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Symmetrized density matrix renormalization group studies of the properties of low-lying states of the poly-para-phenylene system

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We report the symmetrized density matrix renormalization group (DMRG) study of neutral and doped oligomers of poly-para-phenylene (PPP) system within an extended Hubbard model. Model parameters are determined by comparing the existing results for an interacting small system. We compute a number of properties in the ground state as well as in the one-photon, two-photon and triplet states to completely characterize these states. Bond-order studies show that the lowest two-photon state corresponds to a localized excitation while one-photon and triplet excitations are extended in nature. The bipolaronic state shows clear evidence for charge separation and disproportionation into two polarons. We find that the extended nature of one-photon and triplet states of the neutral system are very similar to those of the bipolaronic ground states. © 1997 American Institute of Physics. [S0021-9606(97)50622-2]

I. INTRODUCTION

Electronic structure of conjugated organic polymers has been a field of enduring interest from both experimental and theoretical standpoints. The insulating behaviour of these systems coupled with different topologies in which they exist has opened up the possibility of a vast variety of qualitatively different excited states. In systems with degenerate ground states, we could have solitonic excitations besides the polaronic or bipolaronic excitations of doped systems.¹ These excitations are primarily a consequence of electron–lattice interactions. The insulating nature of the polymers implies fairly long-range electron–electron interactions. In neutral systems, this leads to the possibility of excitonic, biexcitonic or indeed exciton-stringlike excitations.² Besides, these low-lying excitations also have spin degrees of freedom leading to their classification as singlets, triplets, etc. The excitations can further be labelled by the symmetry label of the irreducible representation according to which a given state transforms. The inter-play of electron–lattice and electron–electron interactions leads to complicated yet very interesting and important physical situations.

The polymers that have attracted much attention in recent years are the poly-para-phenylene-vinylene (PPV) and poly-para-phenylene (PPP) systems. Both these polymers have the *para* position of the phenyl rings in conjugation. It was suggested earlier by Soos *et al.*³ that such a system can be mapped onto a strongly dimerized polyacetylene chain and a set of isolated ethylenic units, in the noninteracting limit. Due to the strong dimerization introduced by the transformation, it is also suggested that the electronic excitations in the presence of correlations would be more like that of a noninteracting system. This has very strong implications for

the fluorescence properties of these polymers. In the noninteracting picture, the lowest singlet excitation is dipole allowed and in these cases we should expect strong fluorescence since from Kasha's rule⁴ it is known that fluorescence occurs from the lowest singlet state. However, in polymers such as polyacetylene (PA) the lowest excited state is a dipole forbidden state⁵ since the dominant effect of electron correlation is not suppressed by the moderate dimerization in these systems. The lowest excited singlet state being dipole forbidden in the ideal limit, we should expect weak fluorescence. This brings into focus the symmetry of the low-lying excitations in these polymers.

Electronic energy levels of doped polymers are also of considerable interest, since polymers are envisaged as active components in light emitting diodes (LEDs). The polymers which have been identified as luminescent semiconductors thus far include PPP, poly-para-phenylene-vinylene (PPV), polythiophene and their derivatives.⁶ To tailor the properties of polymers for such applications, it is necessary to understand the doped states in these systems that lie below the conduction band. Many different experimental techniques have been employed to study these “in-gap” states. They are photoinduced absorption (PA),^{7–9} photoconductivity (PC) measurements,¹⁰ electroluminescence (EL)¹¹ and photoluminescence (PL),^{2,12} to name a few. These studies have often been carried out using pump-probe techniques to elicit the dynamics and decay of the electronic excited states.¹³

Theoretical studies of conjugated polymers have been approached from two different standpoints. In one approach, quantum cell models such as the Pariser–Parr–Pople model with static electron–lattice interactions have been studied employing mainly exact diagonalization techniques for small system sizes. The study of large system sizes has not been quite satisfactory in any of the approaches to these models, until recently. However, the advantage of model Hamiltonian

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studies is that they allow exploring the parameter space freely to elicit information in different limits of the models.

The second approach has been pioneered by quantum chemists who employ empirical Hamiltonians such as those obtained from intermediate neglect of differential overlap (INDO) approximation.¹⁴ Using such Hamiltonians, oligomers of several units are studied within the framework of a Hartree–Fock solution followed by limited configuration interaction (CI) calculations.¹⁵ The issues that are addressed in these studies revolve around the optimal geometries of molecules, effects of derivatization of monomers and to a limited extent the spectroscopic characteristics of the system.¹⁶ The main advantage of these calculations over the quantum lattice models is that we can study systems with rather large unit cells within a realistic approach but rather poorly (when only single or double CI are performed) for excited state properties, although the ground state properties such as geometries are known to be predicted quite accurately by these methods.

In recent years, the density matrix renormalization group (DMRG) method has been successful in providing accurate solutions to model Hamiltonians with short-range interactions in low dimensions.¹⁷ Inclusion of symmetry in the DMRG procedure has further allowed access to excited states.¹⁸ The minimal model that can support an excitonic state is the ‘‘U-V’’ model. Reliable solutions of quantum cell models for excited states can clarify the physics of various kinds of ‘‘in-gap’’ excitations. In this paper, we have placed emphasis on the nature of the excitations and relative positions of the excitations rather than on comparison between theory and experiment. The absolute comparisons are made difficult by the substituent groups in the actual system, and furthermore the ‘‘U-V’’ model parametrization is not likely to include the effective long-range interactions that are present in the actual system. We employ the DMRG technique to study the low-lying excitations in the PPP system within the ‘‘U-V’’ model in the neutral state and with both electron and hole doping. In Fig. 1 is shown the schematic diagram of the left-half of the PPP system we have studied. We follow the labelling of the sites and bonds as given in Figs. 1(a) and 1(b), respectively. In Section II, we introduce modification to the usual DMRG procedure.¹⁷ This is followed by Section III, Results and Discussion. Section IV summarizes the contents of the paper.

