson and B. Kohler, Synth. Met. **9**, 241 (1984).

[4] J. Orenstein *et al.*, Phys. Rev. B **30**, 786 (1984).

[5] S. Kivelson and D. Heim, Phys. Rev. B **26**, 4278 (1982).

[6] Z. Soos and S. Ramasesha, Phys. Rev. B **29**, 5410 (1984); S. Mazumdar and S. Dixit, Phys. Rev. Lett. **51**, 292 (1983), and Phys. Rev. B **29**, 1824 (1984).

[7] J. E. Hirsch, Phys. Rev. Lett. **51**, 296 (1983); D. Campbell *et al.*, Phys. Rev. Lett. **52**, 1717 (1984).

[8] G. Hayden and E. Mele, Phys. Rev. B **32**, 6527 (1985); B. Horovitz and J. Solyom, Phys. Rev. B **32**, 2681 (1985).

[9] D. Baeriswyl and K. Maki, Phys. Rev. B **31**, 6633 (1985).

[10] E. Feenberg, *Theory of Quantum Fluids,* Pure and Applied Physics Series Vol. 31 (Academic, New York, 1969).

[11] S. Chakravarty and C. Woo, Phys. Rev. B **13**, 4815 (1976); X. Sun, M. Farjam, and C. Woo, Phys. Rev. B **28**, 5599 (1983).

[12] F. Wu and M. Chien, J. Math. Phys. **11**, 1912 (1970).

[13] During the revision of this manuscript, we received a preprint from S. Kivelson, W. Su, J. Schrieffer, and A. Heeger. They included some off-diagonal terms (bond charge interaction) and also found that the dimerization will decrease monotonically with increasing the electron repulsion.