

Long-range electron transfer across a π -conjugated chain: Role of electron correlations

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We consider a prototype polyene chain donor- π (bridge)-acceptor. The distance between the donor and the acceptor is varied by increasing the number of atoms in the bridge and the rate of electron transfer k_{ET} is studied for a series of different donors $D=\text{NH}_2$, OCH_3 , SCH_3 , and a fixed acceptor $A=\text{NO}_2$. We observe a large k_{ET} even at a D - A separation of ~ 45 Å, unexpected from the standard noninteracting theories. Such a long-range electron transfer is primarily due to the formation of bound electron-hole pair (exciton) across the donor-bridge-acceptor atoms. Calculations at various levels, semi-empirical (with inclusion of configuration interactions) and many-body models (using density matrix renormalization group theory), have been performed to accurately account for such electron correlations.

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I. INTRODUCTION

Electron transfer (ET) between well separated donor and acceptor groups is dominant in many chemical and biological processes. These processes include design of electronic switches and wires in molecular level to photosynthesis and respirations in biological systems.^{1,2} Typically in many systems of interest, the spatial separation between the donor and the acceptor ranges from 10 to 30 Å.³ Because of this separation, there is no direct overlap between the donor and the acceptor groups. The electron transfer coupling is mediated via the intervening orbitals, called the bridge states. In most of the studies, the model used is a donor-bridge-acceptor (DBA) complex, wherein the donor and the acceptor states couple to the bridge in the form of a macromolecule. The intervening bridge can be water, conjugated organic molecules and polymers, a protein backbone, or even DNA. In many of the systems, these bridge states can lead to substantially altered electron transfer rates k_{ET} with respect to vacuum tunneling.⁴ The rate is also known to significantly depend on the conformational degrees of freedom of the bridges.⁵ However, the exact role of the bridges in controlling electron transfer is very poorly understood particularly for systems with strong electron correlations⁶ and weakly bonded species such as the hydrogen bonded systems.⁷

For most systems, these electron transfer rates fall off exponentially with distance ($\ln k_{ET} \propto -\beta r$). The inverse decay length, β , typically varies from 0.2 to 1.5 Å⁻¹, depending on the systems under consideration. Small β values have been observed for many proteins, artificial peptide chains, DNA segments, or a conjugated oligomeric backbone.^{8,9} This exponential decay appears in the Marcus theory of nonadiabatic electron transfer¹⁰ that assumes that the rate of ET depends on the electronic coupling element H_{DA} according to

$$k_{DA}(R_{DA}) = \frac{2\pi}{\hbar} |H_{DA}|^2 \text{FC}, \quad (1)$$

where FC is the Franck-Condon-weighted average density of states. The electronic tunneling matrix element in turn is related to the distance of separation between the D and A as

$H_{DA} \propto \exp(-\beta r/2)$. The theory assumes that the time scale of the electron transfer process is much faster than the time associated with the reorganization of the solvent nucleus or thermal disordering.

To date, most theoretical work has focused on the properties of the bridging medium and the position of D - A levels with respect to the HOMO and LUMO energies of the bridge.¹¹ Furthermore, these theories assume that the role of the bridge is to provide virtual orbitals that create an effective electronic coupling between the donor and the acceptor.¹²⁻¹⁴ This mechanism often reduces the problem of the whole system consisting of the donor, acceptor, and bridge subspaces to an effective two-state Hamiltonian consisting only of the donor and the acceptor states. There have been some alternative approach to this charge-transfer problem in recent years. Davison *et al.* have studied the charge transfer through a Hückel and extended model bridge using Green's function formalism.¹⁵ On the other hand, a completely new approach for an extended bridge with narrow band donor and acceptor groups predict the charge-transfer mechanism to be long ranged, involving a Kondo-singlet across the donor- (acceptor)-bridge atoms.¹⁶ Most often, however, in many of the models, explicit electron-electron interactions in the bridge are completely ignored, while it is well known that electron correlations often lead to qualitatively different descriptions.

