Polaron versus bipolaron in conducting polymers: a density matrix renormalization group study

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Competition between polaron and bipolaron in conjugated polymers with nondegenerate ground state is systematically studied in the extended Hubbard-Peierls model with the symmetry-breaking Brazovskii-Kirova term, using the density matrix renormalization group method combined with lattice optimization in the adiabatic approximation. We demonstrate that the relative stability of a bipolaron over two separated polarons sensitively depends on both on-site Hubbard $U$ and nearest-neighbor repulsion $V$. When $U$ is much larger than $V$, the bipolaron state is more stabilized compared with mean field calculations.

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The formation of a bipolaron, in which two electrons are trapped in a self-induced lattice deformation, is an important subject in many areas of condensed matter physics, such as amorphous semiconductors [1], insulating crystals [2], high temperature superconductors [3,4], and low-dimensional materials [5]. A simple model of localized linear electron-lattice coupling gives us a criterion for bipolaron formation as that the electron-lattice coupling is strong enough to surpass Coulomb repulsion between the two electrons — the situation being called "negative effective $U" [1]. However, real situations are more delicate in the sense that bipolarons possess internal degrees of freedom to allow modification of wavefunctions and lattice deformations so as to reduce Coulomb repulsion and yet to increase binding by lattice distortion. In addition, a purely electronic mechanism of negative effective $U$ has been proposed [1].

In one-dimensional conjugated polymers, polarons and bipolarons belong to the category of solitonic nonlinear excitations [1]. Solitons can exist in polymers with degenerate ground states, such as in trans-polyacetylene, whereas polarons and bipolarons are candidates for major charge carriers in polymers without ground state degeneracy, such as in polythiophene and poly(p-phenylene vinylene). Experimentally, the existence of bipolarons in doped conjugated polymers has been controversial [6-8].

The initial assignments of bipolarons relied upon the observation of two peaks in doping-induced absorption spectra [9]. However, theoretical calculations [10,11] as well as experimental studies of doped oligomers [7,10] have established that the two-peak feature actually corresponds to a polaron rather than a bipolaron. On the other hand, the existence of bipolarons has been suggested by the observation of a single photoinduced absorption peak in an improved sample of polythiophene [12].

On the theoretical side, models with neglecting electron-electron (e-e) interactions predict that a bipolaron (BP) is always energetically more stable than a separated pair of polarons (2P) [4]. The effect of long-range e-e interaction was studied systematically within the unrestricted Hartree-Fock (UHF) approximation [13], and it was shown that the interaction significantly suppresses the stability of BP. A recent study in the extended Hubbard-Peierls model by using the density matrix renormalization group (DMRG) method [14] has shown that BP is favored over 2P even for a very large on-site repulsion $U$ [1]. However, off-site interactions were not taken into account in that study, and, in view of the spatial extensions of a polaron and a bipolaron, it is very important to take those interactions as well.

In the present paper, we investigate this problem systematically by using the DMRG method and by taking both on-site $U$ and nearest neighbor repulsion $V$ into account. The DMRG method developed originally by White [15] for quantum spin systems is quite a powerful method to treat strongly correlated electron systems in one dimension. For the present purpose we combine the DMRG method with lattice optimization by using the Hellmann-Feynman force equilibrium condition. We will demonstrate that higher order correlation effects beyond the mean field approximation are crucial for the formation of BP and that the stability of BP is very sensitive to both $U$ and $V$.

The model Hamiltonian is the one-dimensional extended Hubbard-Peierls Hamiltonian,

\[
H = - \sum_{i,s} t_{i,i+1} [c^\dagger_{i,s} c_{i+1,s} + h.c.] + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i (n_i - 1)(n_{i+1} - 1) + \frac{K}{2} \sum_i y_i^2 + \Gamma \sum_i y_i. \tag{1}
\]

Here, the creation operator of a $\pi$ electron with spin $s$ at site $i$ is denoted by $c^\dagger_{i,s}$, and the number operators are defined as $n_{i,s} = c^\dagger_{i,s} c_{i,s}$ and $n_i = \sum_s n_{i,s}$. The transfer integral, $t_{i,i+1}$, is assumed in the form
where δ₀ is the Brazovskii-Kirova symmetry-breaking parameter to lift the degeneracy of the ground state \( | \psi \rangle \) the change of bond length between \( i \)-th and \( (i+1) \)-th sites, and \( \alpha \) the electron-lattice coupling constant the Su-Schrieffer-Heeger type \([19]\). The parameter \( K \) the spring constant for the change of bond length, a the last term in eq. (1) is added to keep the chain length constant. We take the dimensionless electron-lattice coupling constant \( \lambda = 2\alpha^2/\pi tK = 0.136 \) and \( \alpha/K \approx 0.08 \) as in Ref. \([15]\). Although the relative stability of BP a 2P depends on the electron-lattice coupling, we fix \( t \) parameter and vary e-e interaction strengths \( U \) and \( V \).

