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Exciton Renormalization in Conducting Molecular Solids

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Abstract—The effects upon exciton properties of a coupling between excitons and charge carriers in a conducting molecular solid are calculated employing a canonical transformation. The conducting nature of the system is predicted to introduce a shift to higher energies of the exciton energy; an *additional* blue shift is predicted if the system is superconducting, yielding in principle a method of detecting the superconducting transition by its effect upon the exciton subsystem. Application of the results to systems other than molecular solids is noted, and a qualitative self-consistent treatment of the effects upon the superconducting properties of the system is given.

I. Introduction

A recent conjecture by Little[1] deals with the possibility of observing superconductivity in an organic solid. Little's idea replaces the electron–phonon coupling felt to be the prime cause of superconductivity in metals with an electron polarization effect; conduction electrons in a conducting subsystem interact via Coulomb forces with non-conducting, tightly bound electrons on polarizable molecules of a second subsystem. Since, in effect, one is dealing with a light electron rather than a heavy ion, superconducting transition temperatures an order or two greater in magnitude than those observed in ordinary superconductors are envisaged.

Although not explicitly done so by Little, his coupling may be re-expressed as an electron–exciton interaction, in which configurational mixing of the ground and excited molecular subsystem

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† This work was initiated while the author was in the Central Research Department, E. I. duPont, Wilmington, Delaware.

states is induced by interaction with the conduction electrons. This results in a reduction of the electron–electron repulsion in the conducting subsystem, and, so Little argues, if sufficiently strong, may lead to an effective attractive interaction; this attractive interaction may then render the Fermi sea unstable with respect to a superconducting state. Little's emphasis was on this aspect of the total system.

Little's conjecture regarding organic superconductors is interesting. Regardless of its superconducting ability, or lack thereof, systems such as Little discusses can well be expected to have unusual properties. Thus, it was considered worth while to examine effects which, in such a model system, might occur in the non-conducting molecular subsystem caused by the coupling to the conduction electron subsystem; that is, the exciton renormalization due to the conducting nature of the system. Furthermore, it is important to do so without regard to how the conducting properties of the molecular solid have been gained, so that, as far as possible in the simple model approach taken, the calculations will not be biased by possible errors involved in the presumed conduction mechanism. We shall examine effects produced assuming the electronic system is poorly conducting, normally conducting, or superconducting. A crude model is also solved to indicate how the excitons may affect the superconducting properties involved.

II. Model

As indicated before, the total system is constructed of two major subsystems. One is what we shall term the electronic system and is that subsystem which can be described in terms of a band or bands of nearly free electrons; this is the conducting part of the system, and when we speak of electrons or conduction electrons, we shall be referring to it. The other subsystem, of course, contains electrons too, but, since they are so strongly paired in the molecular binding sense, we shall refer instead to the elementary excitations of this system when discussing it. This subsystem behaves as a molecular solid and its elementary excitations are the tightly bound Frenkel excitons.

We shall be less than completely general from the start by endowing our model solid with certain properties felt to be characteristic of organic solids, conducting or otherwise. The molecular excitation energy (exciton energy band mean) is assumed considerably larger than the electron bandwidth; whereas exciton energies are usually of the order of several electron volts, we shall assume the electronic band width to be of the order of a few tenths of a volt. We shall neglect the zero-order bandwidth of the excitons although band *broadening* due to renormalization effects will be studied. The excitons considered, then, are really completely localized molecular excited states.

There are several comments to be made concerning this assumption. First, it most likely is a good approximation to the type of system Little has discussed. Secondly, molecular exciton bandwidths *are* generally considerably smaller than the energy of the band center; and we are here interested in the *shift* of the exciton energy compared to *changes* in the bandwidth, both quantities being calculable in our model. Also, the use of localized excitons points out clearly the fact that the effects calculated do not depend on intermolecular overlap. Thus, in principle, these effects should be valid in a case where the excitons are localized atomic excitations in a metal. Finally, it must be pointed out that the mixed commutation rules obeyed by excitons render the representation of the present problem extremely complicated if one attempts to include the exciton bandwidth; it is felt that the generality gained does not compensate for the insight lost due to a more complicated symbolism. It might be argued that this approach over-emphasizes the hard-sphere nature of the exciton (that property which gives it mixed commutation rules); however, it is very clear that to treat the excitons in the present calculation as boson-like quasiparticles is to *qualitatively* change the results. It is believed that the zero bandwidth approach is a more nearly correct representation of the system than other similar approximations.

Throughout the discussion, linear subsystems are assumed; that is, the electron and exciton coordinates may be expressed in terms of a site index as along a linear chain. The physical separation of two particles (or quasiparticles) is given by the difference in their site indices. In short, one may picture the total system as two one-dimensional chains side by side, one corresponding to a highly conjugated polyene representing the conducting subsystem and the other a stack of weakly interacting molecules representing the exciton subsystem. This is, in fact, the model Little discusses. However, the one-dimensionality of the problem is used explicitly only in estimating exciton bandwidth broadening to allow an explicit result to be obtained. For the other more important aspects of the present discussion it is used only for simplicity of presentation and conception. It is not necessary for the arguments advanced here, or, for that matter, in Little's discussion.

III. Interacting Subsystems

We presume that only the ground and first excited state of the excitable molecule need be considered, so that the exciton has a simple character: it is either present at a given site (molecule excited) or absent (molecule unexcited). The molecular subsystem wave function is, to zeroth order, taken to be a product function of individual molecular wave functions, each molecular wave function specifying the site on which it is centered and the state of excitation of the molecule at that site.

The electronic and molecular systems are coupled by electrostatic interactions involving both the electrons and nuclei of each system. Let ϕ_n represent a localized electron's wave function centered at site n in the conducting subsystem, and let ψ_{mj} stand for the (many electron) molecular wave function for the molecule at lattice site m and state of excitation j (where $j=0$ for the ground state and $j=1$ for the excited state) in the molecular subsystem. The electrostatic coupling will induce configuration interaction between configurations. These interactions are:

(1) Nuclear–nuclear repulsion. This is some constant for a system of rigid nuclei and will not affect the electronic structure

of the system, the word electronic in this instance being used in its most general sense as referring to *all* electrons in the system.

(2) Conduction electron–molecular nuclei. This interaction results from the electronic charge distribution $\phi_n\phi_{n'}$ interacting with the molecular nuclei and will introduce into our second quantized Hamiltonian a term of the form $C^+_{n\sigma}C_{n'\sigma'}$. This will cause a renormalization of the conduction electrons and will be assumed to have been incorporated in the zeroth order electron Hamiltonian. $C^+_{n\sigma}(C_{n\sigma})$ is the creation (destruction) operator for an electron of spin σ located in the spatial orbital ϕ_n (localized on site n).