In this work, we perform a quantitative estimation of the role of the bridge as well as the donor-acceptor groups for an effective charge transfer across the bridge. The bridge energetics has been found to influence the strength of the donor-acceptor coupling because of strong mixing between donor and acceptor and bridge orbitals.^{17,18} Furthermore, the most frequently used bridges are the π -conjugated chains, which are known to be highly correlated systems.^{19,20} In the DBA system, the process of electron transfer takes place with an electron originally at the donor state, transferring to the acceptor state via the bridge states. In the presence of interactions, the probability of electron transfer to an empty site is larger than it is to a partially occupied site. The probability of the relevant site being empty, partially occupied or doubly occupied depends very strongly on the electron correlation

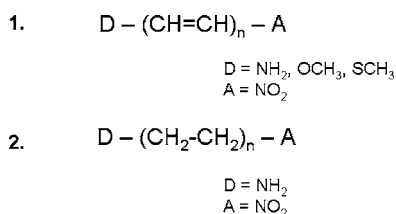


FIG. 1. Model systems considered for study.

strength. Thus, incorporating electron-electron interactions is crucial to the study of electron-transfer processes.

In the next section, we discuss the electron-transfer process in a π -conjugated bridge of varying length with a range of donor strengths. We find that there is a significant amount of ET for a π -conjugated system even when the D and A are separated by a very large distance ~ 45 Å. In Sec. III, we study the charge-transfer process for a model conjugated chain with and without electron-correlations by employing the density matrix renormalization group (DMRG) method²¹ and show that strong electron correlation is indeed required for long-range ET. We conclude with a summary of all the results in the last section.

II. SEMIEMPIRICAL CALCULATIONS

We consider a series of π -conjugated systems shown in Fig. 1. In the top (case 1), the bridge is considered to be a linear polyene chain of length n varying from 2 to 30. The acceptor group is fixed as $A=\text{NO}_2$, and the donor group is varied $D=\text{NH}_2, \text{OCH}_3$, and SCH_3 . All the geometries are optimized using the AM1 parametrized Hamiltonian, a part of semi-empirical MOPAC package.²² We have also verified that these geometries correspond to the minimum energy structure by further optimization at the B3LYP/6-311G++(d,p) level.²³ No symmetry constraints were used in the optimizations. In case 2, we consider that the donor and the acceptor are separated by a saturated alkane chain. These two model cases serve as a good contrast in the mechanism of electron transfer (ET). The former is expected to follow the bridge mediated ET due to the extended conjugation between the donor and the acceptor (through the p_z orbitals of the intervening atoms). In the following, we show that the case 1 is indeed very different and shows long-range ET purely because of electron correlations.

The geometry optimized structures were used for configuration interaction (CI) calculations to obtain energies and the dipole moments in the CI basis using the Zerner Intermediate Neglect of Differential Overlap (INDO) method.²⁴ The levels of CI calculations have been varied but we restrict our discussions to results obtained using singles CI (SCI) only as this gives a reliable estimate of the states involved in charge transfer. The CI approach adopted here has been extensively used in earlier works, and was found to provide excitation energies and dipole matrix elements in good agreement with experiments.²⁵⁻²⁷ For the Hartree-Fock determinant, we use varying number of occupied and unoccupied molecular orbitals to construct the SCI space until a proper convergence is obtained.

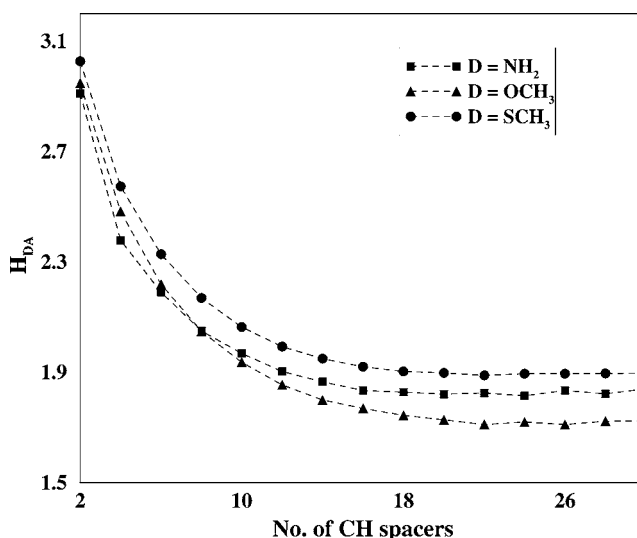


FIG. 2. ET coupling matrix H_{DA} (in eV) with respect to the increase in the number of olefinic spacers for different donors D and fixed $A=\text{NO}_2$.

