Stable Biexcitons in Conjugated Polymers

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Theoretical evidence for stable biexcitons are found within the Coulomb-correlated model for π-conjugated polymers, for realistic Coulomb interaction parameters. High energy picosecond photoinduced absorption, not anticipated within one-electron theories of π-conjugated polymers, is explained as a transition from the optical exciton to the biexciton.

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While early work on conjugated polymers emphasized the role of electron-phonon interactions [1], more recent theoretical and experimental studies suggest that the behavior of these systems is strongly influenced by electron-electron Coulomb interactions [2]. Within Coulomb-correlated models, the lowest optical transition is to a charge-transfer (CT) exciton. Excitons have been demonstrated in polydiacetylenes (PDAs) [3] and in poly-paraphenylenevinylene (PPV) [4], and the third harmonic generation spectrum of *cis*-polyacetylene has been interpreted within the CT exciton model [5]. In conventional *inorganic* semiconductors, the biexciton, or the bound state of two excitons, has been demonstrated [6,7]. It is clearly of interest to determine whether the CT excitons in conjugated polymers bind to form biexcitons, and if so, any possible role they play in the photophysics of these systems.

In the present Letter, we show that stable biexcitons can occur within the standard Coulomb-correlated model for conjugated polymers with realistic interaction parameters [2]. Picosecond photoinduced absorption (ps PA) in conjugated polymers [4,8–10], not understood within the one-electron electron-phonon coupled model [1], can be explained naturally using the biexciton concept.

The theoretical model we consider is the extended Hubbard model [2]

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

Here $c^\dagger_{i,\sigma}$ creates an electron of spin σ on site i, t is the one-electron hopping integral, δ is a bond-alternation parameter, and U and V are the on-site and nearest-neighbor Coulomb interactions. Equation (1) applies to linear chain polymers only. Recent work has shown that the primary excitations in systems like PPV can also be described within effective linear chain models [11]. Parameter values that are considered realistic are $t = 2.5$ eV, effective $\delta = 0.1-0.3$, and moderate Coulomb interactions $U/t = 3$, $V/t = 1$ [2].

The straightforward approach to proving stable biexcitons [6,7], determination of a nonzero energy gap between the lowest two-exciton state(s) and a higher energy two-exciton continuum, is not possible within Eq. (1) for moderate Coulomb interactions. Even for the accurate determination of the *lowest* even parity excited state ($2A_g$), configuration interaction (CI) calculations involving at least quadruple excitations (QCI) become necessary for long chains [12]. This is even more true for the very high energy two-exciton states. QCI calculations of the complete energy spectra are currently possible only for $N \leq 10$ atoms. Since the energy spectra of such short chains are discrete for a moderate Coulomb interaction, an approach different from the standard one is called for.

Our approach is based on the observation that the *lowest* short chain wave function of a given class (here "class" implies spin wave, exciton, continuum, etc.) already exhibits the behavior of the lowest state of the *same* class on a long chain. With an increase in N, the energy of this lowest state decreases and additional states appear above it, but the wave function characteristics of the lowest state remain basically unaltered. Note that the widely used practice of extrapolating finite chain energies of the lowest optical exciton ($1B_u$), the $2A_g$, and the lowest triplet state (1^3B_u) to obtain their $N \to \infty$ values [13,14] has the same implicit principle. We have recently shown how the lowest state of the one-electron–one-hole ($1e$-$1h$) continuum within Eq. (1) can be determined from finite chain calculations [15]. Here our problem reduces to *identifying* the lowest two-exciton state, and the determination of the particular *wave function behavior* that will demonstrate the binding of the two excitons.

Our demonstration of stable biexcitons for realistic parameters within Eq. (1) is reached in several steps. First, we arrive at the wave function behavior that identifies a bound biexciton from physical reasoning. Second, we establish the validity of this criterion in the strong-coupling limit (large U and V). Identical behavior of the biexciton wave function within theoretical models that describe *other* kinds of one-dimensional correlated semiconductors has been found. These latter results establish the universality of our physical criterion of biexciton stability. As a final step, we perform exact and QCI short chain numerical calculations, and applying the criterion for biexciton stability, we conclude that stable biexcitons exist within Eq. (1) for realistic parameters.

