Binding energy of $1B_u$ singlet excitons in the one-dimensional extended Hubbard-Peierls model

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Using a symmetrized density-matrix renormalization-group formulation, we have investigated the electronic binding energy of the lowest optically allowed exciton ($1B_u$) within an extended Hubbard-Peierls model (with parameters U, V, and δ) for conjugated chains with $N=80$ sites. Three symmetries, the C_2, spin parity, and electron-hole symmetries, have been applied to construct the projector operator. Analysis of our results on the ratios between exciton binding energies and exciton energies, sheds light on the current experimental and theoretical controversy on exciton binding for polyacetylene and polyparaphenylene vinylene. We show that in the absence of dimerization, the exciton binding energy is vanishingly small for U/t up to 5 and V/t up to 2.3; for a finite dimerization, it is only when V is large enough that the exciton gets to be significantly bound. This result questions the applicability to conjugated polymers of the strong correlation picture, in which the exciton binding energy is equal to V. [S0163-1829(97)03623-0]

The role of electron correlation in conjugated polymers has long been a subject of intense scrutiny. It has been shown that electron correlation affects strongly the polymer geometry (mostly bond alternation),[1] excitation spectra,[2] and nonlinear optical response[3] and it is generally accepted that an exciton is mainly responsible for the low-lying photoexcitations. However, the location of the conduction-band edge and the exciton binding energy are still unclear from both experimental and theoretical standpoints. Early experimental estimates in polyacetylene (PA) led to $E_b \sim 0.1$ eV.[4] Recently, in the context of investigations on the remarkable photocurrent and luminescence properties of polyparaphenylene vinylene (PPV), the value of the exciton binding energy became a hotly debated issue. Not less than four models of binding have been proposed: (i) very weak binding (semiconductor band model), $E_b \sim 0.025$ eV;[5] (ii) weak to intermediate binding, $E_b = 0.2$ eV;[6] (iii) intermediate binding, $E_b \sim 0.4$ eV;[7-9] and (iv) very strong binding, $E_b \sim 1$ eV, with a theoretical explanation based on the strong correlation picture.[10] Earlier quantum-chemical calculations show that the exciton binding energy is extremely sensitive to both the level at which electron correlation effects are treated and the basis size, and usually provide too large a binding energy in comparison to experiment.[11,12]

In this work, we apply a symmetrized density-matrix renormalization-group (DMRG) theory to calculate the $1B_u$ single exciton energy and charge excitation band gap within an extended Hubbard-Peierls model for a wide range of pa-

rameters U, V, and δ. We present a thorough investigation of the $1B_u$ exciton binding energy behavior within a reasonable parameter space for the extended Hubbard-Peierls model; this model has been widely applied in studying electron correlation effects in conjugated polymers[1] (even though longer range terms, such as next-nearest-neighbor interactions, are neglected and might be important). It is of prime interest, however, to provide accurate results within the Hubbard-Peierls model and to analyze their implications in real polymeric materials; we hope in this way to shed some light on the binding-energy issue in conjugated polymers.

The DMRG technique has been developed by White, who showed that the RG scheme in the density-matrix representation is much more accurate than previous RG approaches.[13,14] Pang and Liang first applied the DMRG formulation to study the Hubbard-Peierls model and examined the correlation effect on the charge- and spin-density distributions for one-particle excitations.[15] Wen and Su studied the doping effect and concluded that the Hubbard U would not cause an insulator-metal transition.[16] We have recently developed a symmetrized DMRG theory which exploits C_2 symmetry, electron-hole symmetry J (which interchanges the creation and annihilation operators with appropriate phases), and spin parity P (spin-up-down symmetry),[17] to form a simple Abel group with eight elements. P can distinguish the even and odd spin states and excludes triplet states from the even parity excited space. The ground state lies in the ${}^eA^+$ space, i.e., even spin ($S=0,2,4,\dots$), symmetric for $C_2(A)$,

and covalent $(+)$; the optically allowed excited states lie in the $^eB^-$ space, i.e., singlet, antisymmetric for C_2, and ionic $(-)$.

We particularly stress the importance of electron-hole symmetry operation, which holds only at half filling. As has been shown previously,[17] the lowest singlet covalent B state (optically forbidden) lies well below the lowest singlet ionic B state that is of major interest with regard to optical properties. If this symmetry operation is not exploited, one always obtains the former state, in DMRG or in exact diagonalization, as the lowest B state, a feature which can cause much confusion.

