PHYSICAL REVIEW B VOLUME 44, NUMBER 20 15 NOVEMBER 1991-II

Electron interaction and optical gap of conjugated polymers

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(Received 28 March 1991)

The controversy regarding whether the optical gap of a polymer is increased or decreased by electron-electron interactions can be clarified by studying the effect of screened Coulomb interactions on the correlation function of the excited states. Since the competition between the diagonal and the off-diagonal parts of the electron interaction depends on the screening, the screening becomes the decisive factor to determine the dependence of the optical gap on the electron interaction. Our theory shows that the electron interaction with weak or normal screening increases the optical gap. However, if the screening is very strong, the optical gap can be reduced by the electron interaction.

I. INTRODUCTION

Experimentally, one of the most prominent features of the conjugated polymer is the finite excitation energy from the ground state to the lowest optically allowed excited state, namely the optical gap. But, theoretically, understanding the physical origin of the optical gap is one of the most controversial issues in this field today. There exists a sharp dispute about the effect of electron-electron interactions on the optical gap. One school shows that the electron interaction increases the optical gap (some groups even think that the main origin of the optical gap is the electron interaction). However, the other school is of the opposite opinion, namely that the electron interaction should reduce the optical gap, which is produced by electron-phonon interactions. Their discrepancy comes from the different descriptions for the electron interaction. The former school uses the extended Hubbard model to describe the electron interaction. Starting from that model, many different theories including the perturbation,[1] Gutzwiller variational,[2] renormalization group,[3] Monte Carlo simulation,[4] valence bond,[5–8] configuration interaction,[9] exact diagonalization,[10] and others have been used to investigate the effect of electron interaction on the dimerization and optical gap. Although their methods and approximations are different, all these approaches reach the same result, namely that the electron interaction increases the dimerization and optical gap. However, the latter school argues that the extended Hubbard model only contains the site-charge repulsion U and V, and misses the bond-charge repulsion W. When W is added to the extended Hubbard model, they find that the dimerization and optical gap is reduced.[11] Nevertheless, the former school is not convinced because the latter takes the extreme case with $W=V$ and makes only first-order perturbation.[12–14] Thus, whether the electron interaction increases or decreases, the optical gap becomes an open question.

It is not surprising that the conclusions of these two schools are completely opposite; the reason is that their model Hamiltonians are different. The question is to what extent these models are suitable. Apparently, the key to settling this dispute is to analyze the limitations of these models and find a better description for electron interaction in polymers. We know that the parameters U and V in the extended Hubbard model are the diagonal matrix elements of the Coulomb interaction, and the bond-charge repulsion W, which is the exchange term, is one of the off-diagonal elements. There are also many other off-diagonal elements, such as the site-bond repulsion X, etc. It has been pointed out by Campbell and coworkers that the parameters U, V, W, X cannot be adjusted artificially at will.[10] The ratios between these parameters should be determined from the Coulomb interaction.

On the other hand, as is well known, the Hubbard model is a good approximation for those systems whose bandwidths are narrow. The off-diagonal elements, therefore, are much smaller than the diagonal elements and they can be neglected. However, the bandwidth of the conjugated polymer is wide and even larger than the electron interaction. In such a case, the off-diagonal elements are not always negligible comparing to the diagonal partner, especially when the screening is strong. Then the results based on selecting some part of the interaction elements with artificial values are questionable. Therefore, it will be more reliable to directly use screened Coulomb repulsion $v(r) \propto (1/r)\exp(-\beta r)$ to describe the electron interaction. In the second quantized representation this interaction includes all diagonal and off-diagonal elements. And in this description, the ratios between all interaction parameters U, V, W, X, etc., can be determined correctly, avoiding any artificiality. This description is general; both the former model (extended Hubbard) and the latter model [KSSH (Ref. 11)] are different approximations of this interaction. So it can be expected that the results based on this interaction will provide a satisfying answer to the above dispute.

Such screened Coulomb repulsion has been successfully used to clear up the confusion about the effect of the electron interaction on the bond alternation of the polymer.[15–18] The bond alternation is a property that is only associated with the ground state of the polymer. But the optical gap involves the excited states. In this paper we are going to use the same interaction to study the effect of the electron interaction on the excited states and the optical gap of the polymer.

In the next section we establish the integral equations for the correlation function of the excited states in an interacting electron system and find the relation between the optical gap and the correlation function of the excited state. Then, in Sec. III, the dependence of the optical gap on the electron interaction will be obtained by solving the integral equations numerically. In the discussion of the results it tells how the controversy about the optical gap can be settled.

