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Shuji Abe [a b] & W. P. Su [a]

[a] Department of Physics, University of Houston, Houston, Texas, 77204-5504, U.S.A.

[b] Eiectrotechnical Laboratory, Umezono, Tsukuba 305

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EXCITONS AND CHARGE TRANSFER STATES IN ONE-DIMENSIONAL SEMICONDUCTORS

SHUJI ABE*,† and W. P. SU*
*Department of Physics, University of Houston, Houston, Texas 77204-5504, U.S.A., and †Electrotechnical Laboratory, Umezono, Tsukuba 305, Japan

Abstract The one- and two-photon absorption spectra of one-dimensional Peierls semiconductors have been calculated by taking account of the effect of exciton. In the one-photon spectrum, the lowest exciton state gains anomalously large oscillator strength as a result of one-dimensionality. In the two-photon absorption spectrum, interband transitions are as important as exciton transitions.

Keywords: Nonlinear optics, polymers, excitons, two-photon absorption, one-dimensional system, optical properties

INTRODUCTION

Nonlinear optical properties of one-dimensional organic semiconductors, such as polydiacetylene, has attracted much attention recently.[1–3] Although there have been substantial theoretical studies on exciton states in such materials,[4] the role of excitons in the nonlinear optical properties has not yet been clarified. One of the authors has recently investigated theoretically the effect of exciton on the linear absorption spectrum in a model of Peierls semiconductors.[5] In the present paper, we further calculate the two-photon absorption spectrum in the same model, and compare the results with the one-photon spectra.

EXCITON EFFECT IN PEIERLS SEMICONDUCTORS

We consider a half-filled, dimerized one-dimensional chain possessing alternated transfer energies t_1 and t_2 ($t_1 > t_2 > 0$).[6] The electronic structure of such a system depends on the degree of dimerization, and is well characterized by the gap parameter Δ and the delocalization length ξ, given by $\Delta = \mid t_1 - t_2 \mid$ and $\xi/a = \sqrt{t_1 t_2}/\Delta$, where a is the interatomic distance (we assume $\xi > a$). Then

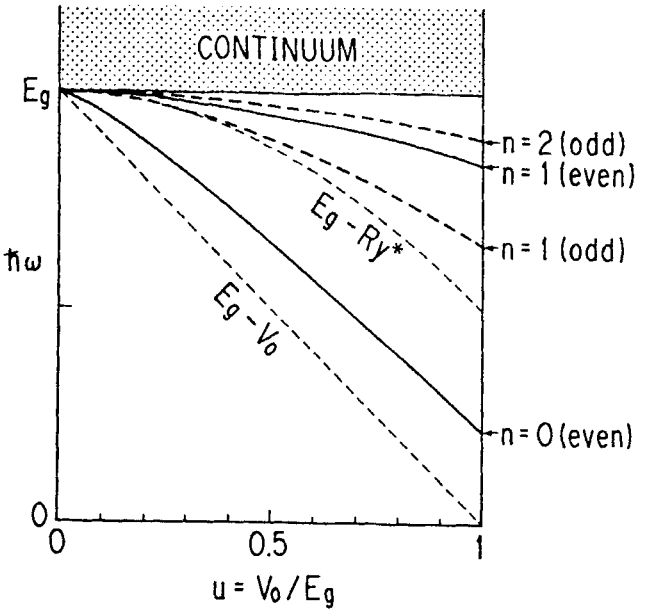

FIGURE 1. Calculated energy levels of exciton with $K = 0$ (center-of-mass momentum) as functions of u. Only the four lowest states are shown. For reference, two energies $E_g - V_0$ and $E_g - Ry^*$ are shown by thin broken lines, where Ry^* is the effective exciton Rydberg energy.

we consider the long-range Coulomb attraction (the exciton effect) between an conduction electron and a valence hole in the continuum limit.

The most crutial point here, which is specific to one dimension, is that the effective attractive potential has a lower-length cutoff, which is considered to be given by the delocalization length ξ.[5] Then this one-dimensional potential problem are solved by using Whittaker functions.[7] The exciton effect is represented by a single dimensionless parameter u defined as $u \equiv V_0/E_g$, where $V_0 \equiv e^2/\epsilon\xi$ is the cutoff energy (ϵ: the dielectric constant) and $E_g \equiv 2\Delta$ is the optical gap.[5]

Figure 1[5] shows the calculated energies of a few lowest exciton states as functions of the interaction strength u. The even-parity (symmetric) states are optically allowed in one-photon transitions, whereas the odd-parity (antisymmetric) states are accessible by two-photon transitions. (Note that the symmetry here refers to that of the exciton envelop wavefunction in the continuum model.)