II. SYMMETRIZED DMRG METHOD FOR PPP SYSTEM

All the carbon sites in the PPP system are taken to be identical and this idealized situation leads to alternancy symmetry in the system. Besides, this system possesses reflection or C_2 symmetry about the central bond of the polymer in the planar geometry. The ‘‘U-V’’ Hamiltonian, which is used to model the electronic states, is spin independent and hence conserves both S_{total}^z and S_{total} . We employ only parity which bifurcates the Hilbert space into space of even and odd total spins.¹⁹ These three symmetries (alternancy, C_2 or reflection and parity) commute with each other resulting in an Abelian group consisting of eight elements and the eight

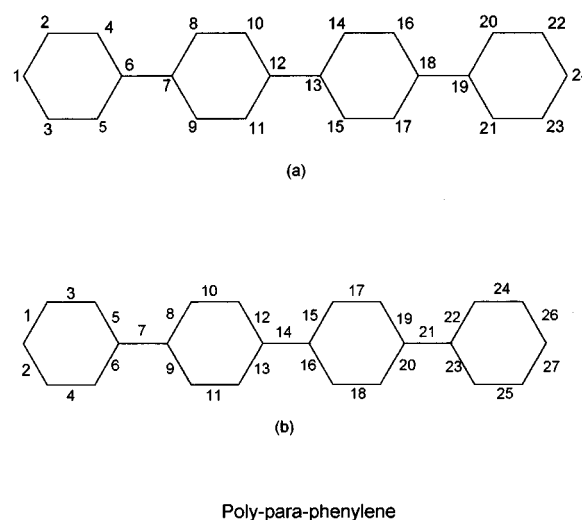


FIG. 1. Schematic diagram of the left half of poly-para-phenylene (PPP) system we have studied. The right half is related by C_2 symmetry. The numbers in (a) and (b) correspond to the site indices and bond indices, respectively. The middle bond is not shown in the figures.

irreducible representations that exist can be labelled by the indices A/B, $+/-$ and o/e corresponding to reflection, alternancy and parity symmetries. The ground state of the singlet for the neutral polymer exists in the $^eA^+$ subspace corresponding to the even spin, ‘‘covalent’’ - A subspace. The first dipole allowed transition is from the ground state to the lowest energy state in $^eB^-$ subspace corresponding to even spin ‘‘ionic’’ B space. The lowest triplet state is to be found in $^oB^+$ subspace. Doping the system leads to breaking of alternancy symmetry and doped states are characterized by total spin, z component of total spin and A/B label. In the symmetrized DMRG procedure, we have taken care to carry out the calculation of the lowest state in each subspace, before identifying the ground state and the excitations.

The oligomers of PPP are constructed starting from a four site initial system. Fig. 2 shows the manner in which the sites are added on the left and right parts of the system to build up the PPP oligomers. The system evolves from the external carbon atoms of the chosen oligomers (Fig. 2) and the carbon sites are progressively introduced in the middle.

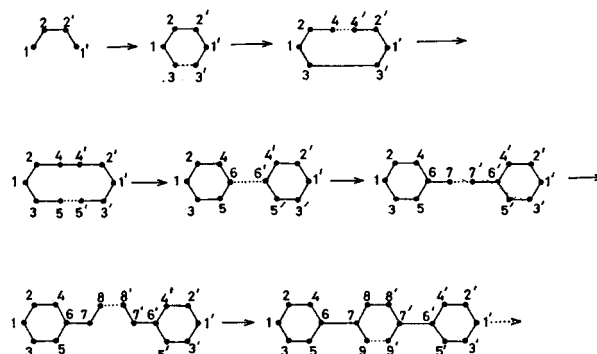


FIG. 2. Schematic diagram of the building up of PPP oligomers by the DMRG method.

TABLE I. Comparison of excitation gaps of DMRG calculation (with cut-off parameter $m=120$) with exact calculation for biphenyl. The intersite electron–electron interaction parameter, V , is 4.5 eV. All the energies are in eV, ΔE_{ST} corresponds to lowest spin gap. The one-photon gap from exact Pariser–Parr–Pople calculation is 4.8814 eV.