The electron transfer coupling element H_{DA} has been calculated using the generalized Mulliken-Hush method for two states, referred to as 1 and 2 (Ref. 28)

$$H_{DA} = \frac{\mu_{12}\Delta E_{12}}{\sqrt{\Delta\mu_{12}^2 + 4\mu_{12}^2}}, \quad (2)$$

where $\Delta\mu_{12}(\Delta E_{12})$ is the dipole moment (energy) difference between the two states, and μ_{12} is the transition dipole between states 1 and 2. As has been discussed earlier, the method considers only the adiabatic states 1 and 2, and assumes that the contribution from the nonadiabatic states to the transition dipole is small enough since the dipole moment operator has a weak distance dependence. Note that, it depends on the calculations whether the nonadiabatic states are well described by the adiabatic states 1 and 2.

The plots of H_{DA} with respect to the number of CH units of the polyacetylene bridge are shown in Fig. 2 for $D = \text{NH}_2, \text{OCH}_3, \text{SCH}_3$, and $A=\text{NO}_2$. All of them have an exponential decay profile for the separation between the D and A . Fitting a single exponential parameter β , for these three donors, we get $\beta=0.277, 0.219$, and 0.237 Å⁻¹ for $D = \text{NH}_2, \text{OCH}_3, \text{SCH}_3$ respectively. Thus, H_{DA} seems to depend on the donor strength although for all three cases we find the range of electron transfer is quite substantial.

A very important inference that can be drawn from our calculation is that even for a bridge length of 45–50 Å, the H_{DA} magnitude is quite significant (~ 1.7) and this value is almost independent of the electronegativity (donor ability) of the ligands. This was also evident from the very low decay exponential parameter $\beta \sim 0.25$. Such low decay features for ET have been reported for DNA (Ref. 29) and has triggered a lot of interest in its molecular electronic properties.³⁰ We propose here that these D and A separated π bridge is also a very good candidate for molecular electronics. While polaron assisted ET is believed to be the mechanism in DNA, we suggest the role of electron-electron interactions leading to

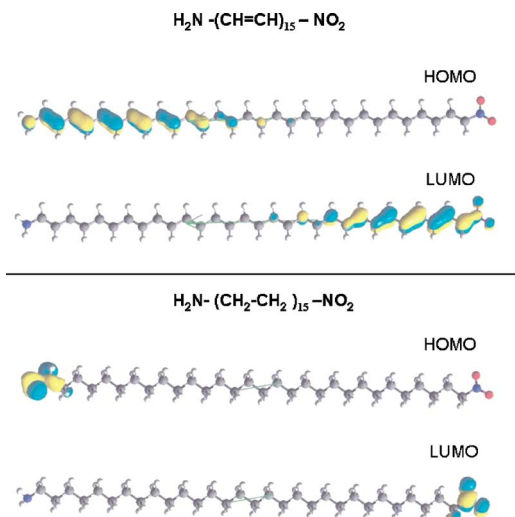


FIG. 3. (Color online) Frontier orbital plots with unsaturated and saturated spacers. The shading of the lobes show the parity. Atom symbols—Red: oxygen, blue: nitrogen, black: carbon, white: hydrogen. Light green arrow shows the direction of the dipole moment

the formation of an electron-hole pair (an exciton³¹) responsible for long-range charge transfer in conjugated polymeric systems.

The formation of exciton is evident from our CI calculations. We have analyzed the oscillator strengths of the lowest few CI states for various system sizes. At smaller chain lengths, the lowest dipole allowed state (the state that has maximum oscillator strength) lies quite high in energy and very close to the single-electron continuum. However, for large chain length ($n > 4$), the exciton stabilization is quite large and the dipole allowed state appears much below the continuum. In fact, as the bridge length increases from $n = 2$, the lowest dipole allowed state shifts its position in the energy spectrum and above $n = 4$ becomes the lowest energy (fundamental) excitation of the system. For smaller chain length, the exciton formation is very weak, since such a small length scale does not provide room for formation of a well bound electron-hole pair. In fact, a critical length scale is necessary for a delocalized electron and a delocalized hole to bind. In contrast to this feature for the conjugated chains (case 1), for the saturated chains $\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2)_n-\text{NO}_2$ (case 2), there are no excitonic bands and the dipole allowed state remains invariant of the chain length enhancements. In fact, the dipole allowed state itself has a small oscillator strength (very weak). This is easy to understand as for the saturated chains, the electron and hole over the D and A respectively, remain uncorrelated for any bridge lengths.