ONE- AND TWO-PHOTON ABSORPTION SPCTRA

The one-photon absorption spectrum in the case of $u = 0$ has a divergence of $(\hbar\omega - E_g)^{-\frac{1}{2}}$ due to the one-dimensional van Hove singularity of the joint density of states.[6] For a finite u, this divergence at E_g is removed in such a way that the interband transitions above E_g and the semicontinuous exciton transitions below E_g are connected continuously at E_g.[7]

Figure 2 shows calculated one-photon absorption spectra for two values of u with assuming a small value of broadening ($\Gamma/E_g = 0.03$). Even for a small $u(= 0.1)$, the lowest exciton state ($n = 0$) takes up a large portion (about half) of the total oscillator strength. The interband continuum forms a continuous tail above the peak, making the peak fairly asymmetric. For a larger $u(= 0.35)$, the $n = 0$ state dominates the spectrum, so that the peak becomes almost symmetric.

The calculation of the two-photon absorption spectrum requires the evaluation of the dipole matrix elements between excited states. Especially, the matrix elements between continuum states must be treated carefully, since they involve a derivative operator, as in the case of non-interacting electrons.[8] Details of the calculations will be reported elsewhere. In contrast to the one-photon absorption, the two-photon transition for $u = 0$ is not allowed at E_g, so that the spectrum starts as $(2\hbar\omega - E_g)^{\frac{1}{2}}$, having a broad peak at a finite energy above the gap.[8]

Figure 3 shows calculated two-photon absorption spectra for the same values of u and Γ as in Figure 2. The exciton effect relaxes the selection rule at the gap, and in fact substantial oscillator strength is accumulated near E_g. For $u = 0.1$, however, the peak is still located above E_g, in contrast to the one-photon absorption. For $u = 0.35$, it is located below E_g at the lowest odd-parity level ($n = 1$), while the continuum states still form a large tail. (The peak around $2\hbar\omega/E_g \simeq 1.55$ is due to one-photon resonance.)

DISCUSSION

The most important feature of the exciton states thus obtained is that the lowest ($n = 0$) state has a quite special character compared with the other states. Usually, the binding energy and the radius of an exciton is measured by the Rydberg energy Ry^* and the Bohr radius a_B^*. In fact, all the states other than $n = 0$ obey this rule. In contrast, the lowest state is determined mostly

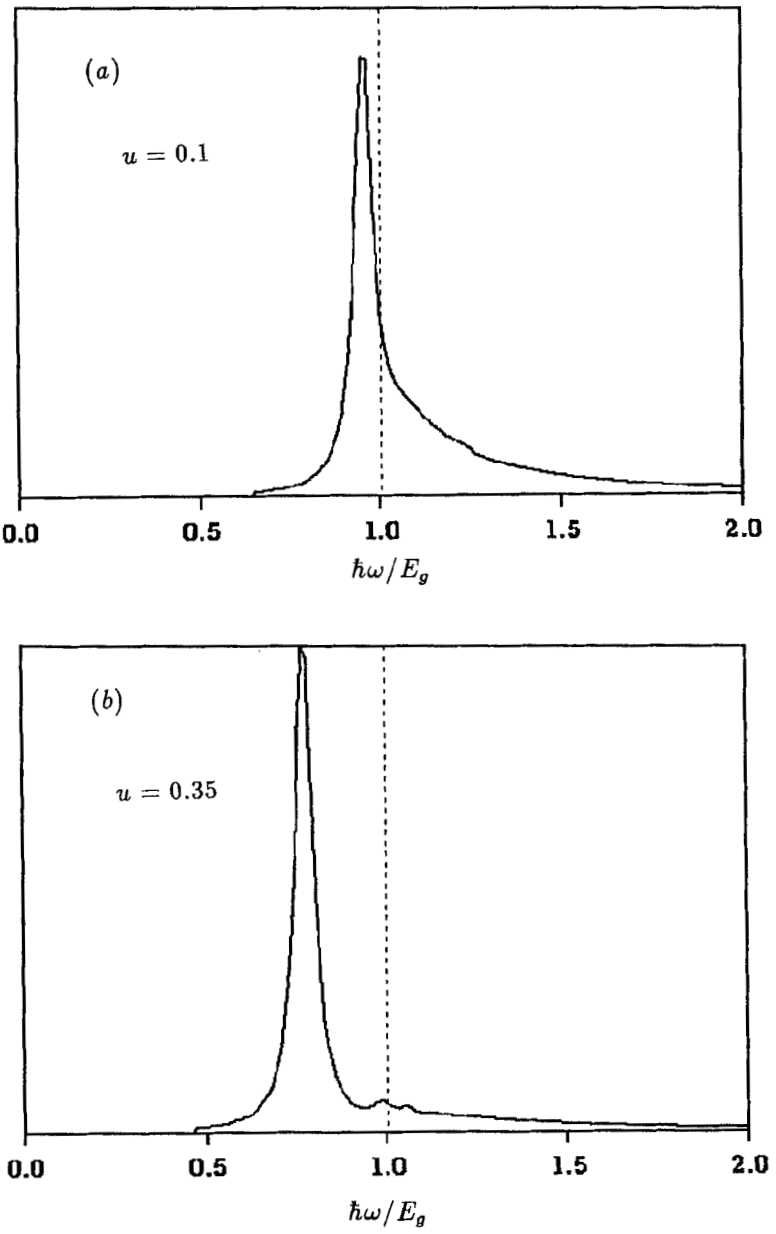

FIGURE 2. Calculated one-photon absorption spectra for (a) $u = 0.1$ and (b) $u = 0.35$.

