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EXCITONIC EFFECTS IN THE OPTICAL PROPERTIES OF CONJUGATED POLYMERS AND FULLERENES

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Abstract Important roles of excitons in the linear and nonlinear optical properties of conjugated polymers and fullerene crystals are demonstrated on the basis of calculations using the conifguration interaction method for the Pariser-Parr-Pople model of interacting π electrons. For polymers we study: (i) the excitonic features in third-order nonlinear optical susceptibilities; (ii) the optical properties of a relaxed exciton polaron; (iii) the role of biexciton-like states in the two-photon absorption spectrum. For fullerenes, we discuss the excitonic nature of photoexcited states in C_{60} crystals.

INTRODUCTION

Delocalized π electrons play important roles in the optical properties of one-dimensional π-conjugated polymers. Many theoretical works from various different points of view have been put forward. The most important difference among the theories may be the strength of electron-electron (e-e) interactions. Models such as the Su-Schrieffer-Heeger model[1] neglect e-e interactions, while strong e-e interactions are taken into account in models such as the Hubbard model and the Pariser-Parr-Pople (PPP) model. The latter models have been studied for small chains, and the results are in agreement with experiments in polyene oligomers.[2] However, appropriate interaction parameters for bulk solids of long polymers are not known. Our basic standpoint[3] is that the e-e interactions are substantially screened in solids because of dense π electrons. We therefore employ the PPP model with weak or moderate e-e interactions.

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With this assumption we use the configuration interaction (CI) method, especially, CI among single excitations (single-CI). This allows us to describe exciton states on a fixed lattice of a perfect chain[4] as well as relaxed exciton polarons[5]. By taking account of CI among double excitations (double-CI), we can treat biexciton states as well.[6]

Fullerens such as C_{60} are also π-conjugated semiconductors. We have studied exciton effects in C_{60} solids by use of a similar approach. This will be briefly discussed in the last section of this paper and more fully in a separate paper[7].

EXCITONS IN CONJUGATED POLYMERS

The basic parameters of the model are the alternation of nearest-neighbor transfer energy, δt, and the interaction potential V_{nm} between electrons at the n-th and m-th sites on the chain. We take a simple form

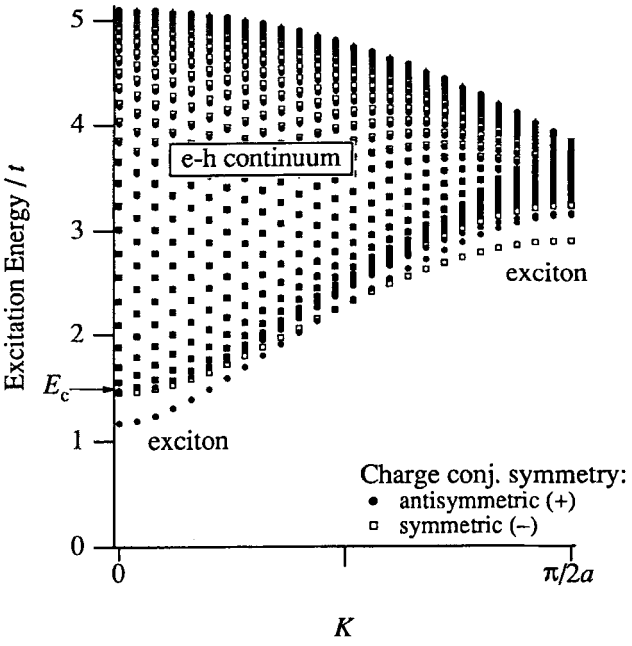

FIGURE 1 Excitation energies plotted against wave number K, calculated by the single-CI method for a ring of N=100 sites with δt=0.2t, U=2t and V=t. Filled circles (empty squares) are + (–) states in terms of charge conjugation symmetry.

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$V_{nm} = V/|n-m|$ $(n \neq m)$ and $V_{nn} = U$ as used in Ref.4. The parameter values used in the following calculations are δt=0.2t, U=2t and V=t.