The physical idea we employ is as follows. Consider first the $U = V = 0$ limit. The lowest two-electron–two-hole ($2e$-$2h$) states that are dipole coupled to the lowest $1e$-$1h$ $1B_u$ state consist of the first e-h pair occupying the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), with a second e-h pair occupying the LUMO and the HOMO, or the LUMO + 1 and the HOMO − 1 orbitals, or the LUMO + 2 and the HOMO − 2 orbitals, and so on. Thus in the noninteracting limit, the spectrum of the absorption from the $1B_u$ to the $2e$-$2h$ A_g states is *identical* to the ground state absorption. In one dimension, such a band absorption spectrum exhibits the square-root singularity at the band edge. The change in the *ground state* absorption upon exciton formation is known. The oscillator strength now concentrates in the $1B_u$ exciton, while the strength of the absorption to the $1e$-$1h$ continuum decreases. The nature of the absorption *from* the $1B_u$ for the interacting models has not been discussed previously, but a compelling intuitive real space argument can be made for one-dimensional systems. We imagine a long chain with the first exciton already formed. For stable biexcitons to exist, the second exciton can occur in only one of two "spots," to the left or to the right of the *first* exciton, at a distance such that binding can occur. In contrast, the second exciton in a two-exciton continuum can appear at arbitrary relative distance from the first exciton. Thus in a long chain, the two-exciton continuum states are superpositions of a very large number of basis functions, while the biexciton is constructed out of a few. The density of states is consequently much larger at the continuum edge, and we expect that the strength of the absorption from the $1B_u$ to the two-exciton continuum edge is *larger* than the oscillator strength of the absorption to the biexciton. Conversely, the observation of a weaker transition strength from the $1B_u$ exciton to the lowest two-exciton state than that to a higher energy two-exciton state is a signature of exciton binding in the lowest two-exciton state.

We establish the validity of this criterion by examining the strong-coupling limit $U \gg V \gg t$. The ground state has all sites singly occupied. The exciton states are even- and odd-parity linear combinations of configurations ...11120111..., where the numbers denote site occupancies. The $1e$-$1h$ continuum consists of all states in which the double occupancy (particle) and the empty site (hole) are separated by more than one site (for example, ...11211...1011...). The biexciton states consist of configurations ...1112020111..., which occur at energy $2U - 3V$, while the lowest two-exciton continuum states have occupancies ...12011...12011..., and occur at energy $2U - 2V$. Thus in the strong-coupling limit, the biexciton binding energy and the exciton binding energy are the same, viz., V. In Fig. 1(a) we show the exact energy states for a periodic ring of $N = 10$ sites for $U/t = 50$, $V/t = 15$, and $\delta = 0.1$. Finite size effects are minimal for these very large Coulomb parameters, and exciton states at $U - V$, the $1e$-$1h$ continuum centered at U, the biexciton at $2U - 3V$, and the two-exciton continuum at $2U - 2V$ are all distinct. Only one of the exciton states at $U - V$ has large dipole coupling with the ground state. In Fig. 1(b) we show the normalized dipole couplings between the optical exciton and all two-exciton states. Note that the dipole coupling with the biexciton B at $2U - 3V$ is smaller than the dipole coupling with the state C at the edge of the two-exciton continuum, in agreement with our prediction. Similar results are obtained with an open chain of $N = 8$ sites.

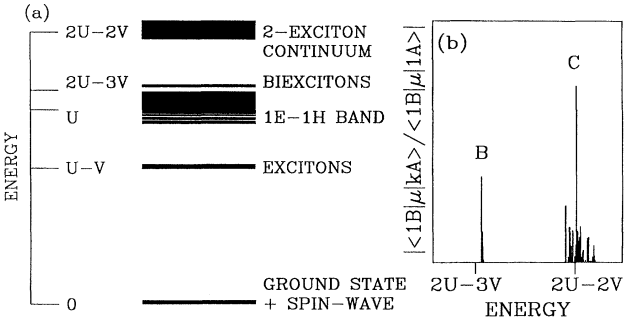

FIG. 1. (a). Total energies of the $N = 10$ periodic ring, for $U/t = 50$, $V/t = 15$, and $\delta = 0.1$. (b) Normalized dipole couplings between the optical exciton and the two-exciton states of (a).

The above result is not limited to the bond order wave (BOW) systems described within Eq. (1) for $U > 2V$. For example, together with our colleagues we have recently established the occurrence of stable multiexcitons (both biexcitons and triexcitons) in a strongly neutral mixed-stack charge-transfer solid [16], a charge density wave (CDW) system. Now in the strong-coupling limit the ground state has the site occupancies ...202020..., while the exciton, the $1e$-$1h$ continuum, the biexciton, and the two-exciton continuum have occupancies ...201120..., 201020210..., ...202011112020..., and ...201120...20112020..., respectively. In Ref. [16], our calculations were limited to energy levels only. Calculations of dipole moments within the CDW Hamiltonian show that the dipole coupling between the CDW optical exciton and the biexciton is again weaker than that between the exciton and the two-exciton continuum edge. Similarly, Ezaki, Tokihiro, and Hanamura have investigated optical absorption from the exciton to the two-exciton states within a Frenkel exciton model that is different from both the BOW and the CDW Hamiltonians, and have also found the weaker dipole coupling of the strongly bound biexciton [17]. The consistency of the results among diverse theoretical models indicates the universal applicability of our criterion.

