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Cluster generalization of the dynamical coherent-potential approximation: Application to exciton-phonon interactions in molecular crystals

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A cluster generalization of Sumi's dynamical coherent-potential approximation (DCPA) for the thermally averaged Green's function of interacting exciton-phonon systems is presented. Numerical solutions are obtained for a simple model Hamiltonian at 0 K and compared to the single-site DCPA and perturbative results. The Green's function is used to compute optical spectra, and it is shown that the bandwidth renormalization imposed by the two-site DCPA has significant effects in the intermediate-coupling regime.

I. INTRODUCTION

The dynamical coherent-potential approximation (DCPA) was introduced by Sumi[1] to study exciton-phonon interactions in molecular crystals in a self-consistent manner. He was able to calculate ground-state energies, effective masses, and zero-temperature optical spectra over the entire range of parameter (exciton bandwidth B, exciton-phonon coupling S) values for a simple (polaron) model containing one vibration at each molecular site and nearest-neighbor exciton interactions; as in the static CPA,[2-4] the scattering of a single site embedded in the effective medium is forced to vanish, leading to self-consistent equations which have to be solved numerically.

Recently,[5] it was pointed out that this single-site DCPA (hereafter called the 1-DCPA), has, on physical grounds, a serious defect; it fails to renormalize the exciton bandwidth (because the self-energy is constrained to be diagonal). While for certain values of B and S (or for certain properties of the system) this may be a reasonable approximation, there are others for which it will not be. For example, one would expect that a calculation of exciton transport in the small-polaron limit ($S \gg B$) would be in error by orders of magnitude if the effective nearest-neighbor exchange interaction is not suitably reduced by Franck-Condon overlaps.

A natural solution to the above problem, if self-consistent (rather than perturbative) solutions are still desired, is to utilize a cluster formulation of the CPA. This approach was suggested in Ref. 5, where equations for a two-site DCPA (2-DCPA) were developed. There are difficulties implementing cluster CPA methods involving nonanalyticities in the averaged Green's function[6-9] and agreement with perturbation theory in various asymptotic limits.[10] Nevertheless, several static cluster CPA equations have been solved and yield quite reasonable results, in some cases despite nonanalytic behavior in extreme regions of parameter space.

In this paper, a 2-DCPA is constructed which has the correct behavior in the relevant perturbative limits ($B/S \to 0, B/S \to \infty$). The self-consistent equations are solved by a matrix continued fraction technique, which allows straightforward generalization to larger clusters and more complex models (e.g., several molecules per unit cell). Extensive numerical calculations have thus far revealed no nonanalytic behavior of the Greeen's functions (although care is required in iterative algorithms to obtain the correct branch of the solution).

Results are presented here for the zero-temperature properties of the simplified model studied in Ref. 1. The ground-state energy and effective mass are studied systematically as functions of B and S, and comparisons are made with the 1-DCPA and perturbation theory. Several optical spectra are also displayed, which reveal significant differences between the 1- and 2-DPCA in the intermediate coupling regime. A method for calculation of finite-temperature Green's functions is outlined (numerical implementation of which is currently in progress) which will allow analysis of the transition from the self-trapped to nearly free exciton regime as a function of temperature. The formalism for application to two molecules per unit cell is given in an appendix.

II. MODEL HAMILTONIAN AND 2-DCPA

We consider a simple model Hamiltonian[1,5,11] for a molecular crystal with one molecule per unit cell and one harmonic vibrational mode per molecule and restrict our study to the case of intraband transitions for the exciton. We include linear and quadratic exciton-phonon "on site" interactions and consider only the diagonal (with respect to phonon population) part of the latter.

In the site representation the Hamiltonain reads ($\hbar = 1$)

$$H = \sum_n E_n A_n^\dagger A_n + \sum_{\substack{n,m \\ n \neq m}} J_{n,m} A_n^\dagger A_m + \omega \sum_n b_n^\dagger b_n + (\omega S)^{1/2} \sum_n A_n^\dagger A_n (b_n + b_n^\dagger) + \Delta\omega \sum_n b_n^\dagger b_n A_n^\dagger A_n \ , \qquad (2.1)$$

where A_n ($A_n^\dagger$) is the annihilation (creation) operator of an exciton at site n (we consider only one-exciton states). Similarly for phonons we define b_n ($b_n^\dagger$). For the crystal we have $\epsilon_n = \epsilon_0$ (site energy) for all n and we consider only nearest-neighbor (NN) interactions, i.e., the exchange integral $J_{n,m} = J = \text{const}$ for n,m NN and zero otherwise. S is the energy gain due to localization; $(\omega S)^{1/2}$ and $\Delta\omega$

represent the linear and quadratic exciton-phonon coupling constants, respectively. ω is the Einstein phonon frequency corresponding to the totally symmetric intramolecular vibration of each molecule. If Z is the number of NN, we define the half-bandwidth associated to the the unperturbed exciton as $B=ZJ$.