In the DMRG calculation, the entire chain consists of four blocks, namely, a left part μ coupled with one new site σ, and their counterparts (μ' and σ') on the right-hand side generated by the C_2 operation. For the left block (for instance, starting from one or two sites), the symmetry operators can be transformed from Fock space to density-matrix eigenstate space, which is block diagonalized with respect to the number of particles and total S_z. The symmetry operations for a new site are defined as $J_i|0\rangle=|\times\rangle$, $J_i|\uparrow\rangle=(-1)^i|\uparrow\rangle$, $J_i|\downarrow\rangle=(-1)^i|\downarrow\rangle$, $J_i|\times\rangle=-|0\rangle$; $P_i|0\rangle=|0\rangle$, $P_i|\uparrow\rangle=|\downarrow\rangle$, $P_i|\downarrow\rangle=|\uparrow\rangle$, and $P_i|\times\rangle=-|0\rangle$ (where $|0\rangle$ represents an empty site and $|\times\rangle$ represents a doubly occupied site; site index i is relevant to the phase of e-h symmetry). Then, for the entire four-block system, the projection operator matrix for a given irreducible representation is formed by a direct product of the matrices of the four blocks by virtue of C_2 symmetry $[C_2|\mu\sigma\sigma'\mu'\rangle=(-1)^\gamma|\mu'\sigma'\sigma\mu\rangle$, $\gamma=(n_\mu+n_\sigma)(n_{\mu'}+n_{\sigma'})$, n is the number of particles in the block]. The linear dependencies of the symmetry adapted combinations are eliminated by a Gram-Schmidt orthonormalization. The symmetrized Hamiltonian is then diagonalized by Davidson's algorithm for the targeted states, these being the ground state, or low-lying singlet and triplet B_u and A_g excited states. The chain is built up to the length desired (in this case, $N=80$), which is referred to as an infinite DMRG. To refine the states obtained from the infinite DMRG procedure, we then apply the finite iteration approach to improve the environments of all the blocks. In this process, the C_2 symmetry is applied only at the last step of each iteration, namely, when the left and right blocks are equal in size. The improvement of accuracy brought by the finite scheme depends on the parameters in the Hamiltonian and the irreducible space. For instance, for more delocalized systems (i.e., small bond alternation δ or small Hubbard U), the improvement is better than in the case of larger δ or U. The finite-scheme iterations are also found to be more important for the description of the $^eB^-$ space than for the $^eA^+$ space. It is important to point out that in our RG scheme, the symmetry adaptation is applied at every iteration step, so that the density matrix whose eigenstates are used for renormalization always comes from the targeted state (ground state or excited state).

To study the exciton binding, we have included the nearest-neighbor density-density repulsion V term, which is the origin of attraction between electron and hole. As has been pointed out before, this term represents a physics that is different from that of the Hubbard model in terms of the excitation spectra.[18] Generally speaking, the long-range character of the Coulomb interaction is important in describing

exciton binding. It is known that the DMRG works extremely well for short-range potentials;[13,14] however, for long-range potentials, convergence is not guaranteed, which can lead to poorer accuracy, especially for long-chain systems. This is the reason why we chose to keep the nearest-neighbor density repulsion term in our model Hamiltonian. The importance of the bond alternation parameter (δ) has been emphasized by Soos, Ramasesha, and Galvão;[19] it provides the simplest way to incorporate the chemical structure in a model study [for instance, δ can induce a $2A/1B$ crossover, i.e., for $\delta<(>)\delta_c$, $E(2A)<(>)E(1B)$ where δ_c is a critical value[20]]. In this context, the extended Hubbard-Peierls model is defined by

$$H = -t\sum_{i,\sigma}[1+(-1)^i\delta](c_{i\sigma}^+c_{i+1\sigma}+\text{H.c.})+U\sum_i n_{i\uparrow}n_{i\downarrow}$$
$$+V\sum_i(n_i-1)(n_{i+1}-1), \tag{1}$$

where t is the hopping integral which is taken to be unity $(t=1)$; δ is the dimensionless bond alternation parameter, U is the Hubbard on-site repulsion, and V is the nearest-neighbor interaction. Note that the condition for occurrence of the spin-density-wave (SDW) or bond-order-wave (BOW) phases is $U>2V$.[1]

Pang and Liang have calculated the charge excitation gap for the Hubbard-Peierls model, which is defined as $E_g=E(N-1)+E(N+1)-2E(N)$.[15] We stress that this is not the optical gap in the extended Hubbard-Peierls model, since this definition excludes the contribution due to Coulomb attraction between electron and hole. Instead, this quantity becomes our definition for the charge excitation band gap which constitutes the continuum edge. Thus, the exciton binding energy is defined as $E_b=E_g-E(1B_u)$. Strictly, this definition is only valid for an infinite chain; for a finite chain, the error is on the order of $1/N$. We note that the finite-size effect for E_g is smaller than for $E(1B_u)$, because $1B_u$ represents two charge carriers on a single chain, while for calculating E_g, there is only one additional charge; the chain ends have then a smaller effect. As a result, for the Hubbard model where E_b is known to be zero, E_b as calculated from the DMRG will be slightly negative and of the order of $1/N$. As noted previously, the covalent singlet $1B$ state lies well below the optically allowed ionic $1B$ state; thus, the binding energy of the former is much larger than that of the latter. Here, we only discuss the ionic $1B$ state.