We now investigate Eq. (1) for the case of weak exciton binding. Our numerical calculations for realistic parameters are for the open chain of $N = 10$ atoms [18], within the QCI approximation. Exact $N = 8$ results are almost indistinguishable from the QCI $N = 10$ results.

For the parameters appropriate for conjugated polymers, not only are finite-chain energy spectra discrete, there is also considerable overlap between the highest $1e$-$1h$ and the lowest $2e$-$2h$ excitations [15], and thus the very *identification* of the lowest two-exciton state is difficult. In order to overcome this problem, we start our calculations with very large δ ($\delta = 0.5$). For moderate $U/t = 3$, $V/t = 1$, and such large δ, all excitations can be described within an effective single-particle picture. We prove this by determining *approximate* molecular orbital (MO) energies that can be used to reproduce all (known) total excitation energies. In Fig. 2 we have shown the $N = 10$ total excitation energies (obtained using QCI) against several representative even and odd parity excitations. The approximate MO energies, with error bars in parentheses, are shown against the individual valence and conduction band levels. From Fig. 2, the $14A_g$ state is the lowest $2e$-$2h$ state in $N = 10$ with $U/t = 3$, $V/t = 1$, and $\delta = 0.5$.

In Fig. 3(a) we have plotted the normalized dipole couplings between the $1B_u$ and all excited A_g states against their normalized energies, for the same parameters. The level labeled 2 is the $2A_g$, the level m is the mA_g state discussed previously in the context of nonresonant nonlinear optics [5,15], while the level B is the $14A_g$ state of Fig. 2, the lowest $2e$-$2h$ excitation. In the band limit, the optical transition from the ground state to the $1B_u$ and that from the $1B_u$ to the lowest $2e$-$2h$ state involve the same MOs, and thus the normalized dipole coupling of nearly 1 for the $14A_g$ also indicates it to be the lowest $2e$-$2h$ state.

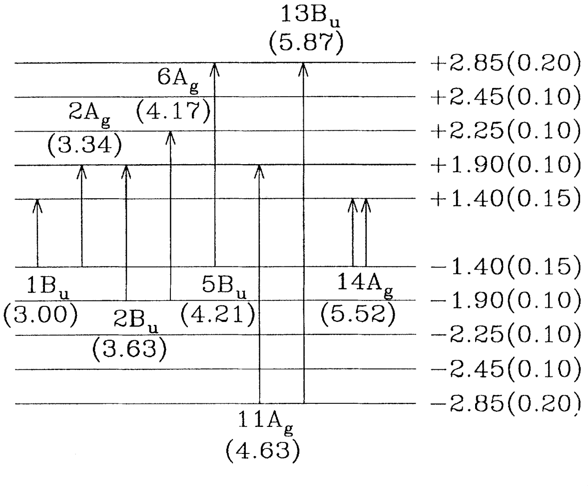

FIG. 2. Decomposition of the QCI $N = 10$ total energies (in units of t) into approximate MO energies for $U/t = 3$, $V/t = 1$, and $\delta = 0.5$. The numbers against the MOs are their approximate single-particle energies, with the error bars included in the parentheses. The vertical arrows indicate the excitations within the MO scheme. The numbers against these are the total excitation energies obtained by QCI. The $14A_g$ is the lowest $2e$-$2h$ excitation for large δ.