(3) Molecular electrons–conduction system nuclei. As above, this term involves only the particles of one subsystem, in this case the excitons. A typical term may represent the interaction of the molecular charge distribution $\psi_{mj}\psi_{m'j'}$ with the electronic nuclei at site n, Z_n. We shall neglect intermolecular overlap and consider only molecular charge distributions such that $m = m'$. Terms such as

$$\bar{V}^{jj}_{|n-m|}\{(-1)^{j+1}\,a^+_m a_m + 1 - j\} \quad j = 0, 1$$

for $j = j'$, and

$$\bar{V}_{|n-m|}(a^+_m + a_m) \quad j \neq j'$$

will occur where $a^+_m(a_m)$ is an exciton creation (destruction) operator for an exciton at molecular lattice site m. The $\bar{V}^{jj}_{|n-m|}$, for example, represent the pertinent matrix elements involved; the use of $|n-m|$ denotes the dependence of the matrix element only upon the site number difference and is a consequence of the translational symmetry of the lattice.

(4) Coulomb-coupling. This is the Coulomb interaction between the charge distributions $\phi_n\phi_{n'}$ and $\psi_{mj}\psi_{m'j'}$; again neglecting intermolecular overlap $(m = m')$ and considering only the dominant electron contribution $(n' = n)$ one will get terms such as

$$V^{jj}_{|n-m|}\,C^+_{n\sigma}C_{n\sigma}[(-1)^{j+1}\,a^+_m a_m + 1 - j] \quad j' = j$$

and

$$V_{|n-m|}\,C^+_{n\sigma}C_{n\sigma}(a^+_m + a_m) \quad j' \neq j$$

It is not a bad approximation to consider the molecular charge distributions $\psi_{m0}\psi_{m0}$ and $\psi_{m1}\psi_{m1}$ to be approximately the same, so that $\bar{V}^{1,1}_{|n-m|} \approx \bar{V}^{0,0}_{|n-m|}$ and $V^{1,1}_{|n-m|} \approx V^{0,0}_{|n-m|}$.† Using this approximation and dropping the remaining exciton-free terms—which may either be treated as constants of the problem or incorporated into the conduction electron renormalization—the final form of the coupling becomes

$$\mathscr{H}_1 = \sum_{n,m,\sigma} (\tfrac{1}{2}\bar{V}_{|n-m|} + V_{|n-m|} C^+_{n\sigma} C_{n\sigma})(a^+_m + a_m) \tag{1}$$

where the factor of $\frac{1}{2}$ before $\bar{V}_{|n-m|}$ compensates for the sum over σ. We note that $\bar{V}_{|n-m|}$ and $V_{|n-m|}$ are expected to be comparable in magnitude and of opposite sign; in later considerations we will, in fact, set $\bar{V}_{|n-m|} = -V_{|n-m|}$.

The electron and exciton creation and annihilation operators have already been introduced. The electron operators obey fermion commutation rules.

$$\begin{aligned} [C_{n\sigma}, C_{n'\sigma'}]_+ &= 0 \\ [C^+_{n\sigma}, C_{n'\sigma'}]_+ &= \delta_{nn'}\delta_{\sigma\sigma'} \end{aligned} \tag{2}$$

where $[A, B]_+$ is the anticommutator, $AB + BA$. The excitons under consideration are considered to arise from singlet spin states. The exciton operators obey "mixed" commutation rules:

$$\begin{aligned} &\text{(a)} & [a_n, a_{n'}]_- &= 0 \\ &\text{(b)} & [a^+_n, a_{n'}]_- &= 0, \quad n \neq n' \\ &\text{(c)} & [a^+_n, a_n]_+ &= 1 \end{aligned} \tag{3}$$

where $[A, B]_-$ is the commutator, $AB - BA$. These commutation rules are "mixed" in the sense that (a) and (b) correspond to those of bosons while (c) is characteristic of fermions. Taken together

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† One can convince oneself of the validity of this approximation by, for example, comparing the charge distributions of the symmetric and antisymmetric forms of the simple diatomic, whose wavefunctions are

$$\psi_\pm = \frac{\phi_2 \pm \phi_2}{\sqrt{[2(1 \pm S)]}}$$

Employing the Mulliken approximation for the cross-terms

$$\phi_1 \phi_2 \approx \tfrac{1}{2} S(\phi_1 \phi_1 + \phi_2 \phi_2)$$

where S is the overlap integral, one finds the distributions $\psi_+ \psi_+$ and $\psi_- \psi_-$ to be the same.

they are precisely the commutation rules for spin raising and lowering operators for $S=\frac{1}{2}$; as such they are sometimes referred to as Pauli commutation rules. Throughout the paper these will be referred to as exciton commutation rules, although it should be understood that they are those for excitons in a particular representation.

IV. Treatment of the Exciton Problem

1. Canonical Transformation

The Hamiltonian of the coupled subsystems is given by

$$\mathscr{H} = \mathscr{H}_0+\lambda\mathscr{H}'$$

$$\mathscr{H}_0 = \sum_{k,\sigma} \epsilon_k C^+_{k\sigma} C_{k\sigma} + \tfrac{1}{2} \sum_{\substack{kk',l\\ \sigma\sigma'}} V^{(c)} C^+_{k+l,\sigma} C_{k\sigma} C^+_{k'-l,\sigma'} C_{k'\sigma'} + \sum_{m} \omega a^+_m a_m$$

$$\mathscr{H}' = \mathscr{H}_1+\mathscr{H}_2 \tag{4}$$

$$\mathscr{H}_1 = \sum_{m,n} \overline{V}_{|n-m|}(a^+_m+a_m) = \sum_{m} \overline{V} a^+_m + \text{h.a.}$$

$$\mathscr{H}_2 = \sum_{n,m,\sigma} V_{|n-m|} C^+_{n\sigma} C_{n\sigma}(a^+_m+a_m)$$

$$= \sum_{\substack{k,l,\sigma\\ m}} V(lm)\, C^+_{k+l,\sigma} C_{k\sigma} a^+_m + \text{h.a.}$$

where h.a. stands for hermitian adjoint and where

$$\overline{V} = \sum_{\delta} \overline{V}_{|\delta|}$$

$$V(l,m) = e^{-ilm} N^{-1} \sum_{\delta} V_{|\delta|} e^{-i\delta l} \tag{5}$$

and a lattice of N sites with periodic boundary conditions has been assumed. $\mathscr{H}'$, the total perturbation, has been broken up into two parts for further discussion. The terms in $\mathscr{H}_0$ are, respectively, the electron "kinetic energy", the electron Coulomb interaction, and the exciton energy; the exciton part of the system is represented by a system of localized, non-interacting quasiparticles with the single energy ω (the analog of the Einstein model for phonons).

k, k', l and n, m, δ refer to crystal-momentum wave vectors and localized site indices, respectively. In further discussion the spin index, σ, will be suppressed, although its presence cannot be neglected. λ is the usual order parameter and will ultimately be set equal to unity. Electron energies are measured relative to the Fermi level and molecular excitation (exciton) energies relative to the unexcited molecule.