We have demonstrated the high accuracy of the symmetrized DMRG scheme in calculating the $1B_u$ state for long-chain systems.[17] The DMRG results are to be regarded as nearly exact for the ground state and a few excited states, such as the lowest-lying triplet states and single B_u and A_g excited states.[20] The accuracy of the calculations is manifested in the following ways: (i) the energy of the target state converges with respect to increasing the dimension (the cutoff) of the truncated density-matrix eigenstates; and (ii) the difference tends to vanish (around 10^{-5}) between 1 (exact value) and the sum of the eigenvalues of the truncated density matrix. This is a natural way to track the precision of a DMRG calculation, as suggested by White.[13,14] Note that in calculating $E(N\pm1)$, we do not apply any symmetry opera-
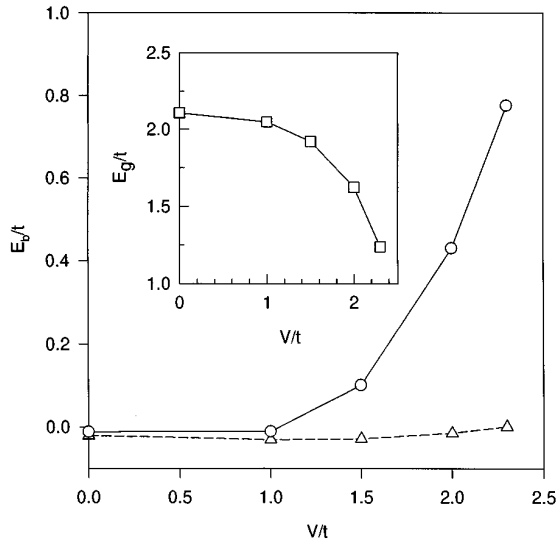
FIG. 1. Dependence of the $1B_u$ binding energy E_b on V/t for $U/t=5$. Circles represent $\delta=0.2$ and triangles $\delta=0.0$. The inset shows the dependence of band gap E_g on V/t for $\delta=0.0$.
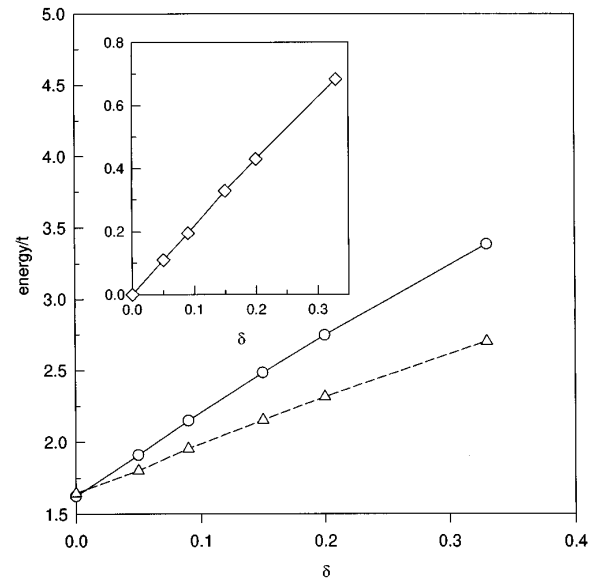

FIG. 2. Dependence of band gap (circles) and $1B_u$ exciton energy (triangles) on alternation δ for $U/t=5$, $V/t=2$. The inset shows their difference, i.e., $E_b=E_g-E(1B_u)$, as a function of δ.

tion. The DMRG cutoff is taken to be $m=100$; since the DMRG is more accurate for stronger correlation, in the case of smaller U values, we set $m=150$ for the $^eB^-$ space in order to have comparable accuracy. The precision on the state energy is poorer for the $^eB^-$ space (10^{-3}) than the $^eA^+$ state space $(\sim10^{-5})$. The accuracy is, however, high enough to give a definite answer concerning the exciton binding energy, which contains an intrinsic error of $1/N$.

The main results of our study are summarized below:

(1) For $V=0$, as expected for the Hubbard-Peierls model, the binding energy E_b is always calculated to be a small negative quantity $O(1/N)$ for any U and δ. This agreement with the physical picture actually serves as a double check for our numerical scheme.

(2) For $\delta=0$ and for fixed $U(=5)$, V does not induce any binding in the SDW/BOW phase $(V<U/2)$. V lowers both the band gap and the $1B_u$ exciton energy, see Fig. 1. The V term is the origin of exciton binding. However, V also increases electron delocalization by largely renormalizing the t term; this eventually increases the electron-hole separation which is largest for $\delta=0$. This result questions the applicability of strong correlation arguments stating that the $1B_u$ exciton binding energy is equal to V.[18]

(3) For fixed electron interaction strength, E_b increases when increasing δ (Fig. 2). This implies that the larger the δ value, the more excitoniclike the lowest charge excitation.