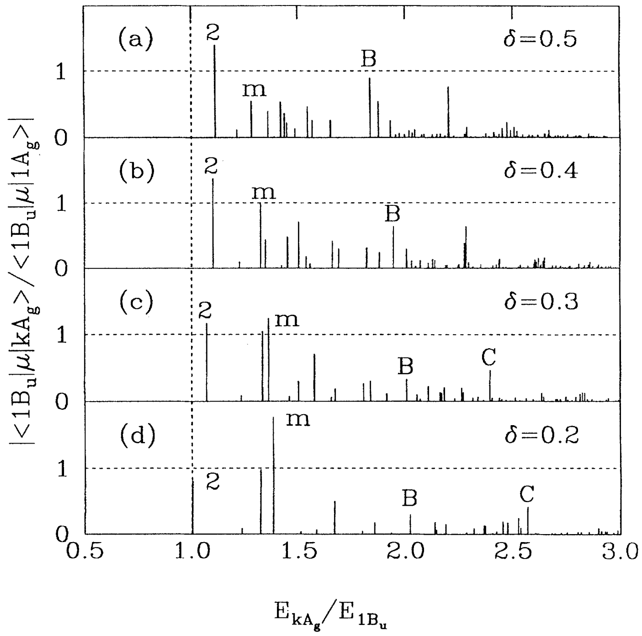

FIG. 3. Dipole couplings between the $1B_u$ and all excited A_g states, normalized by the dipole coupling between the ground state and the $1B_u$, plotted against the normalized energies of the A_g states, for different δ and $U = 3$, $V = 1$. The emergence of a level C above B for $\delta \leq 0.3$ that is more strongly dipole coupled to the $1B_u$ than B, indicates that B is a biexciton (see text).

Having identified the lowest $2e$-$2h$ state for the weakly correlated case, we now increase the correlation contribution to the optical gap by gradually reducing δ. For smaller δ, the wave functions are highly correlated and simple descriptions of the kind in Fig. 2 are not at all possible. For each δ, we again plot the normalized dipole couplings of all excited A_g states with the $1B_u$ against their normalized energies. These results are shown in Figs. 3(b)–3(d). For $\delta = 0.2$, the $2A_g$ is degenerate with the $1B_u$ within the QCI calculation, but occurs below the $1B_u$ for $N = 8$, for which exact calculations were done. Thus $\delta \leq 0.2$ is close to the realistic δ in the PDAs, while $\delta = 0.3$ is closer to PPV [11]. The gradual reduction in δ along with the result of Fig. 3(a) allow us to continue to demarcate between $1e$-$1h$ and $2e$-$2h$ excitations. It is clear from Fig. 3 that the major effect of reducing δ (increasing correlations) is a redistribution of dipole moments of A_g states with the $1B_u$: The relative shifts of energy are small within this range of parameters. There should be no doubt whatsoever that in all cases the level labeled B is the lowest two-exciton state.

In long chains, as the effective correlations increase, we expect the level B to be lowered in energy, in contrast to what is observed in Fig. 2. This increase in energy of *all* 2*e*-2*h* states is a finite size effect that is understandable. For $\delta = 0.5$, the excitations are bandlike. As δ decreases, the ground state begins to have strong covalent contributions, and thus the exciton begins to resemble the single ion pair discussed for the strong-coupling limit of Eq. (1). Unlike the strong-coupling limit though, the particle-hole pair is not localized to nearest neighbors but is spread out over several sites. Since the particle and the hole also tend to avoid the ends of an open chain, the two-exciton states in weakly correlated short chains are effectively "squeezed," which raises their energies relative to the $1B_u$ with a single ion pair (in other words, finite size effects associated with various eigenstates increase with their energies [15]). What is more significant in the present context, however, *is the clear emergence of a level C above B, for* $\delta \leq 0.3$, *which is more strongly dipole coupled to the* $1B_u$ *than B is.* As discussed above, this is a distinct signature of stable biexcitons in the long chain limit.

The occurrence of stable biexcitons below the two-exciton continuum can explain a longstanding mystery in the photophysics of conjugated polymers. In many conjugated polymers a high energy (1.4–1.8 eV) ps PA that is *distinct* from PA due to bipolarons or triplet excitons has been observed [4,8–10]. No such PA is expected within single-particle electron-phonon coupled models [1]. Our results show that within the Coulomb-correlated model a natural explanation of the PA emerges as the optical transition from the exciton to the biexciton. An alternate explanation to ps PA has recently been suggested using a two-polaron mechanism [19], within which dissociation of the exciton occurs immediately after its creation due to interchain migration of the electron or the hole, creating two polarons in short polymer segments. PA within this picture corresponds to polaron absorptions of short chains. The observation of the ps PA in the PDAs [9] with long chains and large interchain separations is against the two-polaron picture. Furthermore, PA at the same energies are seen in thin films and solutions of PPV derivatives [20]. Interchain migrations of electrons and holes are not possible in solutions, and therefore the solution studies are also against the two-polaron mechanism. Finally, in polyphenyleneacetylene [21], ps PA and photoluminiscence decay together for up to 3 ns, strongly supporting the biexciton picture for PA. In Ref. [16], a novel two-photon absorption experiment using the pump-probe technique was used to prove the biexciton nature of the final state to which PA occurs in a charge-transfer solid. We propose a similar experiment to confirm the mechanism of PA in conjugated polymers in which the $2A_g$ is above the $1B_u$.

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