We apply the finite-system DMRG algorithm \([14]\) to treat the electronic ground state. The open boundary condition is imposed to the system with \( N \) sites. The lattice is treated within the adiabatic approximation. The bond variable \( y_i \) is determined by using the Hellman-Feynman force equilibrium condition \([15,17]\),

\[
y_i = -\frac{1}{K} (2\alpha p_{i,i+1} + \Gamma),
\]

where \( p_{i,i+1} = \sum_s < c_{i,s}^\dagger c_{i+1,s} > \) with \( \cdots \) denoting the ground state expectation value. The condition \( \sum y_i = 0 \) gives \( \Gamma = -(2\alpha/N - 1) \sum_m p_{m,m+1} \). Thus the lattice configuration \( \{ y_i \} \) and the electronic ground state must be determined in a self-consistent fashion. We take an iterative method as follows: (i) Set an initial lattice configuration \( \{ y_i^{(0)} \} \). (ii) Calculate the electronic ground state by the infinite-system DMRG method for \( \{ y_i^{(1)} \} \). (iii) Carry out the finite-size DMRG procedure to refine the ground state. (iv) Calculate new lattice configuration \( \{ y_i^{(1)} \} \) from eq. (3). (v) Replace \( \{ y_i^{(0)} \} \) with \( \{ y_i^{(1)} \} \) and go to step (ii). The procedure is continued until the difference between \( \{ y_i^{(0)} \} \) and \( \{ y_i^{(1)} \} \) becomes negligibly small. In the present DMRG calculations, we truncate the Hilbert space by keeping \( m = 80 \) states in each block, which turned out to be sufficient to achieve negligible \( m \)-dependence of calculated results. We have also checked the accuracy of our DMRG calculations by comparing with the results of numerical exact diagonalization up to 12 sites, with the exact solution of the Hubbard model, and with exact numerical results in the non-interacting case \((U = V = 0)\).

We consider the doping of two electrons in a finite chain to examine the formation of BP or 2P. We present results for the system size \( N = 120 \) and the total electron number \( N_e = 122 \). Here electrons with up and down spins are added to the half-filled system so as to give \( S_z = 0 \). To obtain a 2P solution, we can equally use two up spin electrons with \( S_z = 1 \) instead, because the interference between the two well-separated polarons is negligible. This saves a lot of CPU time especially when 2P is less stable

\[
t_{i,i+1} = [1 - (-1)^i \delta_0] t + \alpha y_i,
\]

In Fig. 1 we show an example of obtained lattice distortions of BP and 2P along with corresponding UHF results for comparison. In this example with \( U = 1.5t \) and \( V/U = 0.5 \), we see that polaronic distortions (especially for a bipolaron) are wider and shallower in the DMRG than in the UHF. However, if we go to much smaller \( V/U \), this tendency is reversed, i.e., the distortion becomes narrower and deeper in the DMRG. This implies that higher order correlation beyond the UHF works in opposite directions with respect to \( U \) and \( V \).

Figure 2 displays the energy difference \( \Delta E \) between the obtained BP and 2P states as a function of \( U \) with constant \( V/U \) for the case \( \delta_0 = 0.05 \). \( \Delta E > 0 \) implies that BP is more stable than 2P. The UHF results are also depicted for comparison. In the case of \( V/U = 0.5 \), BP is more stable than 2P for \( U > U_c \) below a critical value \( U_c \approx 1.8t \). The above behavior is qualitatively similar to the UHF result, although \( U_c \) is substantially larger. We could not find out a metastable BP state for \( U > U_c \) in the DMRG calculation in contrast to the UHF result. In this case the iteration procedure always leads to a 2P state with \( S_z = 0 \) even if we start from a BP configuration. This is the reason why the DMRG curve for \( V/U = 0.5 \) in Fig. 2 is terminated at \( U_c \) above which the 2P state is the only self-consistent solution.
On the other hand, $\Delta E$ for $V/U = 0.25$ in Fig is always positive and does not show any indication of crossing $\Delta E = 0$ even for much larger $U$. That is, it is always stable in this case. This is completely different from the UHF result, which is not very sensitive to $V$. We note that this result is consistent with Ref. [17] in the limiting case of $V = 0$.

The destabilization of the BP state with increasing $U$ is understandable at the UHF level as follows [17]. In restricting our consideration to the effects of $U$, a bipolaron with spatial extension $\xi_{BP}$ costs energy $\sim U/\xi_{BP}$, while a polaron with an extension $\xi_{P}$ hardly costs energy because of largely spin-polarized excess charges in the case of large $U$. Higher order correlation may reduce the probability of double occupancy, thus weakening the $U$-dependence of $\Delta E$ in the DMRG method.