(4) For fixed δ (e.g., 0.2), small V values hardly enhance E_b; however, a larger V strongly enhances E_b (see Fig. 1). We note that the exciton is bound only when V is large enough relative to U.

To relate our results with experimental findings, we present in Table I, the DMRG results for the $1B_u$ exciton state and binding energies for three sets of correlation strengths and bond alternation parameters. The alternation parameter for PA is 0.07 according to its bond-length alternation. Soos $et~al.$ have proposed an effective parameter $\delta=0.2$ for systems containing phenylene rings.[21] We note that PPV can actually be considered as a regular copolymer of polyparaphenylene and PA;[22] thus, we consider the effec-

tive bond alternation for PPV to be within the range 0.15–0.2. Note that V/U is fixed at 0.4 in Table I, i.e., a relatively large nearest-neighbor interaction strength for shorter-range interaction (smaller V/U value), the binding energy is smaller than those in Table I. In a one-dimensional correlated system, it has been shown that the $1B_u$ state is nearly responsible for the whole oscillator strength of the lower-lying excitations, while the continuum band state hardly shows up in the linear absorption spectrum;[18] as a result, we take the optical-absorption data to set the $1B_u$ state energy: 1.8 eV for PA and 2.4 eV for PPV. We then obtain the t values for different (U,V)'s using these experimental energies;[23] namely, the bare t is evaluated as $E^{exp}(1B_u)/E^{theo(t=1)}(1B_u)$, which is in the range of 1–2 eV for the parameters in Table I. The binding energies obtained in this way are also reported in the same Table. Given the uncertainty in t value, Table I provides accurate $relative$ values between the exciton state energy and its binding energy.

TABLE I. $1B_u$ exciton binding energies and, in parentheses, $1B_u$ state energy (for $t=1$); V/U is fixed at 0.4. If we take the experimental $1B_u$ energy values for PA ($\delta=0.07$) and PPV ($\delta=0.15$–0.2), then the E_b values can be scaled in absolute units (eV) and are given underlined.

δ	U	
	3	5
0.07	0.042	0.149
	(0.947)	(1.879)
	0.080	0.143
0.15	0.123	0.328
	(1.327)	(2.152)
	0.222	0.366
0.20	0.18	0.430
	(1.54)	(2.312)
	0.28	0.446

We stress that these theoretical $E_b/E(1B_u)$ ratio can help in clarifying the controversy on the exciton binding energy. In fact, the usefulness of such a comparison between the theoretical results with experimental data has been pointed out earlier.[10]

For PA, we noted above that previous quantum-chemical calculations yield a range of huge E_b values, while the experimental estimate corresponds to an E_b value as small as about 0.1 eV.[4] Our results are fully consistent with this experimental estimate, within the whole range of parameters given in Table I, even under strong correlation strength. Namely, the theoretical ratio $E_b/E(1B_u)$ is in good agreement with experiment, regardless of the t value chosen. It is interesting to mention that we also performed a single CI calculation for Hamiltonian (1), an approach which is widely used in exciton theory;[10–12,24] we then find E_b to be 0.6 eV for $\delta = 0.07$, $U = 5$, and $V = 2$ (the $1B_u$ state energy again taken to be at 1.8 eV). This E_b value is notably much larger than the DMRG value, which questions the accuracy of previous single CI-based theoretical calculations.

For PPV, our results, namely, the ratios $E_b/E(1B_u)$ are in agreement with the experimental findings by Campbell *et al.*,[6] Friend, Bradley, and Townsend[7] and Kersting *et al.*,[8] as well as the results of the phenomenological calculations by Gomes da Costa and Conwell.[9] We find a weak to intermediate binding energy even when we use strong correlation parameters; the latter is in contradiction to the results provided by the results provid-

ing strong binding, based on a single CI approach[10] (which thus appears as too crude an approximation).

We note that incorporation of lattice relaxation effects would not lead to an increase in binding energy:[25] from quantum-chemical extensive CI calculations, the lattice relaxation of the $1B_u$ state is found to be comparable to the sum of those of the anion and cation (negative and positive polarons). Among other effects neglected in the present study, are interchain interactions and intrachain long-range interactions. These effects deserve further investigations.

To conclude, we have performed DMRG calculations on an extended Hubbard-Peierls model. We have presented the dependence of exciton binding energy both on alternation δ and nearest-neighbor interaction V. Our results provide reliable values for the ratio of $E_b/E(1B_u)$ in PA and support the experimental findings that the exciton binding energy in PPV occurs in the weak-to-intermediate range (0.2–0.45 eV).

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