II. THEORETICAL FRAMEWORK

By using the screened Coulomb repulsion to describe the electron interaction, the Hamiltonian of our system reads

$$H = H_0 + H_{\text{int}} + (K/2)\sum_l (X_{l+1} - X_l - a)^2 . \tag{2.1}$$

H_0 describes the interaction between the electron and the lattice of the polymer,

$$H_0 = \sum_i \left[\left[\frac{\hbar^2}{2m} \right] \nabla_i^2 + \sum_l V(x_i - X_l) \right] , \tag{2.2}$$

where $V(x_i - X_l)$ is the potential produced by the atom at X_l and exerting on the electron at x_i. The eigenvalues and eigenfunctions of H_0 are $\varepsilon(k)$ and ϕ_k. H_{int} is the electron interaction

$$H_{\text{int}} = \sum_{(i,j)} v(r_{i,j}) , \tag{2.3}$$

$$v(r) = (U_0/r)\exp(-\beta r) , \tag{2.4}$$

where U_0 and β are the strength and the screening factor of the electron interaction in the polymer. The last term in (2.1) is the elastic energy and K is the elastic constant.

The optical gap is the threshold of an interband optical absorption. In the system with electron interaction, an excited state such as $2\,^1A_g$ can exist within the gap, but it is dipole forbidden from the ground state, whose symmetry is $1\,^1A_g$. The lowest many-body excited state in this paper has the symmetry ^1B_u, which is dipole allowed, and the transition from the ground state to this lowest excited state produces the optical gap.[19]

The calculation of the optical gap for a system with an intermediate electron interaction is an important but difficult problem. The polymer has a wide bandwidth of about 10 eV, and the electron interaction in the polymer is about 5 eV. It means that the electron interaction is neither weak enough to use the perturbation nor able to be treated by the strong-limit approximation. It is an intermediate case. The various methods mentioned in the Introduction have enabled some progress for this subject, but they are not able to deal with the Coulomb interaction. Meanwhile, the exact calculation methods for the optical gap suffered from the finite-size effect. In this paper we use the Feenberg-Jastrow variational method,[20] which can work for the Coulomb repulsion and for any length of the polymer chain. We are going to determine the dependences of the optical gap on both the strength and the screening of the electron interaction in the intermediate region of strength and for any screening. Then it can be quantitatively shown how the electron interaction increases or decreases the optical gap.

Following the Feenberg-Jastrow ansatz,[20] the wave function of an interacting electron system is

$$\Psi(1,2,\ldots,N) = D(1,2,\ldots,N)\exp\left[\sum_{i,j} u_{ij}\right] , \tag{2.5}$$

where $D(1,2,\ldots,N)$ is the Slater determinant consisting of occupied states ϕ_k, and u_{ij} is the correlation factor determined by the variational principle. As is known, the first part of the wave function (2.5) represents the individual particle mode and the second part represents the collective mode.[21,22] Actually, in momentum space the second part can be written as

$$\sum_{i,j} u_{ij} = \sum_k C_k \rho_k^* \rho_k ,$$

where C_k is the Fourier transform of $u(r)$ and ρ_k is the density fluctuation, which depicts the plasma in the case of Coulomb repulsion or the zero sound in the case of short-range repulsion. This many-body wave function (2.5) is a functional of the electron's occupation configuration. In the half-filled case, the most interesting states in our study are the ground state $\Psi_g(1,2,\ldots,N)$ with full valence band and empty conduction band and the lowest single-particle excited state $\Psi_e(1,2,\ldots,N)$ with one electron excited from the valence band to the conduction band. Since the collective mode is not excited in this excitation, Ψ_g and Ψ_e have the same u_{ij} but different D_e and D_g, which possess reversed symmetries.[23] The optical transition is allowed between them and the optical gap E_g is

$$E_g = E(\{\Psi_e\}) - E(\{\Psi_g\}) \ . \tag{2.6}$$

The energy $E(\{\Psi\})$ of the wave function Ψ (2.5) is

$$\begin{aligned} E(\{\Psi\}) &= \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \\ &= \sum_{\text{occ}} \varepsilon(\kappa) + \tfrac{1}{2} \int d1 \int d2 [P(1) - n_0] v(1,2) [P(2) - n_0] \\ &\quad + \tfrac{1}{2} \int d1 \int d2 [P(1,2) - P(1)P(2)] v(1,2) + \frac{\hbar^2}{8m} \int d1 \int d2\, P(1,2) (\nabla_1 u_{12})^2 \\ &\quad + \frac{\hbar^2}{8m} \int d1 \int d2 \int d3\, P(1,2,3) (\nabla_1 u_{12}) (\nabla_1 u_{13}) \ , \end{aligned} \tag{2.7}$$