We can write (2.1) in the $\vec{k}$ representation by transforming the site operators A_n via the usual expression

$$A_{\vec{k}}=N^{-1/2}\sum_n A_n \exp(i\vec{k}\cdot\vec{R}_n) \tag{2.2}$$

with $\vec{R}_n$ the nth site lattice vector and N the total number of sites; $A_{\vec{k}}$ annihilates an exciton with momentum $\vec{k}$ and energy $\epsilon(\vec{k})$ with

$$\begin{aligned}\epsilon(\vec{k})&=\epsilon_0+B\Omega(\vec{k})\ ,\\ \Omega(\vec{k})&=\frac{1}{Z}\sum_{n\neq 0}{}'\exp(i\vec{k}\cdot\vec{R}_n)\ ,\end{aligned} \tag{2.3}$$

where the prime means summation over NN.

We decompose the Hamiltonian into an effective Hamiltonian H_{eff} and the remainder Hamiltonian $H'=H-H_{\text{eff}}$. In the 2-DCPA the effective Hamiltonian consists of the zeroth-order exciton and phonon Hamiltonians, with the former containing a renormalized (energy-dependent) site energy $\Sigma_D(E)$ and bandwidth $\Sigma_N(E)$; thus

$$\begin{aligned}H_{\text{eff}}(E)=&\Sigma_D(E)\sum_n A_n^\dagger A_n+Z^{-1}\Sigma_N(E)\sum_{\substack{n,m\\ n\neq m}}{}'A_n^\dagger A_m\\ &+\sum_n b_n^\dagger b_n\ ,\end{aligned} \tag{2.4}$$

where we have taken ω as our energy unit ($\omega=1$).

The remainder of the Hamiltonian is

$$\begin{aligned}H'=&[E_0-\Sigma_D(E)]\sum_n A_n^\dagger A_n+Z^{-1}[B-\Sigma_N(E)]\sum_{\substack{n,m\\ n\neq m}}{}'A_n^\dagger A_m\\ &+(S)^{1/2}\sum_n A_n^\dagger A_n(b_n+b_n^\dagger)+\Delta\omega\sum_n A_n^\dagger A_n b_n^\dagger b_n\ .\end{aligned} \tag{2.5}$$

An exact form for H_{eff} (which would, of course, include effective interactions between all sites) leads to the vanishing of the thermally averaged T matrix associated with H'. In practice it is not possible to force the entire T matrix to vanish. It was suggested in Ref. 6 that an homomorphic partition of H' [Eq. (2.5)] be utilized to define a two-site scattering perturbation, thus guaranteeing the analyticity of the resultant averaged Green's function. However, we have found that this prescription leads to incorrect results in perturbative limits (either as $S\to 0$ or as $B\to 0$), a behavior analogous to that discovered by Van der Rest *et al.*[10] when the homomorphic CPA is applied to static disorder.

We have therefore chosen to use a type of cluster CPA previously employed by Antoniou and Economou,[12] in which the two-site T matrix vanishes. This T matrix contains the diagonal (Σ_D) and off-diagonal (Σ_N) self-energies, where the former includes contributions from both one- and two-site (diagonal) scattering. This variant of the cluster CPA has not found to be subject to nonanalyticities of the sort uncovered by Nickel and Butler[7] (see also Refs. 8 and 9), and it allows us to guarantee the correct behavior of the 2-DCPA in *both* relevant perturbative limits (this is shown in Sec. III).

In a series of extensive numerical calculations, we have not uncovered any anomalous mathematical behavior (e.g., negative densities of states or exponentially growing wave functions) and, hence have concluded that the approximation is well behaved. A detailed investigation of the formal properties of our method (which may be quite different from the static CPA, as the coherent potentials are *nonlocal* in energy) would require lengthy diagrammatic analysis[8,9] and will not be presented here.