Interestingly, the actual decay of ET in $\text{H}_2\text{N}-(\text{CH}=\text{CH})_{15}-\text{NO}_2$ is much smaller. The H_{DA} at a separation of 1.41 Å is 3 (from Fig. 2) and that at 38.5 Å is 1.7. Using Eq. (1) and assuming the Franck-Condon rule to be valid, we get the decay to be only 32% to that for no separation. This is very different from the case 2 in Fig. 1, where the D and A are separated by a saturated spacer and the rate decays to zero after $n = 3$.

Such a feature is very well illustrated in Fig. 3, where we

plot the wave functions corresponding to highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for two of the model systems: D and A separated by unsaturated and saturated spacers by large distance $\text{H}_2\text{N}-(\text{CH}=\text{CH})_{15}-\text{NO}_2$ and $\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2)_{15}-\text{NO}_2$, respectively. The HOMO plot shows the ground state features with electron localized around the donor while the LUMO plot shows the redox process, the lowest charge transfer state. There is a distinct difference between the two systems. While for $\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2)_{15}-\text{NO}_2$, the electron is localized either on the D or A corresponding to HOMO and LUMO, respectively, $\text{H}_2\text{N}-(\text{CH}_2\text{CH}_2)_{15}-\text{NO}_2$ shows very large delocalization of charge carriers from the D and A groups into the bridge orbitals.

In Fig. 4, we show the molecular orbitals (MOs) coefficients for the atoms in donor and the acceptor groups (N atom in NH_2 group and N and O atoms in NO_2 group). The MO coefficients $\sum_i c_{mi}$ (where i index runs for each atomic site and m indexes the molecular orbitals) are extracted for both HOMO and LUMO states. The HOMO state corresponds to the HF ground state and thus represents the system before charge transfer. On the other hand, the corresponding LUMO coefficients represent the state after charge transfer. As can be seen, the MO coefficients before charge transfer are mostly located near the electron donating π orbital of the N atom in NH_2 group. After the charge transfer however, the electrons are distributed over the p_z orbitals of three atoms: N and two O's of the NO_2 group.

III. QUANTUM MANY BODY CALCULATIONS

For a quantitative understanding of the charge-transfer processes in such systems, we have used quantum many-body models. We consider the bridge to be a one-dimensional chain with N atoms (N even) and the donor (D) and the acceptor (A) atoms are attached to its two ends. The Hamiltonian can be written as

$$\begin{aligned}
 H = & -t \sum_i [\{ \sum_{\sigma} (c_{i\sigma}^{\dagger} c_{i+1\sigma} + \text{H.c.}) \} + U n_{i\uparrow} n_{i\downarrow} + V (n_i - n_{av}) \\
 & \times (n_{i+1} - n_{av})] + \epsilon_D n_D + \epsilon_A n_A \\
 & + \sum_{\sigma} [t_1 (c_{i\sigma}^{\dagger} c_{D\sigma} + c_{N\sigma}^{\dagger} c_{A\sigma} + \text{H.c.})], \quad (3)
 \end{aligned}$$

where t is the transfer integral, U the Hubbard on-site potential, and V is the nearest-neighbor Coulomb interaction parameter in the bridge. ϵ_D and ϵ_A are the on-site energy of donor and acceptor atoms, respectively. t_1 is the hopping term between the $D(A)$ atoms with the bridge atoms 1(N). $c_{i\sigma}^{\dagger}$ creates an electron with spin σ at site i , and $n_i = n_{i\uparrow} + n_{i\downarrow}$, is the electron number operator at site i .

The U - V model or the extended Hubbard model is the minimal model to capture the physics of a quasiparticle like exciton, a bound electron-hole pair. In the large U ($U = \infty$) limit, the exciton is stabilized by V , since the Hubbard repulsion U describes the electron-hole continuum. However, this is for an isolated bridge with half-filled band. When the donor (D) and the acceptor (A) species are very weakly at-