The procedure employed is to remove terms to first-order in λ by a canonical transformation.[2] If $\tilde{\mathscr{H}}$ represents the transformed Hamiltonian, then

$$\tilde{\mathscr{H}} = e^{-iS}\mathscr{H}e^{iS} = \mathscr{H} + i[\mathscr{H},S]_- - \tfrac{1}{2}[S,[S,\mathscr{H}]_-]_- + \dots \tag{6}$$

To remove the terms linear in λ, one chooses S such that

$$\lambda\mathscr{H}' + i[\mathscr{H}_0,S]_- = 0 \tag{7}$$

so that

$$\tilde{\mathscr{H}} = \mathscr{H}_0 + \frac{i\lambda}{2}[\mathscr{H}',S]_- + 0(\lambda^3) \tag{8}$$

contains terms of order λ^2 or higher (S is of order λ). An explicit expression for S may be given by expressing Eq. (7) in the interaction representation, defined by

$$A_I(t) = e^{+i\mathscr{H}_0 t} A\, e^{-i\mathscr{H}_0 t} \tag{9}$$

where $A_I(t)$ is in the interaction representation, and units where $\hbar = 1$ have been assumed. Since

$$i\frac{dA_I(t)}{dt} = [A_I(t),\mathscr{H}_0]_- \tag{10}$$

Eq. (7) may be expressed as

$$S = -\lambda \int_{-\infty}^{0} e^{i\mathscr{H}_0 t}\mathscr{H}' e^{-i\mathscr{H}_0 t}\, dt \tag{11}$$

In the present case we will define $S = S_1 + S_2$ corresponding to the two contributions to $\mathscr{H}' = \mathscr{H}_1 + \mathscr{H}_2$. This dichotomy is made in order to point out certain features associated with the two terms.

The form of S given by Eq. (11) is particularly convenient if the eigenfunctions of $\mathscr{H}_0$ are known. S_1 which corresponds to the $\mathscr{H}_1$ part of $\mathscr{H}'$ is given immediately by

$$S_1 = \sum_m \frac{i\lambda \bar{V}}{\omega} a_m^+ + \text{h.a.} \tag{12}$$

Of course, $\mathscr{H}_1$ need not be treated by a perturbation technique since $\mathscr{H}_0 + \mathscr{H}_1$ represents an exactly soluble problem so far as the exciton portion is concerned. We must, however, treat $\mathscr{H}_2$ by some approximate method and since $\mathscr{H}_1$ and $\mathscr{H}_2$ are comparable in magnitude and "oppose" each other (in sign) we shall treat them both to the same order of approximation.

If we choose to ignore the Coulomb interaction, one obtains for S_2 corresponding to $\mathscr{H}_2$ of $\mathscr{H}'$:

$$S_2 = \sum_{k,l,m} \frac{i\lambda V(l,m)\, C_{k+l}^+ C_k a_m^+}{\epsilon_{k+l} - \epsilon_k + \omega} + \text{h.a.} \tag{13}$$

This is the only term where the Coulomb interaction enters in; we may choose to include it, in which case we might take as an ansatz:

$$S_2' = \sum_{k,l,m} \alpha_{klm} C_{k+l}^+ C_k a_m^+ + \text{h.a.} \tag{14}$$

However, with this form of S_2' it will be noted that $[\mathscr{H}_0, S_2']_-$ will contain biquadratic electron terms (terms with four electron operators, as, for example, the Coulomb interaction itself), due to the presence of the Coulomb term in $\mathscr{H}_0$. Since $\mathscr{H}'$ contains only quadratic electron terms, the biquadratic terms in $[\mathscr{H}_0, S_2']_-$ must be simplified, as in the treatment of Nakajima (as outlined in Bardeen and Pines[3]) who employed a Hartree approximation. Using this approach and the chosen form of S_2' yields the condition

$$\lambda V(l,m) + i V_l^{(c)} \sum_p (n_p - n_{p+l})\, \alpha_{plm} = -i\alpha_{klm}(\epsilon_{k+l} - \epsilon_k + \omega) \tag{15}$$

where $n_p = \langle C_p^+ C_p \rangle$ is the expectation value of the electron number operator for momentum state p, averaged over the ensemble. Equation (15) is solved to give

$$\alpha_{klm} = \frac{i\lambda V(l,m)}{\epsilon_{k+l} - \epsilon_k + \omega} D(\omega, l) \tag{16}$$

where $$D(\omega, l)^{-1} = 1 + V_l^{(c)} \sum_k \frac{n_k - n_{k+l}}{\epsilon_{k+l} - \epsilon_k + \omega} \tag{17}$$

$D(\omega,l)^{-1}$ has just the form of the self-consistent field frequency-dependent dielectric constant.[4] Comparing Eqs. (16) and (13) we see that inclusion of the Coulomb interaction in deriving S_2' has effectively caused a screening of the interaction term in S_2'

$$V(l,m) \to V(l,m)\,D(\omega,l)$$

We should point out that, *for the present problem*, inclusion of the Coulomb interaction in S_2 does not appear to be a critical matter since we shall assume an electron bandwidth small compared to ω. Thus, a term like $\omega + \epsilon_{k+l} - \epsilon_k \approx \omega$ and $D(\omega,l)$ is approximately unity. Use of a somewhat better-than-Hartree approximation in the matter exhibits the same behavior.† We will consider the effects of $D(\omega,l)$ to be incorporated into $V(l,m)$ and shall, henceforth, use the expression given by Eq. (13).