The appropriate two-site scattering Hamiltonian H_{12} in the effective medium is

$$H_{12}(E)=H_{\text{eff}}(E)+H_A(E)+H_B \tag{2.6}$$

with

$$\begin{aligned}H_A(E)=&[\epsilon_0-\Sigma_D(E)]\sum_{n=1,2}A_n^\dagger A_n\\ &+[B-\Sigma_N(E)]\sum_{\substack{n,m=1,2\\ n\neq m}}A_n^\dagger A_m\end{aligned} \tag{2.7}$$

and

$$H_B=\sum_{n=1,2}A_n^\dagger A_n[(S)^{1/2}(b_n+b_n^\dagger)+\Delta\omega(b_n^\dagger+b_n)]\ . \tag{2.8}$$

The conventional CPA method is to make the T matrix, associated with $H_{12}(E)$, vanish (and, hence by translational invariance with every perturbation H_{ij}, where ij are NN).

We define the thermally averaged (retarded) exciton Green's function matrix elements as

$$iG_{nm}(t)=\Theta(t)\langle\langle\exp(iHt)A_n\exp(-iHt)A_m^\dagger\rangle\rangle\ , \tag{2.9}$$

where n,m are site indices, $\Theta(t)$ is the unit step function and $\langle\langle\ \rangle\rangle$ represents the canonical average over the phonon population (at temperature β^{-1}). The Fourier transform of $G_{nm}(t)$ is

$$G_{nm}(E)=\int_{-\infty}^{+\infty}dt\,\exp(iEt)G_{nm}(t) \tag{2.10}$$

with the imaginary part of E a positive infinitesimal. For a 2-DCPA only two componetns of $G_{nm}(E)$ must be computed, the $n=m$ component and the n,m component with n,m NN (e.g., G_{11} and G_{12} if $H_{\text{scat}}=H_{12}$; translational invariance guarantees $G_{11}=G_{22}$ and $G_{12}=G_{21}$).

For convenience of notation, in what follows, any quantity with no subscripts is to be considered a 2×2 matrix. By translational invariance (when applicable) the diagonal (off-diagonal) elements are equivalent and labeled with a subscript D (N) (for example, we already have defined the components of the self-energy matrix Σ as $\Sigma_{11}=\Sigma_{22}=\Sigma_D$ and $\Sigma_{12}=\Sigma_{21}=\Sigma_N$). We now proceed to define several Green's functions using definitions (2.9) and (2.10). $\underset{\sim}{G}(E)$ is the Green's function associated with the Hamiltonian

$H_{12}(E)$ [Eq. (2.6)]. Similarly $\underline{G}(E)$ and $\underline{F}(E)$ are the Green's functions associated with $H_{\mathrm{eff}}(E)$ [Eq. (2.4)] and $H_{\mathrm{eff}}(E)+H_A(E)$ [Eq. (2.7)], respectively. We also define the auxiliary Green's function $\underline{D}(E)$, prior to thermal averaging such that $\bar{\underline{G}}(E)=\langle\langle \underline{D}(E)\rangle\rangle$.

For the noninteracting case ($S=\Delta\omega=0$) we have the Green's function $\underline{G}^0(E)$ defined as

$$\begin{aligned} G_D^0(E)&=N^{-1}\sum_{\vec{k}}[E-\epsilon_0-B\Omega(\vec{k})]^{-1}\,, \\ G_N^0(E)&=N^{-1}\sum_{\vec{k}}\Omega(\vec{k})[E-\epsilon_0-B\Omega(\vec{k})]^{-1} \\ &=B^{-1}[(E-\epsilon_0)G_D^0(E)-1]\,. \end{aligned} \tag{2.11}$$

Similarly for the effective Hamiltonian we have

$$\begin{aligned} G_D(E)&=N^{-1}\sum_{\vec{k}}[E-\Sigma_D(E)-\Sigma_N(E)\Omega(\vec{k})]^{-1}\,, \\ G_N(E)&=\Sigma_N^{-1}(E)\{[E-\Sigma_D(E)]G_D(E)-1\}\,. \end{aligned} \tag{2.12}$$

Define the matrix $\underline{V}(E)$ ($V_D=V_{11}=V_{22}$, $V_N=V_{12}=V_{21}$ as previously stated) as

$$\begin{aligned} V_D(E)&=\Sigma_D(E)-\epsilon_0\,, \\ V_N(E)&=\Sigma_N(E)-B\,. \end{aligned} \tag{2.13}$$