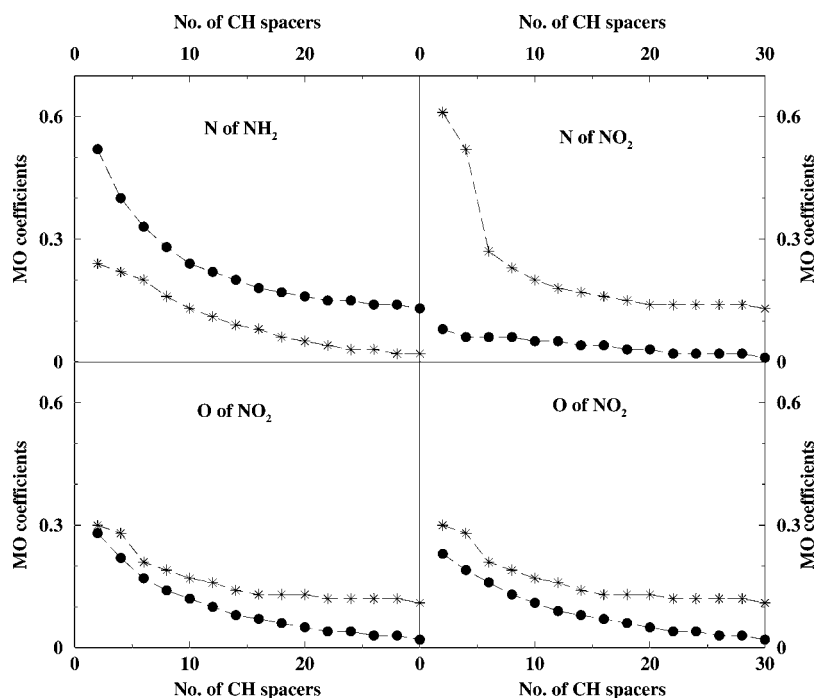


FIG. 4. Coefficients of molecular orbital occupancy on the N atom of NH₂ and the N atom and two O atom of NO₂ before (circles) and after (stars) ET.

tached to the bridge, the electron transfer from D (hole transfer from A) can be mediated through the noninteracting electron-hole states or an excitonic state of the bridge. However, depending on the electron correlations in the D and A orbitals, the probability of intermixing of the D and A states with the bridge states can vary and to account for the electron transfer in such cases, we need to consider the whole system as a macromolecule coupled strongly with its constituents. In our calculations, we have considered two extreme cases for the donor and acceptors in terms of its electron correlations. Case A with no Coulomb repulsion at the donor and acceptor sites which allows any occupancy of the D/A sites and case B where we have set infinite Coulomb repulsions in D and A ,³² which prevents double occupancy of these sites. Note that for both cases, bridge is described by correlated model. The other case with uncorrelated bridge has not been studied, since it has been described elsewhere.¹⁶

The bridge is assumed to be a half-filled conjugated polymer insulator. From the half-filled extended model literature, it is known that the ground state is a spin-density wave (SDW) state for $U > 2V$, while it is a charge-density wave (CDW) state for $U < 2V$. We are interested in charge transfer mechanism through a bridge with SDW ground state representing organic conjugated polymer, and thus we set $U = 5, V = 1$, and $t = 1$, without loss of generality.⁶ The total number of electrons in the D -bridge- A system is $N + 1$, where N is the number of orbitals in the bridge sites and $N + 2$ is the total number of orbitals of the whole DBA system. This system thus represents a linear correlated chain with one less electron than the half-filled limit. We present below the charge transfer efficiency of this system with bridge chain length varying from 2 to 30.

The charge transfer occurs mostly through the lowest energy excited state of the bridge, which is induced experimentally by interaction with light. The density matrix renormalization group (DMRG) method has been used to study the

ground and the excited states of the system.²¹ Since the bridge is a one-dimensional chain, the accuracy of the method is extremely good. In DMRG method, we target the ground state and the lowest dipole allowed states, and the density matrix is averaged over these states at every iteration. The dipole allowed state is recognized as the state to which the dipole moment operator acting on the ground state gives nonzero value. In the DMRG basis the transition dipole moment between two states is defined as

$$\mu_{ij} = \langle \psi_i | \hat{\mu} | \psi_j \rangle, \quad (4)$$

where $\hat{\mu}$ is the dipole moment operator acting between the states ψ_i and ψ_j . The H_{DA} is then calculated from the Mulliken-Hush formula given in Eq. (2).