Consider first that part of the transformed Hamiltonian involving only the terms arising from $[\mathscr{H}_2, S_2]_-$; denote this part of $\bar{\mathscr{H}}$ as $\bar{\mathscr{H}}_2$ where $\bar{\mathscr{H}} = \bar{\mathscr{H}}_1 + \bar{\mathscr{H}}_2 + \mathscr{H}_0$. Then one obtains

$$\bar{\mathscr{H}}_1 = \sum_m [a_m^+, a_m]_- \times \\ \times \left\{ \frac{(\bar{V})^2}{\omega} + \sum_{k,l} C_{k+l}^+ C_k \frac{\bar{V}\, V(l,m)}{\omega} \cdot \frac{(2\omega^2 - (\epsilon_{k+l} - \epsilon_k)^2)}{\omega^2 - (\epsilon_{k+l} - \epsilon_k)^2} \right\} \tag{18}$$

and

$$\bar{\mathscr{H}}_2 = \sum_{m,m'} \sum_{\substack{kk' \\ l,l'}} [2(\epsilon_{k'+l'} - \epsilon_{k'} + \omega)]^{-1} V(l,m)\, V^*(l',m') \times \\ \times \{a_m^+ a_{m'} [C_{k+l}^+ C_k, C_{k'}^+ C_{k'+l'}]_\pm - C_{k'}^+ C_{k'+l'} C_{k+l}^+ C_k [a_{m'}, a_m^+]_\pm\} - \\ - V(l,m)\, V(l',m')\, a_m^+ a_{m'}^+ [C_{k+l}^+ C_k, C_{k'+l'}^+ C_{k'}]_- + \text{h.a.} \tag{19}$$

where one must use the commutator *or* the anticommutator *for both terms* involving the $a_m^+ a_{m'}$ terms in $\bar{\mathscr{H}}_2$. In the derivation of Eq. (18) and Eq. (19) use was made of the commutation rule

$$[a_m, a_{m'}]_- = 0$$

valid for excitons *or* bosons and all m and m'.

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† This involves adding to S_2' a term biquadratic in the electron operators and requiring such biquadratic terms which arise in Eq. (7) to cancel.

It is at this point that the particular statistics of the a-particles enter the problem. For, while the excitons here considered and bosons obey the same commutation rules for what we shall call the transfer terms ($m \neq m'$; those terms which are off-diagonal in the Fock space where $a_m^+ a_m$ is the particle number operator, and cause transfer of the quasiparticle from one site (state) to another), the diagonal terms ($m = m'$) differ:

$$[a_m, a_m^+]_+ = 1 \quad \text{(excitons)}$$

$$[a_m, a_m^+]_- = 1 \quad \text{(bosons)} \qquad (20)$$

This difference is best illustrated by writing out the operator terms multiplying $V(l,m)V^*(l,m')$ in Eq. (19) for the two cases. For bosons one would obtain

$$a_m^+ a_m [C_{k+l}^+ C_k, C_{k'}^+ C_{k'+l'}]_- - C_{k'}^+ C_{k'+l'} C_{k+l}^+ C_k \quad \text{(bosons)}$$

while for excitons one obtains

$$a_m^+ a_m [C_{k+l}^+ C_k, C_{k'}^+ C_{k'+l'}]_+ - C_{k'}^+ C_{k'+l'} C_{k+l} C_k \quad \text{(excitons)}$$

We shall be taking the coefficient of $a_m^+ a_m$, properly averaged over the electronic ensemble, to give a measure of the a-particle renormalization energy. Then, in so far as the renormalization in $\mathscr{H}_2$ is concerned, boson (for example, phonons) renormalization would involve averages over *quadratic* electron terms (the commutation of the biquadratic term reduces it to quadratic terms) whereas the exciton renormalization will involve an average of biquadratic terms (the anticommutator does not simplify). Explicit expressions for these terms will be derived in later considerations.

Note that an attractive biquadratic electron term free of exciton or boson encumbrance is generated in either case. This term, representing an attractive electron–electron interaction, is usually held responsible for the necessary electron–electron attraction in theories of superconductivity in metals (where it arises from the electron–phonon coupling).

The exciton renormalization involved in $\mathscr{H}_1$ is also dependent upon statistics; if boson statistics were assumed, $\mathscr{H}_1$ would contain *only* electron operators. Even so, for either case quadratic electron terms are involved. As will be shown in the following sections it is the presence of biquadratic electron terms in $\mathscr{H}_2$ which, so to speak, allows the molecular subsystem to differentiate between the electron system being an insulator (bad conductor), a metal (good conductor) or a superconductor.

2. Exciton Renormalization

The present problem deals with excitons which exhibit Pauli commutation rules. In this section we shall calculate the effect of the electron–exciton interactions on the exciton system by averaging electron operators over the electronic ensemble whenever they occur in conjunction with exciton terms. We shall consider both diagonal and transfer exciton terms and, with suitable approximations, shall perform the electronic averages over both normal metallic and superconducting states, as well as a Heitler–London state which we shall take to represent an insulator. Without loss of generality we shall consider the electron system to contain, on the average, one electron per lattice site. Furthermore, we shall simplify matters by taking the potentials $\bar{V}_{|n-m|}$ and $V_{|n-m|}$ to be completely local; that is, $\bar{V}_\delta = \bar{V}_0$, $V_\delta = V_0$ for $\delta = 0$, and both are zero otherwise.

a. *Diagonal Terms*

Let the renormalized exciton energy be $\tilde{\omega}$ where

$$\tilde{\omega} = \omega + \omega_1 + \omega_2$$

The renormalization terms arising from $\mathscr{H}_1$, ω_1, may be readily calculated. The coefficient of $a_m^+ a_m$ in $\mathscr{H}_1$ is

$$\omega_1 = \frac{2(\bar{V}_0)^2}{\omega} + \frac{2\bar{V}_0 V_0}{\omega} \sum_{k,l,\sigma} \frac{1}{N} \langle C_{k+l,\sigma}^+ C_{k,\sigma} \rangle \cdot \frac{2\omega^2 - (\epsilon_{k+l} - \epsilon_k)^2}{\omega^2 - (\epsilon_{k+l} - \epsilon_k)} \tag{21}$$

A basic assumption of the present model is that the (unrenormalized) molecular excitation energy, ω, is large compared to the electron bandwidth. This allows the simplification

$$\omega^2 - (\epsilon_{k+l} - \epsilon_k)^2 \to \omega^2$$

We conserve crystal momentum in averaging over the electronic system (set $l=0$) and define

$$n = \left\langle \sum_{k,\sigma} C^{+}_{k\sigma} C_{k\sigma} \right\rangle$$

as the total number of electrons so that ω_1 is

$$\begin{aligned} \omega_1 &= \frac{2(\bar{V}_0)^2}{\omega} + \frac{4\bar{V}_0 V_0}{\omega}\left(\frac{n}{N}\right) \\ &= \frac{2(\bar{V}_0)^2}{\omega} + \frac{4\bar{V}_0 V_0}{\omega} \end{aligned} \tag{22}$$

since we presume an electron subsystem where $n=N$. The expression for ω_1 is *independent* of the conducting nature of the electron subsystem.