Method	One-photon gap	Two-photon gap	ΔE_{ST}
Exact	4.8490	3.3752	2.3665
DMRG	4.8857	3.1301	2.4394

This procedure is very accurate compared to the procedure that builds the oligomer starting from the middle of the total system. This is because, in the latter, we have to rebuild the central bonds each time and the repeated renormalization of the operators at this site reduces the accuracy of the procedure. Besides, the inside-out procedure does not introduce interactions between the new sites and thus the density matrix of the half-blocks are not good representatives of the density matrix of the half-block of the complete oligomer. The order in which the sites are introduced also avoids interaction between sites that are introduced several iterations apart. In our scheme, a newly added site interacts atmost with a site introduced two iterations previously. This procedure should therefore be as accurate as a quasi-one-dimensional system with nearest and next nearest neighbour interactions or the ladder systems.²⁰ This process of construction retains the symmetries of the full Hamiltonian at every stage and hence we can target the lowest state in the desired subspace at each iteration. The symmetrized DMRG procedure is implemented along the lines described in an earlier paper.¹⁸

The geometry of phenyl groups in PPP are taken to be of equal bond lengths (corresponding to the value of 1.397 Å in benzene) with uniform transfer integrals $t_0=2.4$ eV. The inter phenyl bonds have a transfer integral of 2.077 eV corresponding to a bond length of 1.508 Å, the system is however taken to be planar; i.e, the dihedral angle between successive phenyl rings is taken to be zero. The U and V parameters are chosen such as to reproduce the Pariser–Parr–Pople values with standard parameters biphenyl for the optical gap. These correspond to $U=11.26$ eV and $V=4.5$ eV. In Table I we compare the exact excitation energies for biphenyl with standard Pariser–Parr–Pople parameters with those of the “U-V” model. We also compare, in this table, the excitation energies from the DMRG procedure for the “U-V” model.

While the chosen U and V parameters well reproduce the one-photon gap from exact Pariser–Parr–Pople calculations of biphenyl, the lowest two-photon gap (3.13 eV) and the lowest singlet-triplet gap (2.44 eV) from the “U-V” model are well below the exact Pariser–Parr–Pople values (4.08 eV and 2.84 eV respectively). This shows that the two-parameter “U-V” model cannot yield all the excitations of the longer range models simultaneously. The smaller than exact Pariser–Parr–Pople values of the two-photon gap and singlet-triplet gap found in the “U-V” model consequently points to stronger correlations than found in the actual mol-

TABLE II. Comparison of energies from DMRG calculations with cut-off $m=120$ with exact calculation for the noninteracting models of eight monomers of the PPP system.

Doping	Hückel	DMRG
0	−158.518	−158.664
+1	−157.272	−156.996
−1	−157.272	−156.432
+2	−156.026	−155.394
−2	−156.026	−155.334

ecule. The choice of our parameters affects the magnitude of the relative gaps, but still retains the ordering of the energy levels found from exact Pariser–Parr–Pople calculations. The qualitative nature of the low-lying excitations is also not likely to be affected by a more strongly correlated parameter set.

Comparisons in Table I also show that the DMRG method is accurate for small systems. For large systems, confidence in the DMRG method can be gained by comparing the DMRG results for the noninteracting system ($U=V=0$) with exact noninteracting results. When the interactions are turned off, the models are exactly solvable by one-electron methods for the largest system sizes we have addressed. We compare the results from the one-electron method with the DMRG results for the noninteracting models of the PPP system for various dopings for the largest system size we have studied, for a DMRG cut-off of $m=120$. The quantities we compare are energies (Table II) and bond orders for the ground states as well as doped states of the longest oligomer of PPP we have studied for different dopings (Figs. 3–4). We find the comparison between DMRG and exact results to be excellent in the noninteracting limit, where DMRG has the least accuracy.²¹ The positive and negative bipolarons in the noninteracting limit are degenerate as is to be expected. This should also be true in the case

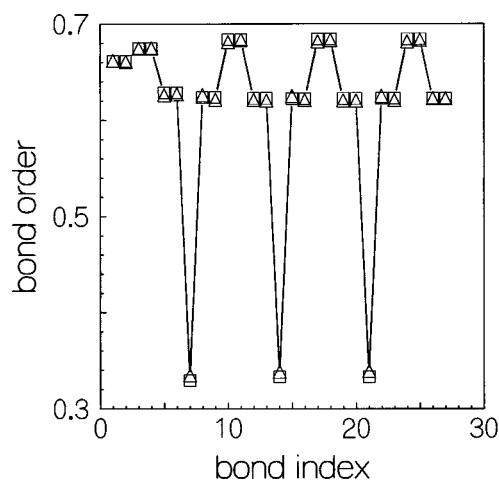


FIG. 3. Comparison of bond orders for neutral PPP system corresponding to the longest system size we have studied, from Hückel and DMRG calculations. Squares represent exact and triangles represent DMRG calculations. The bond index is as shown in Fig. 1(b).

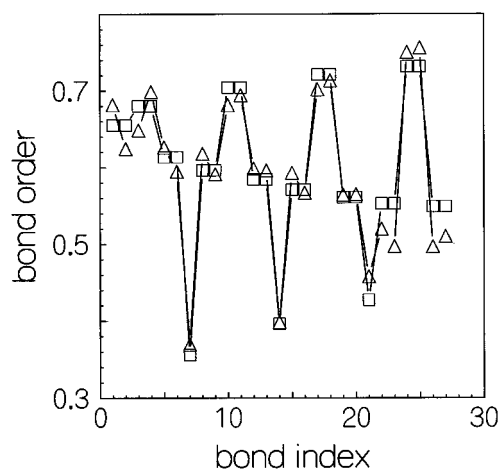


FIG. 4. Comparison of bond orders for positive bipolaron of PPP system corresponding to the longest system size we have studied, from Hückel and DMRG calculations. Squares represent exact and triangles represent DMRG calculations.

of positive and negative polarons, but is not. Interestingly, the small discrepancy can be traced to the fact that the ground state of the negative polaron switches from ‘A’ space to ‘B’ space on going from even number of rings to odd number of rings in the PPP system. While this has been incorporated in targeting the ground state of the negative polaron, we have not checked for the space in which the ground state is found at intermediate stages of the DMRG iterations when the “molecule” is not an oligomer of PPP. Thus, the difference in the energies between the positive and negative polarons reflects upon the accuracy of the DMRG schemes. Because of the desired accuracy of the infinite DMRG procedure we have chosen not to carry out the finite DMRG procedure which is very computer intensive for the cut-off m that we have imposed.^{17,22}

III. RESULTS AND DISCUSSION

We have carried out “U-V” model calculations of PPP systems with up to eight phenyl rings, for neutral as well as hole and electron doped cases. We have obtained energies and bond-orders of ground state and also for a few low-lying excited states. Besides, we have computed charge and spin densities, charge-charge and spin-spin correlation functions.