We have plotted the electron-transfer coupling element (H_{DA}), defined earlier, as a function of chain length for the two cases discussed above. Figure 5(a) shows the H_{DA} for the case with no Coulomb repulsion at the donor and acceptor sites (case A), for a few representative values of the donor strengths (orbital energies ϵ_D). It can be seen that the H_{DA} falls off quite rapidly as expected, and is quite short ranged. An exponential fit to the curves give a value of around 0.5 \AA^{-1} for β , the parameter in the exponential. This type of large β exponential fall of electron transfer rate is expected from the well-known Marcus' theory.¹² Figure 5(b) shows similar plots for the case with large Hubbard repulsion at the donor and acceptor sites (case B). In this case too, the H_{DA} falls off exponentially, but the fall is much slower and long ranged. An exponential fit to these curves give a β value of around 0.2 \AA^{-1} . The value of β for case A is larger than that for case B, indicating that the range of transfer is smaller for the first case. It is very interesting to note that for the π -conjugated bridge considered in the previous section, we obtained β to be of the same order as the case B with correlated bridge. Thus our model calculations are quite justified

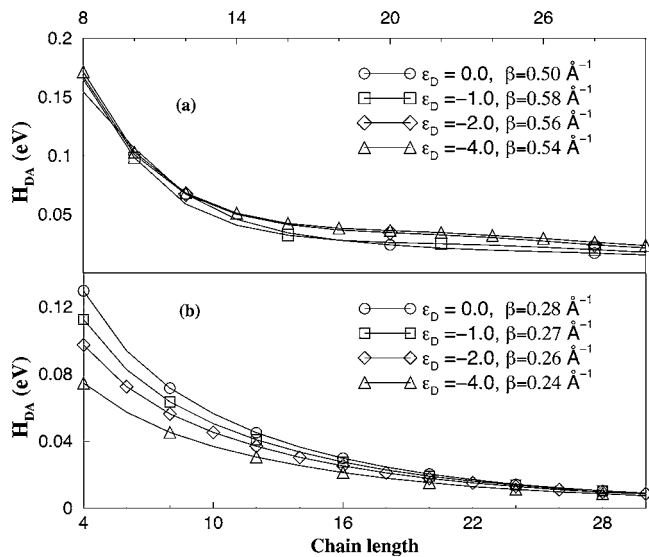


FIG. 5. ET coupling matrix H_{DA} with respect to the bridge length for case A (above) and case B (below) for different values of the donor strengths ($\epsilon_D=0.0$ to $\epsilon_D=-4.0$).

in realizing the ET kinetics for real molecular systems with strong correlations.

To understand the mechanism behind the charge transfer which results in long range and short-range transfer for case B and case A, respectively, we have plotted the ground-state charge densities in Fig. 6 for both cases. Figure 6(a) shows the ground-state charge densities for case A. It can be seen that the presence of a strong donor (a large negative value of ϵ_D) and the absence of any Coulomb repulsion at the donor favors an increase in the charge density at the donor. The acceptor on the other hand, which is always kept at the same strength (with a value of $\epsilon_A=0$ as for the bridge), prefers to retain the average charge density that a system with one less electron would have, as a change in the electron number at

this site, will not result in any change in the total energy. The extra charge density at the donor site is compensated by the reduction in the charge density at the bridge site next to the donor. The hopping energy between the donor and the first site of the bridge favors the presence of a hole (reduced charge density) at the first bridge sites, so that the system can be stabilized by this kinetic energy. A further stabilization is effected by the presence of the nearest-neighbor Coulomb repulsion between the donor and this first bridge site. On the other hand, the last bridge site shows an increased charge density and the last but one bridge site has a reduced charge density. This can be attributed to the fact that hopping between the last bridge site and the acceptor site gets renormalized because of the absence of any Coulomb repulsion at the acceptor, and hence stabilizes the system. The reduced charge density at the last but one bridge site also allows for hopping between this site and the last bridge site. The presence of the extended Hubbard Coulomb repulsion energy V between these sites further enhances the kinetic stabilization. This excess electron and hole is formed due to the correlations in the bridge; they are not free but are rather bound. We refer to this kind of a quasiparticle as an ‘‘exciton.’’ The exciton is formed at the ends of the bridge closest to the donor and the acceptor sites and is not spread over the chain. It has rather small volume and is quite localized.