ω_2 is given by the coefficient of $a^{+}_{m} a_m$ in $\mathscr{H}_2$ and is (h.a. included)

$$\omega_2 = \sum_{k,k',l} \frac{V(l,m)\, V^{*}(l,m)}{2} \frac{2}{\omega^2 - (\epsilon_{k'+l'} - \epsilon_{k'})^2} \langle [C^{+}_{k+l} C_k, C^{+}_{k'} C_{k'+l}]_{+} \rangle \tag{23}$$

where again we have conserved crystal momentum by setting $l'=l$. Simplifying ω_2 according to our previously stipulated method, we obtain

$$\omega_2 = \frac{2V_0^2}{\omega N^2} \sum_{\substack{k,k',l \\ \sigma,\sigma'}} \langle C^{+}_{k+l,\sigma} C_{k,\sigma} C^{+}_{k'\sigma'} C_{k'+l,\sigma'} \rangle \tag{24}$$

The spin index, σ, has been temporarily reinserted as a reminder that it is important in the procedures which follow.

We now proceed to evaluate ω_2 for three different cases.

(1) *Insulator*

This is the limit of poor conductivity, and the electronic state representing it will be taken to be one in which electrons are completely localized; that is, a Heitler-London state dominated by the Coulomb repulsion where each site *always* has only one electron in the orbit ϕ_m. For this particular case, it is more appropriate to write the electron average involved in ω_2 in local space:

$$\omega_2 = \frac{2V_0^2}{\omega N} \left\{ \sum_{n,\sigma} \langle C^{+}_{n\sigma} C_{n\sigma} \rangle + 2 \sum_{n} \langle c^{+}_{n\sigma} C_{n\sigma} C^{+}_{n,-\sigma} C_{n,-\sigma} \rangle \right\} \tag{25}$$

The first term in brackets is simply n, and the second term vanishes due to the Heitler-London restriction of only one-electron per site, regardless of spin. Thus, the *net* renormalization, $\tilde{\omega}-\omega=\omega_1+\omega_2$, for the insulator model is

$$\tilde{\omega}-\omega = \frac{2}{\omega}(\bar{V}_0+V_0)^2 \quad \text{(insulator)} \tag{26}$$

Just as with the $\mathscr{H}_1$ perturbation to $\mathscr{H}_0$, this particular problem, in which $C^+_{n\sigma}C_{n\sigma}+C^+_{n,-\sigma}C_{n,-\sigma}=1$ is a c-number, could have been solved exactly. Now for the coupled subsystems under investigation $\bar{V}_0\approx -V_0$, and we see that the exciton renormalization in the insulator will vanish in this approximation. This is consistent with our idea of weakly interacting subsystems of molecules—that is, a molecular solid. The cancellation of terms for the insulator is due to the vanishing of the second term in Eq. (25) which prevents "ionic" structures in the electron subsystem. In a metal, no such restriction exists and, as we shall see, a net renormalization effect is calculated in the limit $\bar{V}_0=-V_0$.

(2) *The Fermi sea*

Consider first Eq. (24) where the average is taken over the Fermi sea at $T=0$°K. Then,

$$\sum_{\substack{kk',l\\ \sigma\sigma'}} \langle C^+_{k+l,\sigma}C_{k\sigma}C^+_{k'\sigma'}C_{k'+l,\sigma'}\rangle$$

$$= \sum_{\substack{k,k'\\ \sigma,\sigma'}}^{l=0} \langle C^+_{k\sigma}C_{k\sigma}C^+_{k'\sigma'}C_{k'\sigma'}\rangle + \sum_{k,l}^{l\neq 0} \langle C_{k\sigma}C^+_{k\sigma}C^+_{k+l,\sigma}C_{k+l,\sigma}\rangle \tag{27}$$

where only the terms for $k'=k$ and $\sigma'=\sigma$ survive the average in the second term. The two terms yield n^2 and $(N-n/2)n$, respectively, so that for $n=N$

$$\omega_2 = \frac{2V_0^2}{\omega}\cdot\frac{3}{2} \tag{28}$$

and

$$\tilde{\omega}-\omega = \frac{2}{\omega}[(\bar{V}_0+V_0)^2+\tfrac{1}{2}V_0^2] \quad \text{(metal)} \tag{29}$$

Thus, in the nearly correct approximation $\bar{V}_0 = -V_0$ the metal indicates a net exciton renormalization of V_0^2/ω.

(3) *The BCS*[5] *ground state*

The BCS ground state for a superconductor is given by

$$\psi_{\mathrm{BCS}} = \prod_k [(1-h_k)^{1/2} + h_k^{1/2} C_{k,\alpha}^{+} C_{-k,\beta}^{+}]\,\phi_{\mathrm{VAC}}$$

$$h_k = \frac{1}{2}\left[1 - \frac{(\epsilon_k-\mu)}{\sqrt{[(\epsilon_k-\mu)^2+\Delta^2)}}\right] \tag{30}$$

where "up" spin (α) has been associated with $+k$ and "down" spin (β) with $-k$ to give the spin and momentum pairing characteristic of the theory. ϕ_{VAC} is the true vacuum state (no particles) for the electrons, and μ represents the *shift* in chemical potential as one passes from normal metallic to the superconducting state. The BCS wave function does not correspond to a fixed number of electrons but has components corresponding to all even numbers of electrons from 0 to, in the present case of N orbital states, $2N$. The presence of μ in Eq. (30) guarantees that the expectation value of the electron number operator will be exactly n (or $n = N$ in the present model). For a system possessing particle-hole symmetry about the Fermi surface, μ is equal to zero.

Using the fact that

$$n = 2\sum_k h_k$$

(at $\tau = 0$) the average of Eq. (24) is done in a straightforward manner to yield

$$\frac{2V_0^2}{\omega} N^{-2}\left\{Nn + \frac{n^2}{2} + 2N^2\left(\frac{\Delta}{A}\right)^2\right\}$$

where A is the BCS parameter which serves to define the (temperature dependent) gap, Δ:

$$\Delta = \frac{A}{N}\sum_k \frac{0.5\Delta}{\sqrt{[(\epsilon_k-\mu)^2+\Delta^2]}}\tanh\left(\frac{\sqrt{[(\epsilon_k-\mu)^2+\Delta^2]}}{2\tau}\right) \tag{31}$$

Again, for $n = N$, and adding in the contribution ω_1 one obtains

$$\tilde{\omega} - \omega = \frac{2}{\omega}\left[(\bar{V}_0 + V_0)^2 + \tfrac{1}{2}V_0^2 + 2V_0^2\left(\frac{\Delta}{A}\right)^2\right] \quad \text{(superconductor)} \tag{32}$$

Since Δ/Λ is at most equal to $\frac{1}{2}$ in the limit of large Λ (see Eq. (31)), the contribution due to the presence of superconductivity is at best comparable to the contribution present in the normal metallic state ($\Delta = 0$). The BCS treatment allows for the possibility of the *absence* of superconductivity; accordingly, Eq. (32) reduces to that calculated for the metal, Eq. (29), as $\Delta \to 0$.