We have plotted the change in energy in the ground state for the PPP system in going from an $(n-1)$ ring system to an n ring system in Fig. 5. We find that there is a clear *even-odd* pattern in the ground state energy per ring. Addition of a phenyl ring to an even ring PPP oligomer stabilizes the polymer by a slightly greater extent than when a phenyl ring is added to an odd ring system. This difference should vanish when we go to a system with a very large number of rings. The above result shows that the finite size effect is persistent even for an 8-ring oligomer, although the magnitude of the effect itself is rather small. The difference

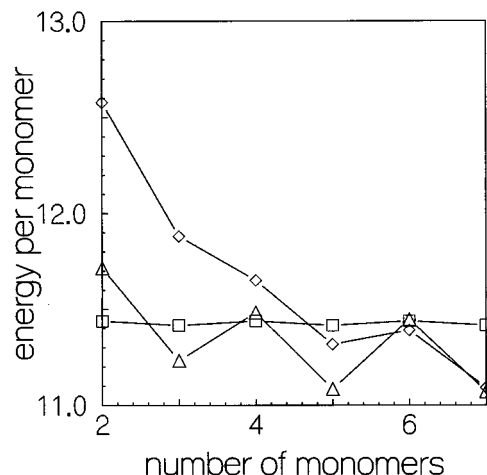


FIG. 5. Change in energy (eV) per monomer vs. number of monomer units for PPP: neutral (squares), polaronic (triangles) and bipolaronic (diamonds) systems.

in energy per ring when a ring is added to an even system as opposed to a ring added to an odd system is 0.024 eV, while the average energy per ring is -11.428 eV.

In Fig. 6, we present excitation energies for the one-photon, two-photon and lowest triplet excitation for the oligomers of PPP. The optical (one-photon) gap shows a sharp drop in going from the dimer to the oligomers and for the long oligomers lies between the values for the 8-ring system (4.67 eV) and for the 7-ring system (4.45 eV). The slight upward trend in the optical gap of the system appears to be an artifact of the DMRG procedure and a larger m value in the truncation could lead to saturation in the gap. This effect is more prominent in the optical gap as the optical excitation is to an extended state. The two-photon gap is slightly more than 1 eV below the optical gap. The two-photon gap also shows finite size effects although it is less pronounced than that in the one-photon gap. We will demonstrate later that the two-photon excitation is a localized excitation. The singlet-

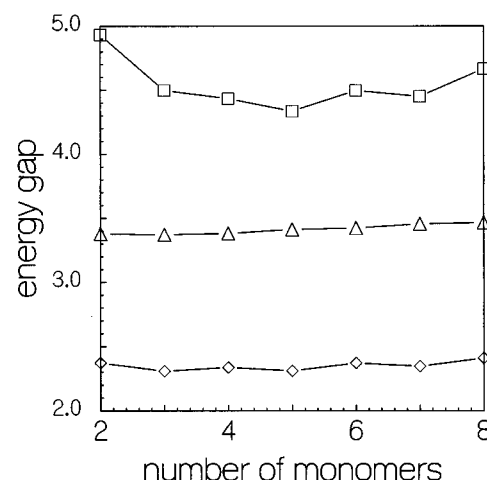


FIG. 6. Energy gaps (eV) for $1^1A_g^+ \rightarrow 1^1B_u^-$ (squares), $1^1A_g^+ \rightarrow 2^1A_g^+$ (triangles) and $1^1A_g^+ \rightarrow 1^3B_u^+$ (diamonds) excitations for PPP system.

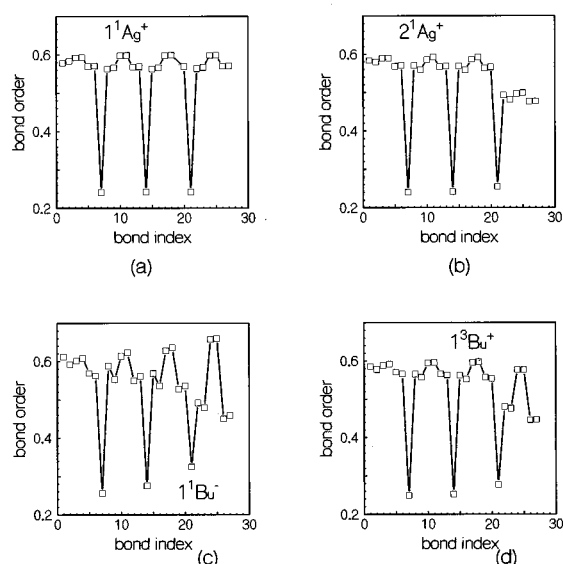


FIG. 7. Bond orders for (a) $1^1A_g^+$, (b) $2^1A_g^+$, (c) $1^1B_u^-$, and (d) $1^3B_u^+$ states of PPP. Bond index corresponds to numbering given in Fig. 1(b).

triplet gap is at an energy of ~ 2.4 eV, which is 2 eV below the optical gap and this gap shows the least finite size effects amongst the excitation gaps we have studied.

