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Excitonic Polarons in Molecular Crystals*

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Band narrowing and band shifts due to excitonic-polaron formation are considered for an electronically polarizable medium. Experimental evidence of such effects in molecular crystals is cited. The central result is that the electron-exciton interaction in the strong-coupling regime leads not only to an indirect attractive electron-electron interaction, but also because of small-polaron formation leads to severe band narrowing. This band narrowing tends to favor the insulating state. The implications of the excitonic polaron for the metal-insulator transition, organic semiconductors, and the question of the possible existence of superconductivity in organic molecular crystals are discussed.

Since Landau first considered the interaction of a charge carrier with a lattice polarization, the coupled electron-lattice or polaron problem has been of continued interest in the study of solids.[1,2] Of particular importance is the *small-polaron* limit, relevant when the binding energy of the electron and the induced lattice polarization is sufficiently larger than the electronic energy bandwidth that the lattice distortion is localized to the immediate vicinity of the electron. Since in this regime the electron must carry the compact lattice polarization as it moves from site to site, small-polaron formation leads to significant band narrowing as well as sizable band shifts.[3]

However, the total polarization in a solid consists of two parts, the lattice polarization and the electronic polarization. In this paper we wish to point out that the electronic polarizability of molecules in the vicinity of a given electron in a molecular crystal leads to small-polaron effects with important experimental consequences. Since the electronic polarizability of the molecules in question can be viewed as arising from virtual excitation of molecular excitons (propagating molecular excited states or Frenkel excitons), the electron together with its tightly bound polarization cloud will be denoted as an *excitonic polaron*. The excitonic or electronic polaron was first considered by Toyozawa.[4] The Toyozawa theory is directly analogous to conventional polaron theory in the weak-coupling limit where a small effective-mass enhancement results. However, excitonic-polaron effects should be particularly important in crystals containing heterocyclic hydrocarbons, since these molecules are known to have large π-electron polarizabilities.[5] Moreover, the narrow bandwidths associated with the relatively weak intermolecular transfer integrals found typically in molecular crystals suggest that the strong-coupling limit is appropriate and the excitonic polaron will be "small" in the conventional sense described above.

As a model we consider a molecular crystal consisting of two perfect rigid-lattice subsystems: a narrow electron energy band containing conduction electrons and a separate subsystem of polarizable molecules whose electrons are paired in σ and π molecular orbitals. The elementary excitations of this polarizable subsystem are propagating excitons.[6] For simplicity we consider only a single exciton band.

Real systems of this kind are explicitly found in nature as demonstrated by the tetracyanoquinodimethan (TCNQ) charge-transfer salts as well as a variety of organic semiconductors. The TCNQ salts are particularly relevant, since experimental data exist on transfer integrals and Coulomb interactions for similar TCNQ$^-$-anion stacking with both polarizable organic cations and nonpolarizable inorganic cations.[7–10] More generally, the model includes schematically systems such as neutral TCNQ or other organic semiconductors where carriers have been injected by photoexcitation or simple thermal activation.

The Hamiltonian describing the model system can be approximated as

$$H = H_e + H_{e-e} + E_E + H_{e-E} \tag{1}$$

where H_e and H_{e-e} refer to the conduction electrons of the narrow band, H_e to the exciton energy of the single exciton band, and H_{e-E} to the conduction-electron–exciton interaction.

The terms representing the conduction electrons will be assumed to be of the form of the Hubbard Hamiltonian[11]:

$$H_e + H_{e-e} = -t \sum_{\substack{ij\\ \sigma}} c^\dagger_{i\sigma} c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow} \tag{2}$$

where t is the transfer matrix element between the ith and jth sites; $c^\dagger_{j\sigma}$ and $c_{j\sigma}$ are, respectively, the creation and annihilation operators of an electron with σ spin; and U is the Coulomb repulsion potential acting when two electrons are simultaneously on the same molecular site.

The exciton energy term is given by

$$H_E = \sum_{\vec{k}} \hbar\omega_{\vec{k}} a^\dagger_{k} a_{\vec{k}} \quad , \tag{3}$$

where $a^\dagger_{\vec{k}}$ and $a_{\vec{k}}$ are, respectively, the creation and annihilation operators for an exciton of wave number $\vec{k}$ and energy $\hbar\omega_{\vec{k}}$. Frenkel excitons have been studied in detail by many authors.[6,12] The molecular excited states propagate through the crystal via exchange-excitation transfer. Since excitons are formally bound electron-hole pairs with at most one per site, such excitations are rigorously neither bosons nor fermions. We shall treat the excitons in the boson approximation, invoking the usual argument that as long as the exciton density is low, the kinematic interaction (by analogy with the Dyson spin-wave theory[13]) should be small.