While the above expressions for metallic and superconductor renormalizations have been derived for $\tau = 0°\,\mathrm{K}$, the same expression may be shown to obtain when the averages are performed at finite temperatures provided one uses a molecular field approximation to separate electron terms greater than quadratic. In the case of the superconductor one first rewrites the electron operators involved in terms of the quasiparticle operators of Bogoliubov[6] and performs the subsequent averaging over the Fock space diagonal in the quasiparticles. Then, $\Delta = \Delta(\tau)$ in general and obeys Eq. (31).

In subsequent discussion we shall assume $\bar{V}_0 = -V_0$. Thus, in the limit of poor conductivity there is no exciton renormalization (Eq. (26)), whereas there does exist an effect in the conductor (Eq. (29)). The essential result of our considerations is the presence of a term in the renormalization involving the *superconducting* nature of the system (Eq. (32)). The presence of this term may be considered a *coherence effect* and allows one, in principle, to detect the transition between normal and superconducting states.

b. *Transfer Terms*

Transfer terms are present only in $\mathscr{H}_2$; it is a straightforward procedure to evaluate these terms which are given by the coefficients of $a_m^+ a_{m'} (m \neq m')$ and $a_m^+ a_{m'}^+$ (and $a_m a_{m'}$). The former will contribute to the exciton bandwidth, while the latter, involving creation or destruction of pairs of excitons, will necessitate a re-diagonalization of the exciton Hamiltonian. The general coefficient of both $a_m^+ a_{m'}$ and $a_m^+ a_{m'}^+$, $T_{mm'}$. is

$$T_{mm'} = -\frac{V_0^2}{2\omega^2} \sum_{\substack{k,l \\ \sigma}} e^{-il(m-m')} N^{-2} (n_{k+l,\sigma} - n_{k,\sigma})(\epsilon_{k+l} - \epsilon_k) \quad (33)$$

where, as before, crystal momentum is conserved, the relations $n_k = n_{-k}$ and $\epsilon_k = \epsilon_{-k}$ are assumed, and the approximation

$$\omega^2 - (\epsilon_{k+l} - \epsilon_k)^2 \approx \omega^2$$

has been made. In general, one must know the k-dependence of ϵ to evaluate Eq. (33). Here we make the simplifying assumption of a cosine band, so that

$$\epsilon_k = b(\cos k - \cos k_0)$$

where b is the band half-width and $b \cos k_0$ is the Fermi energy, ϵ_{F}. If this is used for ϵ_k, then Eq. (33) becomes

$$\begin{aligned} T_{mm'} &= -\frac{V_0^2}{2\omega^2 N^2} \sum_{k,l} [2\, e^{-il(m-m')}(1 - \cos l)][n_k b \cos k] \\ &= \frac{V_0^2}{2\omega^2}\left(\frac{n}{N}\right)(\bar{\epsilon} + \epsilon_{\mathrm{F}})\, \delta_{m=m'\pm 1} \end{aligned} \tag{34}$$

where $\bar{\epsilon}$ is the average electronic energy

$$\bar{\epsilon} = \frac{1}{n} \sum_k n_k \epsilon_k \tag{35}$$

Thus, in the present case for $n = N(\epsilon_{\mathrm{F}} \to 0)$, the coefficients of the exciton terms $a_m^+ a_{m'}$ and $a_m^+ a_{m'}^+$ are both given by

$$T_{mm'} = \frac{V_0^2}{2\omega^2} \bar{\epsilon} \delta_{m=m'\pm 1} \tag{36}$$

We note that the assumed cosine nature of the electron band leads to a nearest-neighbor-only interaction for the exciton terms ($m = m' \pm 1$).

3. DIAGONALIZATION OF THE TRANSFORMED EXCITON HAMILTONIAN

The results of the preceding sections show that that part of the transformed Hamiltonian concerned with excitons, $\mathscr{H}_x$, may be written as (with $\bar{V}_0 = -V_0$)

$$\begin{aligned} \mathscr{H}_x = \sum_m & A a_m^+ a_m + 2B(a_m^+ a_{m+1} + a_m^+ a_{m-1}) + \\ & + B(a_m^+ a_{m+1}^+ + a_m^+ a_{m-1}^+) + B(a_m a_{m+1} + a_m a_{m-1}) \end{aligned} \tag{37}$$

where

$$\begin{aligned} A &= \omega + \frac{2}{\omega}\left[\tfrac{1}{2}V_0^2 + 2V_0^2\left(\frac{\Delta}{\Lambda}\right)^2\right] \\ B &= \frac{V_0^2\bar{\epsilon}}{2\omega^2} \end{aligned} \qquad (38)$$

and where the nearest-neighbor exciton coupling effect has arisen from use of a cosine electron energy dependence. Because of the nearest-neighbor nature of $\mathscr{H}_x$ *and* the one-dimensionality of the problem, the exciton operators can be transformed to fermion operators[7] and the resulting Hamiltonian diagonalized by a Bogoliubov-Valatin[6] transformation. The resulting quasiparticles obey Fermi-Dirac statistics and have a wavevector energy dependence given by

$$E_k^2 = A^2 + 16B^2 + 8AB\cos k \qquad (39)$$

Since A is much larger than B (since $\bar{\epsilon}/\omega$ is presumed small), the mean energy of the exciton band is A, while $8B$ may be taken as a measure of the exciton bandwidth.

Let $\bar{\epsilon} \approx b$. In the absence of superconductivity ($\Delta = 0$), the ratio of the shift of the exciton band center to the band broadening caused by the electron–exciton coupling is

$$\frac{A-\omega}{8B} = \omega/4b$$

For $\omega \sim 1$ eV and $b \sim 0.1$ eV—not unreasonable values for our model conducting molecular solid—the ratio is 2.5. What is perhaps more important is the mean energy shift induced by the superconducting nature of the system relative to the bandwidth. This ratio is given by

$$\left(\frac{\Delta}{\Lambda}\right)^2 \bigg/ \left(\frac{b}{\omega}\right)$$

In order for the effect of superconductivity to be experimentally detected, this ratio should be at least comparable to unity. The ratio Δ/Λ is determined by Eq. (31). For a cosine band, explicit evaluation of (Δ/Λ) as a function of the width parameter b indicates that, for $b/\omega = 0.1$, the ratio is unity at approximately $b/\Delta \approx 0.67$. For $\omega = 1$ eV, $b = 0.1$ eV, this gives $\Lambda = 0.15$ eV and $\Delta = 0.048$ eV. The ratio is approximately 0.1 for $b/\Lambda = 1.25$, so that $\Lambda = 0.08$ eV and $\Delta = 0.008$ eV. We may generalize to say that the effect should be detectable provided $\Lambda \gtrsim b$. Some other values for the same b are: $b/\Lambda = 1.73$ for $\Lambda = 0.058$ eV and $\Delta = 0.0017$ eV, and $b/\Lambda = 0.044$ for $\Lambda = 2.29$ eV and $\Delta = 1.14$.