Then from (2.6) and (2.7)

$$\underline{F}(E)=\underline{G}(E)-\underline{G}(E)\underline{V}(E)\underline{F}(E)=\underline{G}(E)[\underline{\mathbb{1}}+\underline{G}(E)\underline{V}(E)]^{-1}\,. \tag{2.14}$$

The equation for $\bar{\underline{G}}(E)$ is

$$\bar{\underline{G}}(E)=Q^{-1}\sum_{n_1,n_2=0}^{\infty}\exp[-\beta(n_1+n_2)]\langle n_1n_2\,|\,\underline{D}(E)\,|\,n_1n_2\rangle\,, \tag{2.15}$$

with Q the harmonic-oscillator partition function

$$Q=\sum_{n_1,n_2=0}^{\infty}\exp[-\beta(n_1+n_2)] \tag{2.16}$$

and $|\,n_1n_2\rangle$ a complete basis set with n_1 (n_2) phonons in site 1 (2) which contains the exciton vacuum.

In Appendix A we derive a recursion relation for the matrix elements $\langle n_1,n_2\,|\,D_{\alpha\alpha'}(E)\,|\,m_1,m_2\rangle$, $\alpha,\alpha'=1,2$ that can be solved via continued fractions expansions. As shown in Appendix A we have

$$\begin{aligned} \langle n_1,n_2\,|\,\underline{D}(E)\,|\,n_1,n_2\rangle^{-1}=\underline{H}(E)-\Delta\omega\,\underline{X}(n_1n_2) \\ -\underline{\Gamma}_1(E,n_1,n_2) \\ -\Gamma_2(E,n_1,n_2)\,, \end{aligned} \tag{2.17}$$

where

$$\underline{H}(E)=\underline{F}^{-1}(E)=\underline{G}^{-1}(E)+\underline{V}(E)\,, \tag{2.18}$$

$\underline{X}(n_1,n_2)$ is a 2×2 matrix with elements

$$[X(n_1,n_2)]_{ij}=\delta_{ij}n_i\Theta(n_i),\quad i,j=1,2, \tag{2.19}$$

$\Theta(n)$ is the usual unit step function, and $\underline{\Gamma}_1$ and $\underline{\Gamma}_2$ is given by

$$\underline{\Gamma}_1(E,n_1,n_2)=\cfrac{S\underline{X}(n_1,n_2)}{\underline{H}(E+1)-\Delta\omega\,\underline{X}(n_1-1,n_2-1)-\cfrac{S\underline{X}(n_1-1,n_2-1)}{\underline{H}(E+2)-\cdots}}\,, \tag{2.20}$$

a finite continued fraction since $\underline{X}(m_1m_2)=\underline{0}$ for m_1 and m_2 less or equal to zero; and

$$\underline{\Gamma}_2(E,n_1,n_2)=\cfrac{S\underline{X}(n_1+1,n_2+1)}{\underline{H}(E-1)-\Delta\omega\,\underline{X}(n_1+1,n_2+1)-\cfrac{S\underline{X}(n_1+2,n_2+2)}{\underline{H}(E-2)-\cdots}}\,, \tag{2.21}$$

an infinite continued fraction.

We can also write $\bar{\underline{G}}(E)$ as

$$\bar{\underline{G}}(E)=\underline{G}(E)+\underline{G}(E)\langle\langle \underline{T}^{12}(E)\rangle\rangle\underline{G}(E)\,, \tag{2.22}$$

where $\underline{T}^{12}(E)$ is the T matrix associated with $H_{12}(E)-H_{\mathrm{eff}}(E)$. As stated above, the customary CPA condition[2–4] is to require $\langle\langle \underline{T}^{12}(E)\rangle\rangle=\underline{0}$. From Eq. (2.22) we can equivalently require

$$\bar{\underline{G}}(E)=\underline{G}(E) \tag{2.23}$$

which is more convenient for numerical implementation. The set of Eqs. (2.15) and (2.23) yields two independent self-consistent equations for the two unknown functions $\Sigma_D(E)$ and $\Sigma_N(E)$.

We recover Sumi's 1-DCPA (Ref. 1) by taking $\Delta\omega=0$ and $\Sigma_N(E)\equiv B$. The off-diagonal equation reduces to an identity and the diagonal equation to the scalar one-site result. Since Sumi's results correctly approach the well-known limiting cases ($B\to0$ or $S\to0$) we expect the same behavior from our calculations, and we defer to Sec. III the comparison of both limiting cases for 1- and 2-DCPA.