By using the cyclic boundary condition, single CI claculations can be carried out easily for very long chains with several hundred sites. Such a length is long enough to distinguish exciton states from the electron-hole continuum in the sense the energy discreteness of the continuum due to the finite size effect is much smaller than the exciton binding energies. In Fig.2 we display an example of calculated excitation energies against wave number K for a ring of 100 sites. we can identify branches of exciton states below the electron-hole (e-h) continuum. The edge of the continuum, E_c, is defined as the interband gap of the Hartree-Fock one-electron states. The excitonic character of each state can be also checked by examining its wave function in real space.[4]

The characteristic features of various third-order nonlinear optical susceptibilities $\chi^{(3)}$ and the linear susceptibility $\chi^{(1)}$ calcualted in the single-CI approximation[8] are summarized in Fig.2. The linear absorption spectrum, Im[$\chi^{(1)}(\omega)$], in Fig.2(a) is dominated by the lowest exciton state, while the contribution of the e-h continuum above E_c is almost negligible. The two-photon absorption (TPA), Im[$\chi^{(3)}(-\omega;\omega,-\omega,\omega)$], shown in Fig.1(b), on the other hand, is large only in the two-photon resonance region for the second lowest exciton and the e-h continuum. The electroabsorption spectrum, Im[$\chi^{(3)}(-\omega;\omega,0,0)$], displayed in Fig.2(c) contains two gross features: the low-energy structure around the lowest exciton energy, corresponding to the Stark shift of the exciton level; and the high-energy structure around E_c. The third-harmonic generation spectrum, Im[$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$], in Fig.2(d) possesses three peaks. In the order of increasing energy, the first one is due to three-photon resonance with the lowest exciton state; the second peak and its high-energy tail originate from three-photon resonance with the states above around E_c. The third peak is due to two-photon resonance with the second exciton and the e-h continuum states above E_c. Many of these characteristic features associated with exciton and e-h continuum states are in fact observed in polymers such as polydiacetylene[9-11] and polysilane[12].

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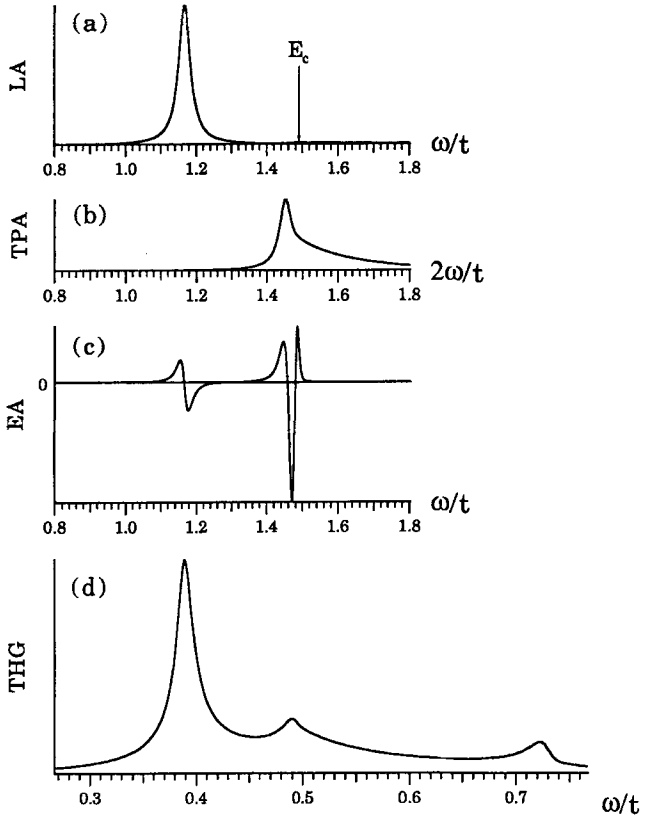

FIGURE 2 Four kinds of optical spectra calculated by the single-CI method for a ring of N=1000 sites with the same parameters as in Fig.1: (a) linear absorption; (b) two-photon absorption; (c) electroabsorption; (d) third-harmonic generation.

BIEXCITONIC STATES IN CONJUGATED POLYMERS

The TPA spectrum in Fig.2(b) was limited to the range of ω much smaller than the one-photon resonance energy. When ω becomes close to the energy of exciton, we need to take into account two-exciton states for intermediate states. For this purpose, we expand our CI basis to include double excitations.[6] Fig.3 is a typical example of calcualted TPA spectrum $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ for N=40. It consists of many positive peaks, which may be grouped into two: the low energy weak peaks and the high energy strong peaks. The former corresponds to the TPA due to excitons discussed in the