V. Effect of Exciton Renormalization on the Super-Conducting State; A Self-Consistent Solution

In the previous discussion interest has been focused on the exciton renormalization problem; whenever electronic terms have appeared, average values computed over a suitable electronic ensemble have been substituted. It has been *assumed* that the electronic state *can* exist in a superconducting state and can be described by the parameters Λ and Δ. In this section a superconducting solution to the coupled electron–exciton system will be derived by assuming a separability of variables and treating the separated problems self-consistently.

A model BCS-like Hamiltonian is taken by truncating the transformed Hamiltonian $\mathscr{H}_0 + \mathscr{H}_2$ after terms of order λ^2. We presuppose that the effects of $\mathscr{H}_1$ are now contained in the exciton energy ω and the electron energy ϵ_k. ω will now contain all renormalization effects *except* those arising from the possible superconducting nature of the system. Pairing of electron spin and momentum is demanded and only diagonal exciton terms are retained. An effective interaction, Λ_c, is introduced which may be taken to represent all contributions to the electron–electron coupling *other* than that induced by the electron–exciton coupling. Thus, a superconducting solution will be obtained even for $\Lambda_1 \to 0$ provided $\Lambda_c < 0$; this, of course, implies that a mechanism other than electron–exciton coupling will be responsible for the superconductivity. If only the exciton–electron mechanism is considered, $\Lambda_c > 0$ and represents an effective Coulomb repulsive interaction.

The resulting *ab irato* Hamiltonian is

$$\begin{aligned}\mathscr{H} = {} & \omega \sum_m a_m^+ a_m + \sum_k \epsilon_k (C_k^+ C_k + C_{-k}^+ C_{-k}) + \\ & + \frac{1}{N}(\Lambda_c - \Lambda_1) \sum_{k,l} C_k^+ C_{-k}^+ C_{-l} C_l + \\ & + \frac{2\Lambda_1}{N^2} \sum_{m,k,l} a_m^+ a_m C_k^+ C_{-k}^+ C_{-l} C_l \\ & \left(\Lambda_1 \equiv \frac{2V_0^2}{\omega}\right)\end{aligned} \tag{40}$$

where in this section we will adopt the shorthand notation that α-spin is associated with explicitly positive k and β-spin with explicitly negative k; that is, $C_{k,\alpha} \to C_k$ and $C_{-k,\beta} \to C_{-k}$. The BCS parameter, Λ, introduced previously, will be related to Λ_c and Λ_1 and is assumed positive (i.e., $-\Lambda$ is attractive). Note that the interaction $(\Lambda_c - \Lambda_1)$ is allowed to act over all k-space here since the exciton energy, ω, is assumed greater than the electronic bandwidth. This is different from ordinary BCS theory (with phonons) in which the averaged interaction acts only over the range of k-space near the Fermi surface for which the phonon Debye energy is greater than $(\epsilon_{k+l} - \epsilon_k)$.

The model Hamiltonian is separated into an exciton part, $\mathscr{H}(\mathrm{I})$, and an electron part, $\mathscr{H}(\mathrm{II})$, by averaging first over electronic operators and then over exciton terms. Thus

$$\begin{aligned}\mathscr{H}(\mathrm{I}) = {} & \sum_m a_m^+ a_m \left\{\omega + \frac{2\Lambda_1}{N^2}\left\langle \sum_{k,l} C_k^+ C_{-k}^+ C_{-l} C_l \right\rangle\right\} \\ \mathscr{H}(\mathrm{II}) = {} & \sum_k \epsilon_k (C_k^+ C_k + C_{-k}^+ C_{-k}) + \\ & + \frac{1}{N}\left\{\Lambda_c - \Lambda_1 \left[\left\langle \frac{1}{N} \sum_m (1 - 2a_m^+ a_m) \right\rangle\right]\right\} \times \sum_{k,l} C_k^+ C_{-k}^+ C_{-l} C_l\end{aligned} \tag{41}$$

The quantities in the pointed bracket, $\langle \ldots \rangle$, are c-numbers obtained by taking the appropriate expectation value over the ground state of the subsystem involved. The electronic Hamiltonian is "solved" by an equations-of-motion method in which

$$C_k^+ C_{-k}^+ C_{-l} C_l$$

is replaced by

$$\langle C_k^+ C_{-k}^+ \rangle\, C_{-l} C_l + C_k^+ C_{-k}^+ \langle C_{-l} C_l \rangle$$

The superconducting gap is given by

$$\Delta = -\frac{\Lambda}{N}\sum_k \langle C_k^+ C_{-k}^+ \rangle = -\frac{\Lambda}{N}\sum_k \langle C_{-k} C_k \rangle \tag{42}$$

where, in the present case

$$\Lambda = -\Lambda_c + \Lambda_1 \left\langle \frac{1}{N}\sum_m (1 - 2a_m^+ a_m) \right\rangle \tag{43}$$

To be consistent with this decoupling of the electronic Hamiltonian, in $\mathscr{H}(\mathrm{I})$ one must use

$$\left\langle \sum_{k,l} C_k^+ C_{-k}^+ C_{-l} C_l \right\rangle \rightarrow \left\langle \sum_k C_k^+ C_{-k}^+ \right\rangle \left\langle \sum_l C_{-l} C_l \right\rangle = \left(\frac{N\Delta}{\Lambda}\right)^2 \tag{44}$$

Define the expectation value of the exciton number operator. $a_m^+ a_m$, by

$$\eta \equiv \langle a_m^+ a_m \rangle = \frac{1}{N}\sum_m \langle a_m^+ a_m \rangle \tag{45}$$

where the last equality holds due to the translational symmetry of the lattice. Using the results of the equations-of-motion treatment of $\mathscr{H}(\mathrm{II})$ and the trivial solution of $\mathscr{H}(\mathrm{I})$ the following equations are obtained which must be satisfied self-consistently:

$$\begin{aligned} \Delta &= \{\Lambda_1(1-2\eta) - \Lambda_c\}\frac{1}{N}\sum_k \frac{0.5\Delta}{\sqrt{(\epsilon_k^2 + \Delta^2)}} \tanh\left(\frac{\sqrt{(\epsilon_k^2+\Delta^2)}}{2\tau}\right) \\ \eta &= (e^{\tilde{\omega}/\tau} + 1)^{-1} \\ \tilde{\omega} &= \omega + \frac{2\Lambda_1 \Delta^2}{[\Lambda_1(1-2\eta) - \Lambda_c]^2} \end{aligned} \tag{46}$$