On the other hand, for the case with large Coulomb repulsion at the donor and acceptor sites (case B), the ground-state charge densities show contrasting behavior, as shown in Fig. 6(b). Here, the charge densities show a dip (reduction) at both the first and the last bridge sites closest to the donor and the acceptor. In this case, the large Hubbard U ensures that there is only a maximum of one electron which is allowed at the donor and the acceptor sites. No matter, however large the strength of the donor, the charge at the donor site does not exceed 1. When the donor and the acceptor energies are kept the same as the bridge ($\epsilon_D = \epsilon_B = \epsilon_A = 0$), the charge densities at all sites, except the bridge sites closest to the donor

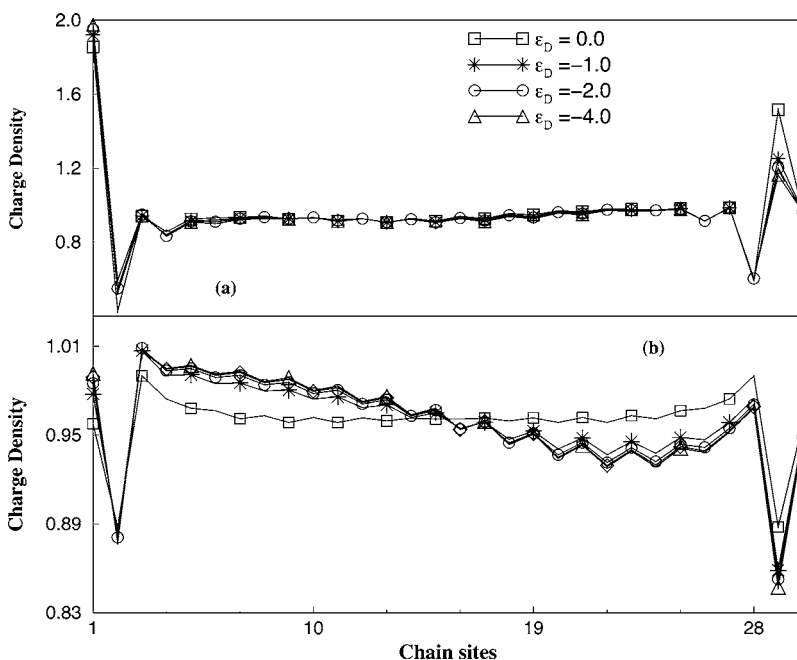


FIG. 6. Charge densities at every bridge site for case A (above) and case B (below) for different values of the donor strengths ($\epsilon_D=0.0$ to $\epsilon_D=-4.0$).

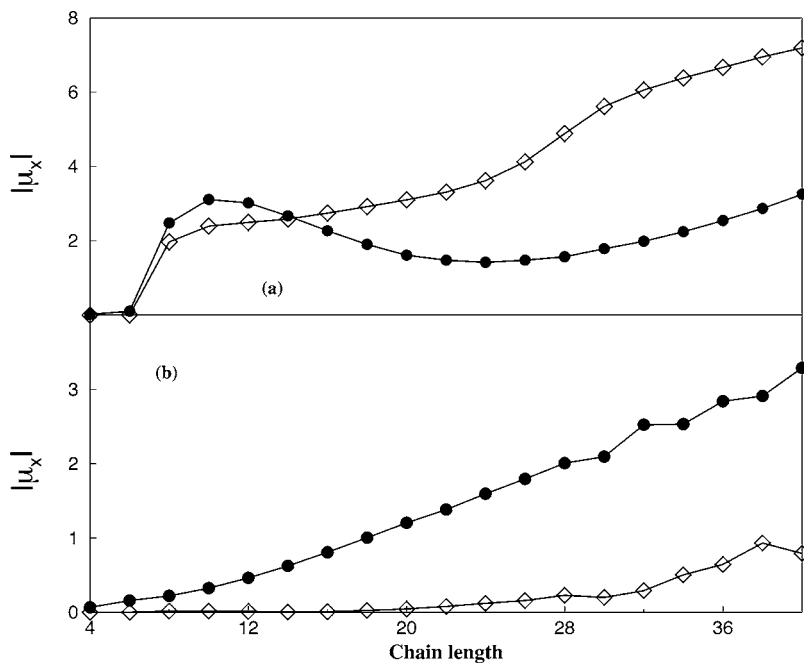


FIG. 7. Modulus of the x component of the transition dipole moment $|\mu_x|$ with respect to chain length for case A (above) and case B (below) for transition from ground state to first excited state (filled circles) and ground state to second excited state (diamonds).

and the acceptor, have an average number of electrons that a system with one less electron from the half filling would have. This reduction in charge at the first and last bridge sites is due to the resulting stabilization that would be brought about by the presence of the hopping energy t and the extended Hubbard energy V . A higher donor strength shows a similar feature at the first and the last sites of the bridge, however, a very prominent increase in the charge density can be seen in the first half of the bridge and a corresponding reduction in the other half of the bridge. This shows that the exciton in this case spreads over the size of almost the length of the entire bridge. This large volume exciton is in fact responsible for the long range electron transfer for the case B.