where $P(1,2,\ldots,n)$ is the n-particle distribution function, which satisfies the following integral equations:[15]

$$P(1|\xi) = P(1|0) \exp\left[\int_0^\xi d\xi' A(1|\xi') \right] \ , \tag{2.8}$$

$$P(1,2|\xi) = P(1,2|0) \exp\left[\int_0^\xi d\xi' K(1,2|\xi') \right] \ , \tag{2.9}$$

where

$$A(1|\xi') = \int d2\, u_{12} P(1,2|\xi') / P(1|\xi') + \tfrac{1}{2} \int d2 \int d3\, u_{23} [P(1,2,3|\xi') / P(1|\xi') - P(2,3|\xi')] \ , \tag{2.10}$$

$$\begin{aligned} K(1,2|\xi') &= u_{12} + \int d3 (u_{13} + u_{23}) P(1,2,3|\xi') / P(1,2|\xi') \\ &\quad + \tfrac{1}{2} \int d3 \int d4\, u_{34} [P(1,2,3,4|\xi') - P(1,2|\xi') P(3,4|\xi')] / P(1,2|\xi') \ . \end{aligned} \tag{2.11}$$

Since the density is not high, and there is no electron condensation under the screened repulsive interaction; the multibody correlation is much less effective than the two-body correlation. Then the three- and four-particle distribution functions can be expanded by the convolution approximation in terms of two-body correlation function,[22] and Eqs. (2.8) and (2.9) are closed. For the ground state Ψ_g, its density $P_g(1)$ and two-body distribution function $P_g(1,2)$ can be obtained directly by solving the combined integral equations (2.8) and (2.9), which has been done in a previous work.[15]

In order to get the optical gap from the Eq. (2.6), we must first know the density $P_e(1)$ and two-particle distribution function $P_3(1,2)$ for the excited state. They can be obtained by defining

$$\tilde{P}(1) = P_e(1) - P_g(1)$$

and (2.12)

$$\tilde{P}(1,2) = P_e(1,2) - P_g(1,2) \ ,$$

which are the differences of the densities and correlation functions between the excited state and ground state. Since the system contains N electrons and Ψ_e is an extended single-particle excited state, both $\tilde{P}(1)$ and $\tilde{P}(1,2)$ are the quantities with the order of $1/N$. Keeping this in mind and applying Eqs. (2.8) and (2.9) to the excited state Ψ_e, the equations for $\tilde{P}(1)$ and $\tilde{P}(1,2)$ can be derived:

$$\frac{\tilde{P}(1|\xi)}{P(1|\xi)} = \frac{\tilde{P}(1|0)}{P(1|0)} + \int_0^\xi d\xi' \left[\int d2\, \tilde{P}(2|\xi') \frac{\delta A(1|\xi')}{\delta P(2|\xi')} + \int d2 \int d3\, \tilde{P}(2,3|\xi') \frac{\delta A(1|\xi')}{\delta P(2,3|\xi')} \right] \ , \tag{2.13}$$

$$\frac{\tilde{P}(1,2|\xi)}{P(1,2,|\xi)} = \frac{\tilde{P}(1,2|0)}{P(1,2,|0)} + \int_0^\xi d\xi' \left[\int d3\, \tilde{P}(3|\xi') \frac{\delta K(1,2|\xi')}{\delta P(3|\xi')} + \int d3 \int d4\, \tilde{P}(3,4|\xi') \frac{\delta K(1,2|\xi')}{\delta P(3,4|\xi')} \right] \ . \tag{2.14}$$