The electron-exciton interaction is responsible for the emission and absorption of virtual Frenkel excitons by the conduction electrons. We consider the strong-coupling limit in which the conduction-electron bandwidth is narrow compared to the electron-exciton interaction. The conduction electron can then be treated as a static point charge at a single lattice site $\vec{r}_j$ interacting with the nearby polarizable medium. In this limit the electron-exciton interaction takes the form[14,15]

$$H_{e-E} = \frac{i\Gamma}{\sqrt{N}} \sum_{\vec{k}} \left(a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}_j} - a^\dagger_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}_j} \right) , \tag{4}$$

where the coupling constant Γ is assumed for simplicity to be k independent, that is, short range. The form of Γ will be discussed below.

This Hamiltonian was previously considered by Chesnut,[14] who focused on the effect of the conducting system on the exciton dispersion relation. The fact that any such effect is small is not surprising, since the linear coupling is equivalent to a displaced oscillator Hamiltonian. As a result, any changes in the exciton dispersion relation are small.

In the case of a single electron in an otherwise empty conduction band, Eq. (1) becomes

$$H = H_E + H_{e-E} + H_e \quad . \tag{5}$$

The first two terms are dominant and must be considered in zeroth order. The electron kinetic energy H_e is to be treated subsequently in tight-binding perturbation theory. Although Eq. (5) is formally identical with the conventional polaron Hamiltonian, there are important physical differences. The polarization in question is electronic in origin, and should be large in magnitude since the coupling constant Γ arises directly from electron-electron Coulomb repulsion. In addition, the fact that typical exciton energies are of order 2 eV as compared with 0.02 eV for typical phonon energies qualitatively changes the problem. Because of this relatively large exciton energy the number of real excitons present will be negligible at all temperatures. This is quite different from the phonon case where presence of thermal phonons greatly complicates the problem.[3]

Under the conditions appropriate to small-polaron formation, the resulting effective tight-binding transfer integral t^* can be obtained by the usual canonical transformation method[1,15]:

$$t^* = te^{-S} \quad , \tag{6}$$

where

$$S = \Gamma^2/(\hbar\omega_0)^2 \tag{7}$$

and the polaron binding energy or band shift is given by

$$E_B = -\Gamma^2/\hbar\omega_0 = -\hbar\omega_0 S \quad . \tag{8}$$

In the above, we have neglected the small-exciton dispersion and replaced ω_k by ω_0. Negligible error is involved, for the exciton bandwidth is much less than the average excitation energy ω_0. The exponentially reduced t^* leads in tight-binding theory to a similarly narrowed conduction band. The results for t^* and the associated polaron band are directly analogous to those obtained in the lattice-polaron problem.[3]

An expression for the coupling constant Γ can be obtained from a simple classical argument. The classical binding energy is of the form

$$E_B = -\tfrac{1}{2}\alpha E^2 , \tag{9}$$

where α is the molecular polarizability and E is the electric field at the molecule due to the electron nearby on the conducting chain; $E = e/a_0^2$. Thus, using Eq. (8), we have

$$\Gamma = \left(\frac{\alpha}{2a_0^3}\right)^{1/2} \left(\frac{e^2\hbar\omega_0}{a_0}\right)^{1/2} . \tag{10}$$

In the above, we assume an interaction only between the electron and its nearest neighbors a distance a_0 away. More than one near neighbor will generally be involved in a real system, thereby increasing S somewhat, depending on the detailed lattice structure.[16]

Using Eqs. (7) and (10), one finds

$$S = \frac{\alpha}{2a_0^3}\,\frac{e^2/a_0}{\hbar\omega_0} . \tag{11}$$

To estimate S we use numbers typical for molecular crystals with exciton bands in the visible portion of the spectrum. Taking $a_0 \sim 3$–5 Å, $\alpha \sim 50$ Å^3, $e^2a^{-1} \sim 3$–4 eV, and $\hbar\omega_0 \sim 2$ eV, one finds S in the range $\frac{1}{2}$–4, thus making a band narrowing by an order of magnitude not unreasonable, especially when multiple nearest neighbors are included. The fact that S can easily be greater than unity justifies *a posteriori* the small-polaron point of view.

The simplest application of the consequences of small-excitonic-polaron formation can be seen in the photoconductivity and semiconductivity of polarizable molecular crystals such as neutral TCNQ. In such organic semiconductors the polaron binding energy shows up as a band shift decreasing the energy gap for thermal or photoexcitation of carrier. In first approximation the energy gap is the charge-transfer energy between two TCNQ^0 molecules, $I - A = U_0$, where U_0 is the Coulomb interaction. When the polaron binding is considered, this is reduced by the binding energy of the electron-polaron and the hole-polaron, implying an effective Coulomb interaction:

$$U_{\text{eff}} = U_0 - 2E_B . \tag{12}$$

This shift is well known[17] and has been observed, for example, in neutral TCNQ by Hiroma *et al.*[18] From their analysis, one finds experimentally $E_B \simeq -2$ eV, which by Eq. (8) leads to a value of $S \simeq 1$, in agreement with the above estimate. We conclude that the excitonic-polaron band shift is an important factor in determining the magnitude of the energy gap in organic semiconductors. In addition, the carrier effective mass should be quite heavy with associated low mobilities, as seen from Eq. (6). Note, however, that activated hopping is *not* expected, because of the very high energy of the excitons.