We have also looked at the excited state charge densities for both cases. For case A, there is not much difference between the ground and the excited state charge densities indicating that the charge transfer has not been mediated by the localized exciton, whereas for case B, the excited state charge densities clearly show the movement of charge density from the donor to the acceptor with a reverse in the density pattern from that found for the ground state.

We also have studied the charge-charge correlations functions between the donor-acceptor and the bridge sites: $\langle n_{D(A)}n_B \rangle - \langle n_{D(A)} \rangle \langle n_B \rangle$, where $n_{D(A)}$ and n_B are the charge densities at the donor (acceptor) and the bridge sites, respectively. The ground-state charge-charge correlations in case A for all strengths of the donor, clearly indicates that the correlations between the donor and the bridge sites are very short ranged and that the exciton is not effective in mediating the charge transfer between the far separated donor and the acceptor. In contrast to this, the correlations in case B shows features in correspondence with the charge density in Fig. 6(b), i.e., the donor is highly correlated with the bridge sites and hence transfer mediated by the exciton is the most likely mechanism of charge transfer between the donor and the acceptor.

Finally, to understand the nature of the excitonic state responsible for longer-range electron transfer, we have plotted the chain axis component of the transition dipole moment between the ground state and the first and second excited states for the two cases discussed above, for a particular donor strength ($\epsilon_D = -4.0$) in Fig. 7(a) and 7(b), respectively. This transition dipole moment enters into the calculation of H_{DA} and hence is a good measure of the strength of the states carrying the charge for transferring to/from the acceptor end. When there is no Coulomb repulsion at the donor and the acceptor sites (case A), the transition dipole moment between the ground state and the first excited state increases and then falls off for longer chain lengths, whereas that between the ground state and second excited state shows a steady increase, clearly indicating that the state carrying the charge is not a well defined electron-hole bound pair state. On the other hand, for the case with large Coulomb repulsion at the donor and the acceptor sites (case B), the transition dipole moment between the ground and the first excited state shows an increase with the increase in the chain length, indicating that this is the state which carries the charge through, from one end to the other even for large bridge length. The same between the ground state and the second excited state has zero value for small system sizes and a very negligible value for larger chain lengths, clearly showing that this state does not play any part in the charge transfer between the donor and the acceptor states. This emphatically proves that for case B, the charge is carried by a well defined fundamental quasiparticle for all the chain lengths resulting in long-ranged electron-transfer.

IV. CONCLUSIONS

To conclude, we have performed semi-empirical as well as many-body DMRG calculations to understand the role of electron-electron interactions in governing the electron transfer in $D-\pi-A$ systems. The electron transfer kinetics are truly

long ranged for strongly correlated conjugated polymeric systems and are not affected much by the strength of the donors. What matters is the extent of interactions in the bridge. It is the mediation of a stable electron-hole pair quasiparticle (exciton) in these systems that is responsible for small inverse decay length β . We have been able to quantify the nature of the exciton from different levels of calculations. The CI calculations clearly indicate the formation of the excitonic state for an optimum size of the conjugated bridge length. But for the saturated bridge case, electrons are localized at the respective sites and thus the electron transfer has a much shorter range. From the quantum many-body long-chain DMRG calculations on systems with small and large correlations between the donor (acceptor) and the bridge sites, we have been able to distinguish the nature of the quasiparticle responsible for the electron transfer in the two cases. Our results show that when the donor (acceptor) and bridge are weakly correlated, the charge transfer is purely by uncorrelated electron and hole, leading to short-range ET observed in earlier theories. On the other hand, when the

donor (acceptor) and bridge sites are strongly correlated, formation of well-bound electron-hole pair spread over the entire chain length is involved in the charge transfer, even for larger chain lengths, giving a very long-range ET. Thus, the exciton formation is a crucial parameter in controlling long-range ET. Formation of such a quasiparticle is known to lead to very interesting optical properties in organic light emitting diodes. The fact that excitons also play an important role in transport mechanism signifies an important contribution towards fabrication of molecular wires where currents can be induced by optical excitations. Also, for biomolecular systems with known long-range ET such as DNA, the identification of the right kind of quasiparticle responsible for charge and field carrying processes can lead to novel applications in biomolecular optoelectronics. This however, requires further study.

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