If we expand $\underline{\Gamma}_1(E)$, $\underline{\Gamma}_2(E)$, and $\underline{D}(E)$ [Eqs. (2.17)–(2.21)] to first order in S, we obtain

$$\begin{aligned} \underline{V}(E)=\omega S\{&N_{\mathrm{ph}}(\omega)\underline{G}(E+\omega) \\ &+[N_{\mathrm{ph}}(\omega)+1]\underline{G}(E-\omega)\} \end{aligned} \tag{2.24}$$

with $N_{\mathrm{ph}}(\omega)=[\exp(-\beta\omega)-1]^{-1}$ the phonon occupation number (we have reincorporated the phonons frequency ω, taken throughout the calculation as our energy unit). For Eq. (2.24) to be a consistent first-order (in S) expression, $\underline{G}(E)$ must be replaced by the noninteracting Green's function $\underline{G}^0(E)$ [Eqs. (2.3) and (2.11)]. If we redefine the energy scale such that the noninteracting exciton site energy $\epsilon_0=0$, we obtain, for the self-energies to lowest order in S,

$$\Sigma_D(E)=\frac{\omega S}{N}\sum_{\vec{k}}\left[\frac{N_{\rm ph}(\omega)}{E-\epsilon(\vec{k})+\omega}+\frac{N_{\rm ph}(\omega)+1}{E-\epsilon(\vec{k})-\omega}\right],$$

$$\Sigma_N(E)=B+\frac{\omega S}{BN}\sum_{\vec{k}}\left[\frac{N_{\rm ph}(\omega)\epsilon(\vec{k})}{E-\epsilon(\vec{k})+\omega}+\frac{[N_{\rm ph}(\omega)+1]\epsilon(\vec{k})}{E-\epsilon(\vec{k})-\omega}\right]. \quad (2.25)$$

The right-hand side of Eq. (2.25) consists of two terms, which represent the one-phonon absorption and emission process, respectively. The expression for $\Sigma_D(E)$ is identical to the one obtained by Davydov[13] using second-order perturbation theory.

Finally, to conclude this section, we note that the structure of Eqs. (2.17)–(2.21) suggests a generalization to an M-site DCPA. Let $G_m(E)$, $m=1,2,\dots,M$, represent the relevant matrix elements of $\underline{G}(E)$ [Eq. (2.10)], with $G_m(E)=G_{ij}(E)$, with i,j mth NN (for $M=2$, $G_1=G_D$, $G_2=G_N$) and $\Sigma_m(E)$ the renormalized transfer integrals, i.e., $\Sigma_m(E)\sim J_{ij}(E)$ with i,j mth NN. If $|n_1,n_2,\dots,n_m\rangle$ denotes the basis set with n_i phonons in site i $(i=1,2,\dots,M)$ and the exciton vacuum, Eqs. (2.17)–(2.21) can be constructed for an M-site DCPA in an isomorphic fashion, with $\underline{D}(E)$, $\underline{H}(E)$, $\underline{G}(E)$, $\underline{X}(n_1,\dots,n_M)$ $M\times M$ matrices. For example, $\underline{G}(E)$ and $\underline{X}(n_1,\dots,n_M)$ will have components

$$G_{ij}(E)=G_m(E),\quad m=|i-j|$$

and

$$X(n_1,\dots,n_M)=\delta_{ij}n_i\Theta(n_i),\quad i,j=1,2,\dots,M\ , \quad (2.26)$$

respectively, so that there will be M independent equations and M unknowns. As the size of the cluster increases so does the degree of difficulty for both obtaining analytic expressions for $G_m(E)$ and the numerical solution of the self-consistent Equation (2.23). In an analogous fashion, our results can be generalized to crystals with more than one molecule per unit cell. As this formulation is of significant practical interest, we have carried out the calculation in detail in Appendix B. Subsequent publications will contain numerical results for this model.

III. ZERO-TEMPERATURE CALCULATIONS

In this section we solve the self-consistent equations [Eqs. (2.15)–(2.23)] for the zero-temperature case $\beta^{-1}=0$. This particular case, besides being the easiest one to implement numerically, provides us with the ground-state properties and allows us to compare with relative simplicity both the 1- and 2-DCPA with the limiting cases $S/B\to 0$ and $S/B\to\infty$. Also some insight is gained concerning the behavior of both DCPA calculations for the various regimes in parameter space, insight needed to proceed, and at a later stage, to the finite-temperature case.