From Eq. (2.6), the optical gap can be expressed in terms of $\tilde{P}(1)$ and $\tilde{P}(1,2)$:

$$E_g=2\Delta+\frac{N}{n_0\Omega}\int_\Omega d1\int d2[\widetilde{P}(1,2)/2-n_0\widetilde{P}(1)]v(1,2)$$
$$+\frac{\hbar^2}{8m}\left[\frac{N}{n_0\Omega}\int_\Omega d1\int d2\,\widetilde{P}(1,2)(\nabla_1 u_{12})^2\right.$$
$$\left.+\int d1\int d2\int d3(\nabla_1 u_{12})(\nabla_1 u_{13})\left[\int dy\,\widetilde{P}(y)\frac{\delta P(1,2,3)}{\delta P(y)}+\int dy\int dz\,\widetilde{P}(y,z)\frac{\delta P(1,2,3)}{\delta P(y,z)}\right]\right], \tag{2.15}$$

where Ω is the volume of the cell and n_0 is the average density. From this expression it can be seen that, although $\widetilde{P}(1)$ and $\widetilde{P}(1,2)$ are infinitesimal, their contribution to the optical gap is finite. In the right-hand side of Eq. (2.15), the first term 2Δ is the dimerization gap; the rest are the effect of the electron interaction on the excitation.

Thus, the core of our theory is to calculate $\widetilde{P}(1)$ and $\widetilde{P}(1,2)$ by solving the integral equations (2.13) and (2.14), from which the density and the correlation function of the excited state can be obtained. Substituting the obtained $\widetilde{P}(1)$ and $\widetilde{P}(1,2)$ into the Eq. (2.15), we can get the optical gap.

III. RESULTS AND CONCLUSION

Following the formalism established in the preceding section, the optical gap with the electron interaction can be calculated step by step.

First, we deal with the band without the electron interaction. For the sake of simplicity, a periodical square-well potential is taken as the electron-lattice interaction, which gives the bandwidth $4t_0=12$ eV and the noninteracting dimerization gap $E_g^0=1.4$ eV. With this band, the noninteracting density $P(1|0)$ and $\widetilde{P}(1|0)$ as well as the two-body distribution function $P(1,2|0)$ and $\widetilde{P}(1,2|0)$ can be obtained straightforwardly.

Next, using the obtained $P(1|0)$ and $P(1,2|0)$ as the initial condition to solve the integral equations (2.8) and (2.9), we can get the density $P(1|\xi)$ and the two-body distribution function $P(1,2|\xi)$ under the electron interaction. Substituting $P(1|\xi)$ and $P(1,2|\xi)$ into Eqs. (2.13) and (2.14), and using $\widetilde{P}(1|0)$ and $\widetilde{P}(1,2,|0)$ as the initial condition, $\widetilde{P}(1)$ and $\widetilde{P}(1,2)$ can be obtained by numerically solving Eqs. (2.13) and (2.14).

Finally, substituting all the obtained $P(1),P(1,2)$ and $\widetilde{P}(1),\widetilde{P}(1,2)$ into Eq. (2.15), we obtain the optical gap.

In our theory, the essential quantity is $\widetilde{P}(1,2)$, which reflects the electron correlation in the excited state. The feature of $\widetilde{P}(1,2)$ is shown in Fig. 1, where there apparently appears the $2k_F$ oscillation, which is the characteristic of the correlation function. Notice that $\widetilde{P}(1,2)$ itself is not the two-body correlation function of the excited state, as is defined in Eq. (2.12); it is the difference of the two-particle distribution functions between the excited state and ground state. So, besides the behavior of $2k_F$ oscillation, the shape of Fig. 1 looks quite different from the two-body correlation function of the ground state, which was shown in Fig. 2 of Ref. 15.

The dependences of the optical gap E_g (in the unit of $E_g^0=1.4$ eV) on both the interacting strength U_0 (in the unit of $t_0=3$ eV) and the screening factor β are shown in Fig. 2. Each curve in Fig. 2 has a fixed screening factor β. From these curves, it can be seen that the weak screening and the strong screening have qualitatively different effects of the electron interaction on the optical gap. In the case of the weak and normal screening, the electron interaction increases the optical gap; the weaker the screening is, the larger the increase is. But if the screening is very strong ($\beta > 3$), the optical gap will be reduced by the electron interaction.

Based on these results, the dispute about the effect of the electron interaction on the optical gap can be clarified. As was mentioned in the Introduction, the ratios between the interaction parameters U,V,W,X cannot be assigned arbitrarily. The merit of using the screened Coulomb repulsion to describe the electron interaction is that it can correctly bring about the ratios. With our band and the Wannier function it is straightforward to calculate the ratios of the off-diagonal elements to the diagonal ones. These ratios depend on the screening; their values are given in Table I, where X is negative. Painelli and Girlando predicted it and discussed its meaning.[24] Combining Table I and Fig. 2, the controversy is easily settled. From Table I it is seen that, if the screen-