We have carried out similar calculations for various $\delta_0$. By plotting the critical value $U_c$ for BP destabilization against $\delta_0$, we obtain the ground state phase diagram in the parameter space of $\delta_0$ and $U$. Figure 3 is the obtained phase diagram for $V/U = 0.5$, where the solid (broken) line indicates the phase boundary between the regions of stable BP and 2P in the DMRG (UHF) results. The phase boundary becomes lower with raising $\delta_0$, because the increment of $\delta_0$ results in the decrement of $\xi_{BP}$ and $\xi_{P}$, thereby enhancing the effect of Coulomb repulsion. Higher order correlation stabilizes the BP state, as mentioned above. In the case of $V/U = 0.25$ we did not find out the region of 2P being more stable than BP for any $\delta_0$ in the DMRG method.

In order to clarify the role of higher order correlation beyond the UHF approximation for the energies of 2P and BP, we have evaluated the fluctuation energies in the obtained DMRG wave functions. The spin fluctuation energy, $U \sum_i (< n_{i\uparrow} - n_{i\downarrow} >) (< n_{i+1\uparrow} - n_{i+1\downarrow} >)$, is always larger for 2P than in BP, destabilizing the 2P state. Its difference between 2P and BP grows with increasing $U$, so that this contribution is more important for smaller $V/U$. On the other hand, the charge fluctuation energy, $V \sum_i s_{i\downarrow} < n_{i\downarrow} - n_{i\uparrow} >(< n_{i+1\downarrow} - n_{i+1\uparrow} >)$, is almost the same for 2P and BP, so that the net effect to the relative stability is negligible. Therefore, the main difference between the DMRG and UHF results comes from spin fluctuations associated with on-site Coulomb repulsion $U$.

In summary, we have investigated the effect of $e-e$ interactions on the spatial profiles and energies of polarons and bipolarons in conjugated polymers by using the DMRG method. We have demonstrated that the relative stability of a bipolaron over a pair of separated polarons is sensitive to both on-site $U$ and nearest neighbor $V$. Spin fluctuations associated with on-site $U$ contribute to the stabilization of a bipolaron compared with the results of the UHF approximation. On the other hand, nearest neighbor $V$ works in the direction of dissociating a bipolaron into two polarons in the same way as the UHF calculation.

The present study is limited to the extended Hubbard-Peierls model with short range interactions, while longer range interactions such as the Ohno potential should be taken into account to discuss situations in real materials. Judging from the roles of $U$ and $V$ clarified in the present work, we expect that the inclusion of longer range interactions would not cause qualitative differences but enhance the tendency of stabilizing polarons by $V$. 

![Fig. 2](image_url) 

FIG. 2. Energy difference between the bipolaron two-polaron states against $U$ calculated by the DMRG method (solid lines) and the UHF approximation (broken lines) for $V/U = 0.5$ and 0.25 with $\delta_0 = 0.05$.

![Fig. 3](image_url) 

FIG. 3. Ground state phase diagram of the two-electron doped system with $V/U = 0.5$. The solid (broken) line indicates the phase boundary between the regions of a bipolaron (BP) and two separated polarons (2P) obtained by the DMRG method (the UHF approximation).
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[1] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).
[2] H. Hiramoto and Y. Toyozawa, J. Phys. Soc. Jpn. 54, 245 (1985).
[3] K. Nasu, Phys. Rev. B 37, 5075 (1988).
[4] D. Emin, Phys. Rev. Lett. 62, 1544 (1989).
[5] A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W.P. Su, Rev. Mod. Phys. 60, 781 (1988).
[6] H. Katayama-Yoshida and A. Zunger, Phys. Rev. Lett. 55, 1618 (1985).
[7] Y. Furukawa, in Primary Photoexcitations in Conjugated Polymers, edited by N.S. Sariciftci (World Scientific, Singapore, 1997).
[8] E.M. Conwell, and H.A. Mizes, Synth. Met. 78, 201, (1996).
[9] K. E. Ziemelis et al., Phys. Rev. Lett. 66, 2231 (1991).
[10] K. Fesscr, A.R. Bishop, and D.K. Campbell, Phys. Rev. B 27, 4804 (1983).
[11] Y. Shimoi, S. Abe, and K. Harigaya, Mol. Cryst. Liq. Cryst. 267, 329, (1995).
[12] Y. Furukawa, J. Phys. Chem. 100, 15644 (1996).
[13] P.A. Lane, X. Wei, and Z.V. Vardeny, Phys. Rev. Lett. 77, 1544 (1996).
[14] D. Baeriswyl, Electronic Properties of Conjugated Polymers III, edited by H. Kuzmany, M. Mehring, and S. Roth (Springer, 1989) p. 54.
[15] Y. Shimoi and S. Abe, Phys. Rev. B 50, 14781 (1994).
[16] S. R. White, Phys. Rev. Lett. 69, 2863 (1992); S. R. White, Phys. Rev. B 48, 10345 (1993).
[17] G. Wen, and W.P. Su, Synth. Met. 78, 195 (1996).
[18] S.A. Brazovskii and N.N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. 33, 6 (1981) [JETP Lett. 33, 4 (1981)].
[19] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1689 (1979); Phys. Rev. B 22, 2099 (1980).