The expression (6) for t^* represents adequately the one-electron aspects of the problem. To generalize to the many-electron system one must consider polaron interactions. Two polarons interact directly via the Coulomb interaction [U in Eq. (2)] and indirectly via the induced excitonic polarization. The indirect interaction arises from the polaron binding energy. For two widely separated excitonic polarons in a crystal, the total binding energy is

$$2E_B = -2\hbar\omega_0 S , \tag{13}$$

whereas if both electrons are simultaneously on the same anion site (within this linear theory),

$$E_B(2) = -4\hbar\omega_0 S . \tag{14}$$

The binding energy is twice that found for the two separated excitonic polarons, implying the existence of an attractive electron-electron interaction which arises indirectly via the excitons. The Coulomb repulsion U in Eq. (2) is in fact to be interpreted as the charge-transfer energy between a state with two sites each having one electron, and a state where one site is neutral and the other doubly negative. Thus, when dealing with the interacting polarons, the resultant interaction may be written as an effective two-body term

$$U^* = U - 2\hbar\omega_0 S = U - 2E_B . \tag{15}$$

Using the effective one-electron transfer t^* and the effective interaction U^* one may rewrite the many-electron Hubbard Hamiltonian as

$$\mathcal{H} = -t^* \sum_{\substack{i,j\\ \sigma}} \tilde{c}^\dagger_{i\sigma}\tilde{c}_{j\sigma} + U^* \sum_{i} \tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow} , \tag{16}$$

where the operators $\tilde{c}_j$, etc., represent the dressed electron, i.e., polarons.

The extension of the small-polaron theory to the many-electron system is not done trivially. Since the electron-exciton coupling is assumed to be large, the N-electron system requires polarization contributions from each exciton mode which are of order unity. In such circumstances, the boson assumption becomes questionable and polaron-polaron interactions must be taken into account. The lowest-order indirect interaction is already included in Eq. (15). Higher-order interaction terms exist in principle, but their magnitude depends on the nonlinear terms in the molecular polarizability, or equivalently on anharmonic terms in the exciton Hamiltonian. Thus, within the harmonic approximation, superposition holds and the generalization to the many-polaron system is valid. Subtle effects on t^* can arise from correlation in the many-particle wave function, but analysis shows[19] that the resultant t^* is if anything narrower than that given in Eq. (6). (This additional narrowing arises from the *double* orthogonality involved in making an electron-hole pair.) These arguments are physically sound and appear to be borne out in the experimental results described below, but the need for further theoretical study of this question is evident.

In anion radical salts such as those based on TCNQ the band narrowing expressed by Eqs. (6) and (12) can have severe consequences. The metal-insulator transition in such systems is determined by the ratio of the Coulomb interaction to the bandwidth.[9,10] Although the full interaction Hamiltonian represents a formidable problem, the high frequency of the exciton together with the strong-coupling assumption implies that one can solve the single-electron–exciton problem first and subsequently consider the interaction between electrons as described above. This approach is well within the spirit of the Hubbard model. In this limit *the excitonic-polaron band narrowing strongly favors the Mott insulating state*. We note in this respect that the experimental results for t^* and U^* in N-methylphenazinium-TCNQ ($t^* = 0.02$ eV and $U^* = 0.17$ eV[9,10]) may be as much as an order of magnitude smaller than in other TCNQ salts not containing polarizable cations.[7] A similarly narrow band is implied in quinolinium $(\mathrm{TCNQ})_2$.[8] Although such transfer integrals are extremely sensitive to details of the lattice structure, we suggest that the implied band narrowing and reduced interaction is of excitonic-polaron origin.

The indirect attractive interaction derived in Eqs. (13)–(15) is the strong-coupling analog of Little's indirect interaction via excitons,[20] which has been suggested as a means of obtaining high-temperature superconductivity. We note, however, that although the attractive interaction varies linearly with S, the bandwidth decreases exponentially. Thus attempts to achieve a strong, indirect, attractive interaction may necessarily result in systems with extremely narrow bandwidth. Consequently, in the strong-coupling limit considered here, as the electron-exciton interaction is increased, it appears likely that an insulating state would always be achieved before the superconducting state.

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