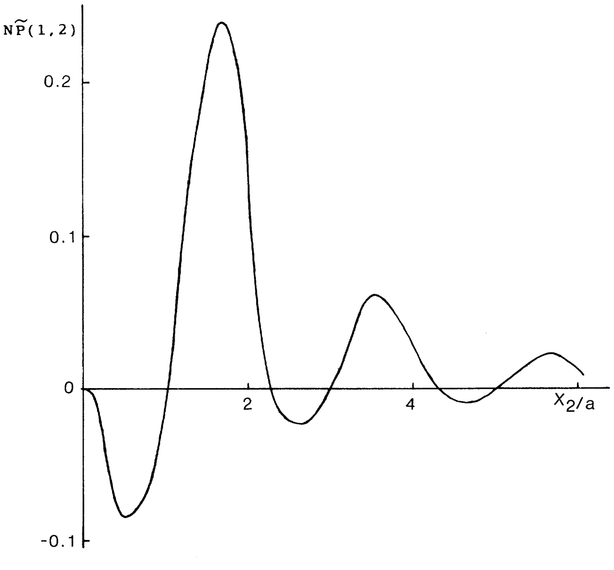

FIG. 1. The curve of $N\widetilde{P}(1,2)$ with $X_1=0$.

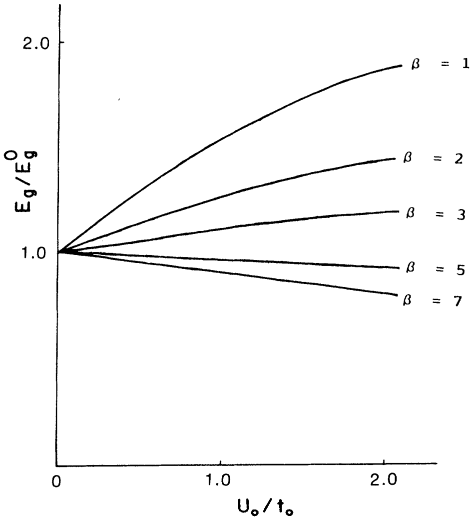

FIG. 2. The dependence of the optical gap E_g on the interaction strength U_0 with different screening β.

TABLE I. Ratios of off-diagonal elements to diagonal elements.

β	1	3	5	7
W/V	0.02	0.10	0.26	0.43
X/V	−0.06	−0.18	−0.45	−0.77

ing is small, the off-diagonal elements W and X are much smaller than the diagonal ones, and they can be neglected. So, in this case, the electron interaction can be described by the extended Hubbard model. At the same time Fig. 2 shows that the optical gap is increased by the electron interaction if the screening is weak. This is exactly the result obtained by the former school. Table I also shows when screening increases, the ratios of W/V and $|X|/V$ rapidly increase. If the screening becomes very strong, the off-diagonal terms can be big enough to compete with the diagonal ones; then the bond-charge repulsion W and the other off-diagonal elements should be considered. Meanwhile, Fig. 2 indicates that the electron interaction will suppress the optical gap if the screening is strong. This is what the latter school claimed. Thus, our theory discloses the origin of the conflicting conclusions between these two schools. It now becomes clear that each side of the dispute has its own limitation: the former is valid in the weak or normal screening, whereas the latter is valid in strong screening.

Here, we see that the behavior of the optical gap is quite similar to that of the dimerization of the polymer, although the optical gap is determined by the excitation of the polymer, whereas the dimerization is only related to the ground state. For the dimerization, it has been discovered that the electron interaction initially enhances the dimerization if the screening is weak, but if the screening is strong enough ($\beta > 1.5$), the electron interaction will suppress the dimerization.[15] For the optical gap, the difference is that it requires even stronger screening, $\beta > 3$; only then will the optical gap be suppressed by the electron interaction.

In summary, our conclusion is that the effect of the electron interaction on the optical gap depends on the screening: for weak and normal screening, the electron interaction increases the optical gap, and the increase can be so large that the electron interaction becomes the main origin of the optical gap; on the contrary, for very strong screening, the electron interaction decreases the optical gap, and the optical gap is mainly produced by the electron-phonon interaction.

ACKNOWLEDGMENTS

This work was partially supported by Project 863 of the National Science Foundation of China. D.L. and T.G. received support from the U.S. Office of Naval Research. We would like to thank Dr. C. Wu, Dr. R. Fu, Professor W. P. Su, Dr. D. K. Campbell, and Professor S. Mazumdar for their helpful discussions. X.S. is very grateful to the Institute for Molecular Science for hospitality during his visit.

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