We find from our studies that the one-photon gap is always above the two-photon gap in the PPP system. This is contrary to the excitation from the mapping of the system to a strongly dimerized chain in the noninteracting limit.³ The one-photon gap from our calculations is almost saturating at 4.56 ± 0.11 eV, while the two-photon gap is saturating at 3.4 eV. The stronger correlations reflected by the choice of our parameters can account for about 0.9 eV in the difference between the one-photon and two-photon gaps. Still, this places the two-photon state ~ 0.25 eV below the lowest one-photon state. However, the difference is sufficiently small and interchain interactions in the solid state would stabilize the *ionic* $1^1B_u^-$ state relative to the *covalent* $2^1A_g^+$ state. This could lead to the $1^1B_u^-$ state being the lowest singlet excited state in the system. This would then explain the strong fluorescence in the PPP system.

In real systems, we would encounter both nonplanarity and broken electron-hole and reflection symmetries. Nonplanarity introduces a blue shift in the optical absorption due to reduced delocalization and shifts in the $2^1A_g^+$ state is largely unaffected as it is a localized state, even in the planar system. Breaking electron-hole and reflection symmetries leads to nonzero oscillator strength to the state derived from the $2^1A_g^+$ state, resulting in moderate fluorescence.

The ground state, the lowest one-photon, two-photon and triplet states show very interesting bond-order patterns. In Fig. 7, we present these data for the 8-ring oligomer. In the ground state, the intra-ring bonds are very nearly identical and the magnitude of the bond-order is close to that of an isolated benzene ring. The inter-ring bond is very weak and has a bond-order of 0.24 and nearly the same for all the inter-ring bonds.

The bond-orders in the lowest one-photon state show very interesting variations. Towards the ends of the oligomer, the rings are benzenelike while as we move to the interior, the rings acquire quinonoidal characteristics. The inter-ring bonds progressively strengthen as we move towards the interior of the oligomer. The bond-order pattern in the lowest two-photon state is qualitatively different from that of the $1^1B_u^-$ state. In this case the rings in the exterior of the molecule are benzenelike and the inter-phenyl bonds in this region have very weak double bond character. In this region, the bond-orders resemble the bond-orders in the ground state. However, in the interior ring, the intra-ring bond-orders although nearly uniform, have a value smaller than that in the exterior. This shows that the excitation is mainly confined to the interior two-rings in the full system. The lowest triplet state shows a strengthening of the inter-ring bond as we move towards the center of the molecule. Furthermore, the bonds involving the carbons at the para position become weaker in the interior rings while those between the ortho and meta carbons become stronger. This supports a quinonoidal structure in the interior of the PPP system, while away from the center the rings tend to be more benzenelike with the inter-ring bonds having rather weak double bond character in this region.

The strong similarity in the bond-order patterns of the lowest triplet and the lowest $1^1B_u^-$ state allows us to visualize the excitations as spread out over the entire oligomer with the quinonoidal character strengthening as we move towards the interior. However, the $2^1A_g^+$ state has a distinctly different characteristic and appears to be a strongly localized excitation, with the excitation essentially confined to two middle rings of the 8-ring oligomer. We would expect this difference between the $2^1A_g^+$ state, the $1^1B_u^-$ state and the $1^3B_u^+$ states to increase when the range of interactions are extended beyond the nearest neighbour. This is because, the extended range interactions allow for stability of structures in which charges are far apart. Such resonance structures have very strong quinonoidal character. The local char-

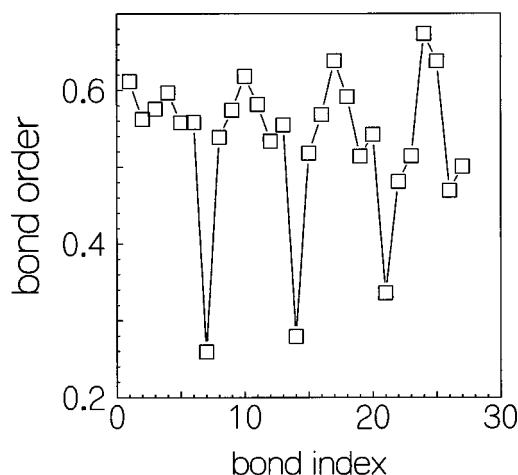


FIG. 8. Bond orders for singly doped PPP system. Bond index corresponds to the numbering given in Fig. 1(b).

acter of the $2^1A_g^+$ state shows that introducing nonplanarity in the system will not shift the two-photon gap significantly. Thus, we should expect the nonplanar PPP system to fluoresce more weakly than the planar modification.

The study of the doped states of the system is important as it is conjectured that the excitations decay to give rise to charged segments. The photoinduced absorption corresponds to excitations from these charged segments. We have shown in Fig. 5 the energy per additional ring for one and two doped charges. We find that the finite size effect is more pronounced in doped systems than in the undoped systems. However, the change in energy for addition of a ring is almost the same as in the polaronic and bipolaronic systems and is very close to the value in the undoped system. The DMRG procedure conserves electron-hole symmetry of the Hamiltonian as observed from the difference in total energies between the oppositely charged species, which corresponds to nU , where n is the number of doped charges in the system.