Here $\tau = k_B T$ and $\tilde{\omega}$ represents the renormalized exciton energy. Δ is positive-definite provided $\Lambda_1(1-2\eta) - \Lambda_c > 0$ and is zero otherwise. Note that it is $\Lambda_1 - \Lambda_c$ which determines the strength of the superconducting transition, whereas it is the factor Δ_1 which largely determines the exciton renormalization. $\tilde{\omega}-\omega>0$ always and is a decreasing function of increasing temperature; thus, for excitons with $\omega \sim 1$–2 eV, η will be effectively zero and will only slightly perturb the electronic properties. The general effect is to lower the transition temperature since, from Eq. (43), Δ is reduced by finite η. The exciton energy, however, is strongly affected by the electronic subsystem. Of course, cross-coupling will be strongest if the excited state of interest is very low in energy, allowing a sizeable value of η to develop. The exciton energy renormalized for superconducting effects agrees with our previous result as it should.

One must take the above considerations only as a crude picture of possible exciton-coupling effects on the superconductor. Contrary to our considerations of exciton renormalization along in Section IV which is a valid perturbative approach to the problem, the present sections suffer from an inability to really justify the *model* Hamiltonian involved in terms of a physical Hamiltonian. In such cases the usefulness of the calculation can only be ascertained by its agreement with reality coupled with the experimental tests and probes it suggests.

VI. Summary and Discussion

The main purpose of this paper has been to demonstrate the reaction of a molecular exciton subsystem to the conducting nature of a partner subsystem capable of electronic conduction. The excitons react by exhibiting both a shift of their mean energy to higher energy and a broadening of the exciton band. The energy shift is measured relative to the exciton energy in an average molecular-solid environment ($\overline{V}_0=-V_0$); it is seen to properly vanish if the conducting system is not conducting at all, but rather insulating (Eq. (26)). For metallic conduction an energy shift is present (Eq. (29)) and is larger than the band broadening; thus, an observable blue shift of the exciton band center is predicted for the coupled exciton-conductor subsystems. If the conducting subsystem is superconducting, an additional shift is calculated (Eq.

(32)). This superconducting shift is dependent upon Δ, the superconducting gap, and is correspondingly temperature dependent. In order to be detectable the superconducting shift must be comparable in size to the exciton band broadening. For *electron* bandwidths of *c*. 0.1 eV, a superconducting gap of the order of a few hundredths to a few tenths of an electron volt is estimated to be necessary. This means transition temperatures where kT_c is of the order of $\Delta(T=0)$, that is, a high-temperature superconductor. Of course, the better one can characterize the exciton spectra the more detectable the superconducting shift. Although a zero-width exciton band in zeroth order was assumed in our model, real bands have finite widths; a reasonable value for spacing of vibrational lines in a typical molecular solid at room temperature is of the order of 0.1 to 0.2 eV. Thus, the shifts, broadening, and bandwidths are likely to be comparable so that metallic or superconductive shifts may require careful analyses in order to be observed.

A simple argument can be advanced to show how a shift to higher energy may be understood in terms of the statistics of the excitons. Consider a completely local problem of the form

$$\mathscr{H} = \omega a^+ a + q(a^+ + a) \tag{47}$$

where q represents some perturbation of the system. This Hamiltonian has the form commensurate with the more general problem treated in this paper, and is easily solved. If the a-particles are bosons, a transformation, $b^+ = a^+ - q/w$, yields the diagonal form

$$\mathscr{H} = \omega b^+ b - \frac{q^2}{w} \quad \text{(bosons)} \tag{48}$$

in which the energy of the boson is unaffected. However, if the a-particles are excitons and exhibit a hard-sphere nature such that $a^+ a + aa^+ = 1$, one must solve the 2×2 determinant explicitly to obtain the eigenvalues

$$\epsilon_\pm = \frac{\omega \pm \sqrt{(\omega^2 + 4q)}}{2} \quad \text{(excitons)} \tag{49}$$

where the energy spacing is now

$$\tilde{\omega} \equiv \epsilon_+ - \epsilon_- = \sqrt{(\omega^2 + 4q)} \quad \text{(excitons)} \tag{50}$$

and has increased due to the fact that coupled levels in this type of problem "repel".

In the exciton renormalization calculations, we did not account for the presence of metallic conductivity or superconductivity, but rather *assumed* their presence. The calculations may be considered a legitimate perturbative treatment of the situation. This implies that energy changes divided by zero order energies not be too large in order for convergence to obtain. Thus, the quantity like V_0^2/ω^2 must be properly small in the perturbative sense. If we take a value of 0.1, then shifts of the order of 0.1ω are indicated; for $\omega \sim 1$–3 eV, such shifts should be easily observable. Of course, the chief sources of error are likely to be hidden within the assumptions of the simple model which was used. Even so, the qualitative behavior should be correct.

If the requirements of detectability are satisfied, the superconducting shift offers a means of detecting the transition of the conducting subsystem to the superconducting state. This may prove useful in systems of the type Little envisages where the usual methods of observing enhanced conduction or the Meissner effect may prove more difficult than in conventional systems because of the possible linear nature of the conduction system and the general sensitivity of conduction properties of organic solids to impurities and imperfections.

It is much more difficult from a rigorous point of view to assess the calculation of the final section (V). It should be regarded more as a kind of hand (and arm)-waving argument concerning the possible effects on the superconducting system due to the presence of coupling to excitons. One can make the following points. First, it is the type of approach which works rather well for ordinary superconductivity (BCS theory). Secondly, the renormalized exciton energies obtained agree with those estimated from the perturbative approach. The self-consistent calculations indicate that the presence of excitons reduces the transition temperature since the parameter $-\Delta$ is reduced for finite η. As mentioned previously, for ordinary exciton energies of an eV or so, the thermal equilibrium value of η is going to be vanishingly small. If very low energy excitons (say, $\omega \sim 0.1$ eV) are involved, however the effect should be sizeable for a high-temperature superconductor.

Finally, the present discussion is not necessarily limited to excitons in molecular solids, but should be valid for any case in which quasiparticles of similar statistics are involved. Thus, polarization of inner shell electrons (acting as pairs) in an ordinary conducting system (i.e., an ordinary metal or semiconductor) should be another example where the present renormalization arguments are valid. If such coupling is important, renormalization of the inner shell electrons should be reflected in modified charge distributions of the inner core; this should be observable as *differences* above and below the transition temperature in measurements sensitive to this property, such as, for example, nuclear quadrupole resonance and the Mössbauer effect.

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