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previous section. The latter is mainly due to double excitations. The fact that the strong TPA appears below the one-photon resonance implies that the exciton-exciton interaction is attractive and a biexciton is formed. However, there is strong mixing between single and double excitations, so that the biexciton components are distributed over many states. For stronger Coulomb interactions, the distinction between the excitonic and biexcitonic TPA becomes ambiguous.[6]

EXCITON-POLARONS IN CONJUGATED POLYMERS

So far we have not considered the coupling of excitations to the lattice, in spite of the fact that we have taken into account the bond alternation due to the SSH-type electron-lattice coupling. Because of this coupling, the optical spectra considered in the previous sections will be much influenced by quantum and thermal lattice fluctuations. This effect has been simulated within the classical approximation by introducing Gaussian disorder to the transfer energies.[13] Averaging over many samples yields asymmetric broadening of resonance peaks.

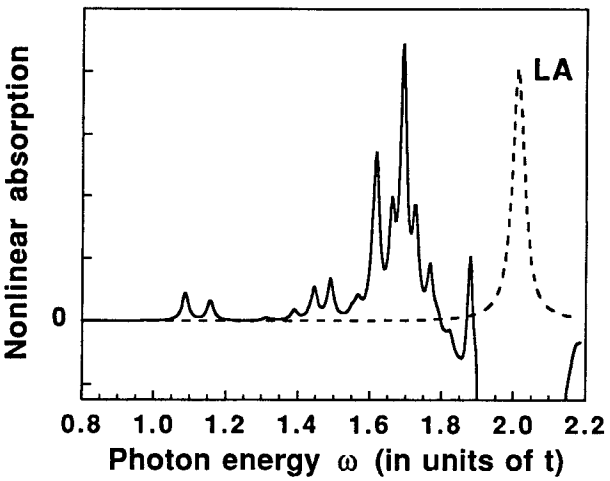

FIGURE 3 Nonlinear absorption spectrum calculated by double-CI method for a ring of 40 sites with the same parameters as in Fig.1. A broken curve is the linear absorption.

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When an exciton is created on a chain, it will be accompanied by lattic relaxation, forming an exciton polaron. This is well known for the SSH model, in which an exciton polaron coresponds to a neutral bipolaron.[14] We have recently studied the exciton polaron in the presense of moderate e-e interactions by use of the single-CI method.[5] Figure 4(a) displays an example of adiabatic potential curves with respect to polaron deformation Q, assuming lattice displacements $u_n = (-1)^n u_0(1-Q\mathrm{sech}[(n-c)/\xi])$ with u_0 being the ground state displacement. (ξ is optimized for the lowest triplet exciton polaron: ξ=2.25 here.) The lowest relaxed excited state is a triplet exciton polaron. Its absorption spectrum, as shown in the lower