Since the ground state of the positively charged polarons is targeted with greater accuracy, we concentrate on the properties of the positive polarons. The properties of the negative polarons are related to that of the positive polarons

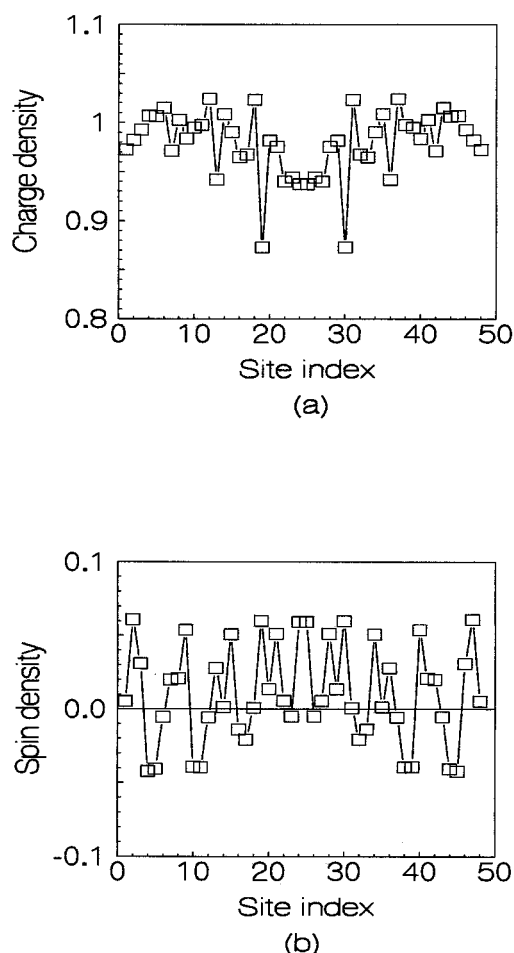


FIG. 9. (a) Charge density and (b) spin densities for singly doped PPP system.

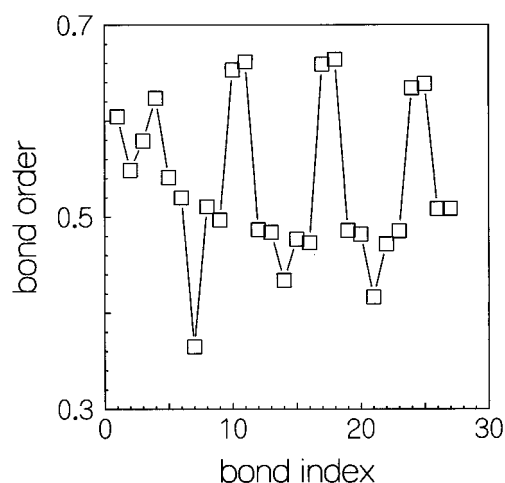


FIG. 10. Bond orders for doubly doped PPP system. Bond index corresponds to the numbering given in Fig. 1(b).

by electron-hole symmetry. The bond orders of the polaron are shown in Fig. 8. The polaron shows slightly pronounced quinonoidal character in the middle of the PPP system, the inter-ring bonds having acquired strong double bond character in the interior. The charge density distribution of the polaron shows [Fig. 9(a)] slight localization in the interior rings. This is consistent with the bond order studies (Fig. 8). The spin density variations of the polarons [Fig. 9(b)] are more towards the ends of the system, consistent with the charge density and bond order data.

The bond order patterns of the bipolarons is shown in Fig. 10. The terminal rings are benzenoid in character while the interior rings have quinonoidal character. This pattern is very similar to the bond order pattern in the $1^1B_u^-$ and the $1^3B_u^+$ states. The charge density distributions (Fig. 11) also show that the excess charge is almost exclusively found at the ends of the system with the interior rings being almost neutral.

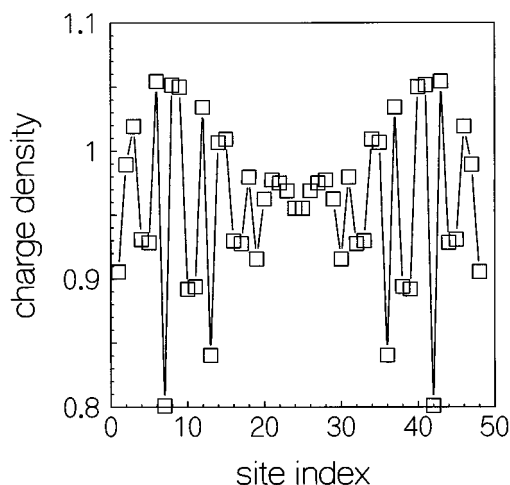


FIG. 11. Charge densities for doubly doped PPP system. Site index corresponds to the numbering given in Fig. 1(a).