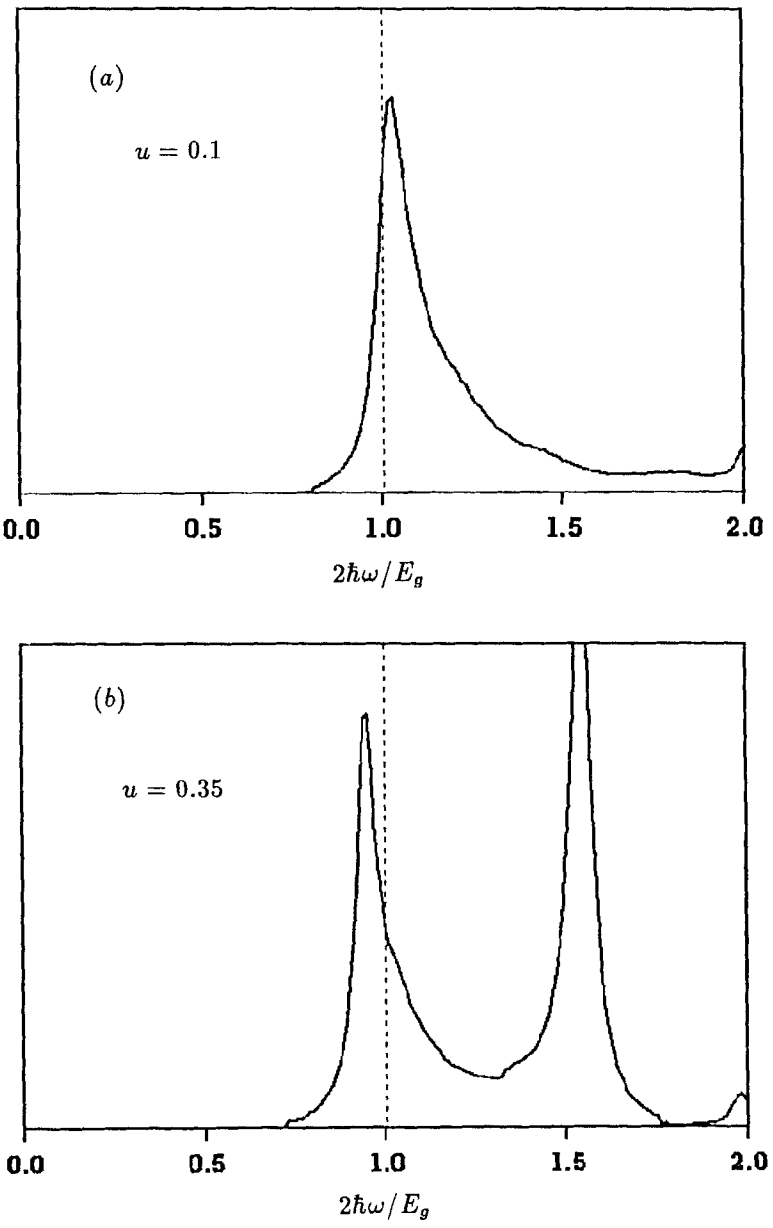

FIGURE 3. Calculated two-photon absorption spectra for (a) $u = 0.1$ and (b) $u = 0.35$.

by the cutoff: its binding energy is close to V_0 and its radius, to ξ. In a sense, the lowest exciton state assumes the smallest size available, so that it is like a Frenkel exciton. All the higher states, in which the electron-hole distance is much larger, may be looked upon as charge-transfered states.

Because of this special character, the $n = 0$ state gains a large portion of the total oscillator strength in the one-photon absorption spectrum. On the other hand, the lowest odd-parity state ($n = 1$) is not special in this sense. This difference results in different behavior in the one- and the two-photon spectra shown above. In short, the contribution from exciton states is relatively smaller in the two-photon spectrum than in the one-photon one.

In the present paper, we have treated the exciton effect in a simple continuum model by assuming an effective potential. More rigorous results will be obtained by calculating excited states in the tight-binding model with considering bare long-range Coulomb interactions between electrons. A numerical study in such a direction is now under way.[9] Also, a necessary next step will be to take the effect of quantum lattice fluctuations[10] into account.

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