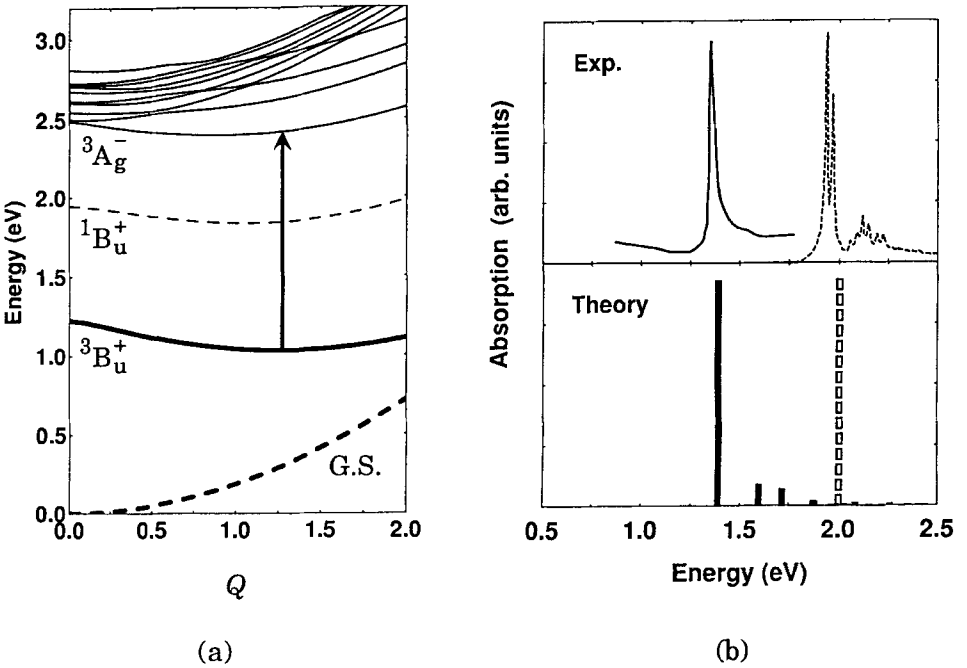

FIGURE 4 (a) Adiabatic potential curves calculated with the single-CI method[5] for the ground state (G.S.), the lowest triplet ($^3B_u^+$) and singlet ($^1B_u^+$) excitons, the second lowest triplet ($^3A_g^-$) exciton and some more excitations, plotted against the polaronic deformation coordinate Q. (b) Photo-induced absorpton[15] observed in polydiacetylene (solid curve) and the calculated absorption spectrum of the triplet exciton polaron (solid bar).[5] Also the experimental[10] (broken curve) and theoretical (broken bar) linear absorption spectra are also shown.

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panel of Fig.4(b), is dominated by a single transition to an excited state of the exciton polaron, the transition being indicated by an arrow in Fig.4(a). This result well explains the photoinduced absorption spectra of polydiacetylene shown in the upper panel of Fig.4(b). Similar spectra have also been observed in poly(*p*-phenylene vinylene). Note that the energy position and the sharp width of the photoinduced absorption cannot be explained without taking Coulomb interactions into account.[14]

EXCITONS IN C_{60} FULLERITES

We have also studied the optical excited states of C_{60}, which are spherical π-conjugated molecules. In this case, it is not so meaningful to distinguish an exciton and an unbound electron-hole pair inside the molecule, although Coulomb interactions are important to describe the excited states.[16] The distinction becomes important when we consider a C_{60} crystal, which is a molecular crystal. We have performed single-CI calculations for a system consisting of four C_{60} molecules with the periodic boundary condition in all the three-dimensional directions.[7] We

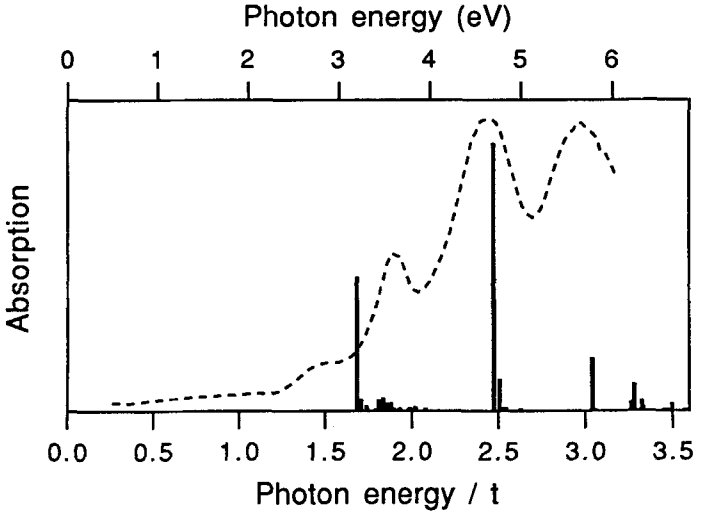

FIGURE 5 Absorption oscillator strengths calculated by the single-CI method for a $(C_{60})_4$ cluster with the periodic boundary condition and $t'=0.1t$, $t_w=0.1t$, $U=4t$, and $V=2t$. The broken curve is the absorption spectrum of a C_{60} film observed by S. L. Ren et al.[17] (top scale).

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take into account intramolecular nearest neighbor transfer energies $t+\frac{2}{3}t'$ $(t-\frac{1}{3}t')$ for double (single) bonds, intermolecular transfer energies t_w, together with intra- and intermolecular Coulomb interactions in the form of the Ohno potential $W(r)=1/\sqrt{(1/U)^2+(r/r_0V)^2}$ with r_0 being the average bond length on a molecule. Figure 5 displays the calculated absorption oscillator strengths. The states with large oscillator strength at about $1.7t$, $2.5t$, and $3t$ may well correspond to the observed absorption peaks at 3.5, 4.6, and 5.7 eV. By analyzing the wave functions of these states, we found that the states are Frenkel-like intramolecular excitons with small intermolecular charge-transfer components.[7] Therefore, exciton effects are also important for the optical properties of fullerites, although in a way somewhat different from conjugated polymers.

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