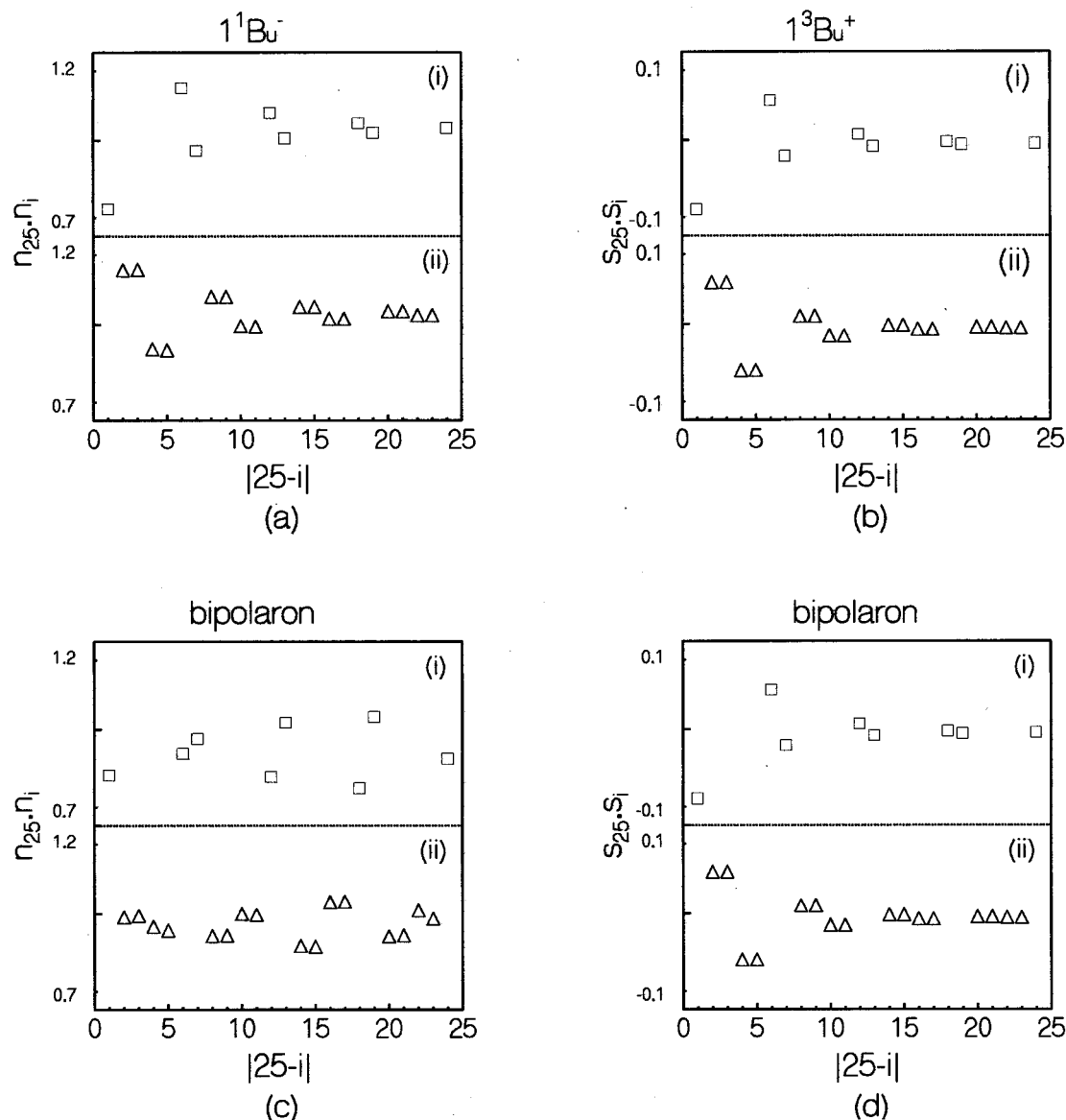


FIG. 12. Charge-charge correlation functions of PPP system for (a) $1^1B_u^-$ state and (c) bipolaron and spin-spin correlation functions for (b) $1^3B_u^+$ and (d) bipolaron. In all the four figures, upper panel corresponds to the correlation of newly added site of the right block with all the para-position sites of the left block while bottom panel corresponds to the correlation of newly added site of the right block with all the ortho- and meta-position sites of the left block.

It is possible to view the bipolarons, $1^1B_u^-$ and $1^3B_u^+$ states—as similar excitations. In the bipolaronic case we can look at the excess charge as being confined to the ends of the chain and the system as being quinonoidal in the interior. The triplet state can be viewed as the unpaired electrons being confined to the ends of the system with the interior rings being quinonoidal. The $1^1B_u^-$ excited state can be viewed as an electron and a hole confined to the ends of the chain with the interior of the system again being quinonoidal.

The most convincing evidence for similarities among bipolaronic ground state and $1^1B_u^-$ and $1^3B_u^+$ excited states of the neutral system comes from comparison of the appropriate correlation functions. The inter-site correlations we have studied are between the 24' [the last site added in the DMRG

procedure for the 8 ring system on the right-half (Fig. 12)], which is at the para-position and the para-position sites of all the rings on the left (shown in upper panels of all the figures) on the one hand and the inter-site correlations between site 24' and the ortho- and meta-position sites of the left-half of the system on the other hand (bottom panels in all the figures). The successive pairs of sites (e.g., 2 and 3, 4 and 5, etc.) are both ortho- or both meta- position sites located on the top and bottom half of the PPP system.

In Fig. 12(a) we show the charge-charge correlation function for the dipole-allowed states ($1^1B_u^-$) and in Fig. 12(b) is shown the spin-spin correlation function for the triplet state. There is a dramatic similarity between the charge-charge correlation function of the $1^1B_u^-$ and spin-spin correlations of the $1^3B_u^+$ state. These excited states can

be viewed as the charge and spin counterparts of each other. The bipolarons also show strong charge–charge correlations [Fig. 12(c)] for sites between which charge–charge correlations of the $1^1B_u^-$ states are strong. However, the excess charges in the bipolarons are more localized towards the ends of the system and hence the charge–charge correlations build up towards the exterior of the system starting from the middle. In the $1^1B_u^-$ state, the correlation function dies down towards the exterior. If we were to deal within a periodic boundary condition, this distribution would have vanished. This is indeed reflected in the similarity between the spin–spin correlation function [Fig. 12(d)] of the $1^3B_u^+$ state and those of the bipolarons. The total picture that emerges from the comparisons of spin–spin and charge–charge correlations of these four states shows that these states are indeed very similar. Experimentally, this similarity should manifest as comparable Stokes shifts in the fluorescence/phosphorescence from these states.

IV. SUMMARY

To conclude, we have carried out DMRG studies of the oligomers of PPP system, within a “U-V” model. The parameters of the model are determined by comparing the exact “U-V” model results with the exact Pariser–Parr–Pople model results for biphenyl. The reliability of the DMRG technique is illustrated by comparing the DMRG results for $U=V=0$, with Hückel results, for the largest system sizes studied. In the PPP system, bond order studies reveal that the $2^1A_g^+$ state corresponds to a localized excitation while the $1^1B_u^-$ and the $1^3B_u^+$ excitations are extended in nature. Furthermore, from the charge–charge and spin–spin correlation studies we find that the lowest one-photon state, the lowest triplet state and the bipolaronic ground state are very similar in nature and correspond to charge/spin separated configurations. The bipolaronic state shows clear indication of disproportionation into two polarons in the polymeric chain.

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- ¹J. L. Bredas and G. B. Street, *Acc. Chem. Res.* **18**, 309 (1985); A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- ²J. M. Leng, S. Jeglinski, X. Wei, R. E. Benner, Z. V. Vardeny, F. Guo, and S. Mazumdar, *Phys. Rev. Lett.* **72**, 156 (1994); P. Gomes da Costa and E. M. Conwell, *Phys. Rev. B* **48**, 1993 (1993); M. Chandross, S. Mazumdar, S. Jeglinski, X. Wei, Z. V. Vardeny, E. W. Kwock, and T. M. Miller, *ibid.* **50**, 14 702 (1994).
- ³Z. G. Soos, S. Etemad, D. S. Galvao, and S. Ramasesha, *Chem. Phys. Lett.* **194**, 341 (1992).
- ⁴M. Kasha, *Discuss. Faraday Soc.* **9**, 14 (1950).
- ⁵Z. G. Soos, S. Ramasesha, D. S. Galvão, and S. Etemad, *Phys. Rev. B* **47**, 1742 (1993).
- ⁶J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990).
- ⁷Y. Shimoi and S. Abe, *Phys. Rev. B* **49**, 14 113 (1994).
- ⁸X. Wei, B. C. Hess, Z. V. Vardeny, and F. Wudl, *Phys. Rev. Lett.* **68**, 666 (1992).
- ⁹J. W. P. Hsu, M. Yan, T. M. Jedju, L. J. Rothberg, and B. R. Hsieh, *Phys. Rev. B* **49**, 712 (1994).
- ¹⁰C. H. Lee, G. Yu, D. Moses, and A. J. Heeger, *Phys. Rev. B* **49**, 2396 (1994).
- ¹¹L. S. Swanson, J. Shinar, A. R. Brown, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. Kraft, and A. B. Holmes, *Phys. Rev. B* **46**, 15 072 (1992).
- ¹²M. Herold, J. Gmeiner, W. Rieb and M. Schwoerer, *Synth. Met.* **76**, 109 (1996).
- ¹³S. D. Halle, M. Yoshizawa, H. Murata, T. Tsutsui, S. Saito, and T. Kobayashi, *Synth. Met.* **49-50**, 429 (1992).
- ¹⁴J. Cornil, D. A. dos Santos, D. Beljonne, and J. L. Brédas, *J. Phys. Chem.* **99**, 5604 (1995); D. Beljonne, J. Cornil, J. L. Brédas, and R. H. Friend, *Synth. Met.* **76**, 61 (1996).
- ¹⁵J. L. Brédas and A. J. Heeger, *Chem. Phys. Lett.* **217**, 507 (1994).
- ¹⁶J. Cornil, D. Beljonne, R. H. Friend, and J. L. Brédas, *Chem. Phys. Lett.* **223**, 82 (1994).
- ¹⁷S. R. White, *Phys. Rev. Lett.* **69**, 2863 (1992); *Phys. Rev. B* **48**, 10 345 (1993).
- ¹⁸S. Ramasesha, Swapan K. Pati, H. R. Krishnamurthy, Z. Shuai, and J. L. Bredas, *Phys. Rev. B* **54**, 7598 (1996).
- ¹⁹S. Sorenson and I. Affleck, *Phys. Rev. B* **49**, 55 771 (1994).
- ²⁰K. Swapan, R. Pati, R. Chitra, D. Sen, H. R. Krishnamurthy, and S. Ramasesha, *Europhys. Lett.* **33**, 707 (1996); *J. Phys. Condens. Matter* **9**, 219 (1997).
- ²¹R. M. Noack and S. R. White, *Phys. Rev. B* **47**, 9243 (1993).
- ²²Y. Anusooya, Swapan K. Pati, and S. Ramasesha, *Phys. Rev. B* (to be published).