We begin by redefining the energy scale such that the noninteracting exciton energy ϵ_0 is set equal to zero, and as before we take the phonon frequency to be our energy unit ($\omega=1$). From Eq. (2.15) with $\beta^{-1}=0$ we have

$$\underline{\bar{G}}(E)=\langle 0,0\,|\,\underline{D}(E)\,|\,0,0\rangle\ . \quad (3.1)$$

We restrict the present calculation to linear coupling only, i.e., $\Delta\omega=0$; finite $\Delta\omega$ does not change qualitatively our results provided both S and B are not much less than 1.[1] From Eqs. (2.17)–(2.21) and Eq. (2.23) we have

$$\underline{V}(E)=\cfrac{S}{\underline{G}^{-1}(E-1)+\underline{V}(E-1)-\cfrac{2S}{\underline{G}^{-1}(E-2)+\underline{V}(E-2)-\cfrac{3S}{\underline{G}^{-1}(E-3)+\underline{V}(E-3)-\cdots}}} \quad (3.2)$$

with the components of $\underline{V}(E)$, given as in Eq. (2.13),

$$V_D(E)=\Sigma_D(E)\ ,$$
$$V_N(E)=\Sigma_N(E)-B\ , \quad (3.3)$$

$\underline{G}^{-1}(E-p)$, $p=1,2,3,\dots$, is a function of $\Sigma_D(E-p)$ and $\Sigma_N(E-p)$ [Eq. (2.12), thus Eq. (3.3) is an equation for $\underline{V}(E)$ in terms of $\underline{V}(E-p)$]. It follows for Eq. (3.3), that for a sufficiently large negative energy $|E|\gg S\Sigma_D(E)$ and $\Sigma_N(E)-B$ approaches zero. We have used in this argument the asymptotic behavior of $\underline{G}(E)$ [Eq. (2.12)],

$$G_D(E)\sim 1/E\quad \text{as}\ |E|\to\infty\ ,$$
$$G_NE(\,)\sim 1/E^2\quad \text{as}\ |E|\to\infty\ . \quad (3.4)$$

In analogy to Sumi's method,[1] properly generalized to our matrix formation, we assume $\Sigma_D(E)=\Sigma_N(E)-B=0$ for $E\le E_m$. We also truncate the infinite continued fraction Eq. (3.3) at $E-p_0$. Then from Eq. (3.3) we are able to calculate $\underline{V}(E_m+p)$, $p=1,2,3,\dots$, by simple iteration. We now proceed to adjust E_m (function of B and S) and p_0 [in principle not only a function of B and S, but also on the value E for which Eq. (3.3) is evaluated]. We start with a sufficiently large $|E_m|$ and p_0 and search for the smallest pair $|E_m|,p_0$ such that $\underline{V}(E)$ lies within a prescribed error from the initial $\underline{V}(E)$. Finally, we calculate $\underline{V}(E)$ for $E=E_m+p+\delta$, $p=1,2,3,\dots$, $0<\delta<1$, and obtain $\underline{V}(E)$ for any desired range and density of points in the energy axis.

For real three-dimensional lattices there is no closed analytic forms for the Green's function $\underline{G}(E)$ [Eq. (2.12)]. This introduces numerical difficulties in the practical evaluation of $\underline{G}(E)$ and $\underline{V}(E)$. Since we are interested in the dynamical aspect of the exciton-phonon system and not on the details of the band structure, we approximate

$\underline{G}(E)$ via the Hubbard density of states model,[14] that corresponds, for the noninteracting exciton, to an hemielliptically shaped density of states. This model reproduces most of the qualitative features of the Green's function for any cubic three-dimensional lattice, and has been used by many authors to overcome the numerical difficulties mentioned above. In the present situation this model provides us with a relatively fast algorithm for $\underline{V}(E)$. In the Hubbard approximation $\underline{G}(E)$ is given by

$$\begin{aligned} G_D(E) &= \frac{2}{\Sigma_N^2(E)}(E-\Sigma_D(E) \\ &\quad -\{[E-\Sigma_D(E)]^2-\Sigma_N^2(E)\}^{1/2}) , \\ G_N(E) &= \frac{1}{\Sigma_N(E)}\{[E-\Sigma_D(E)]G_D(E)-1\} . \end{aligned} \tag{3.5}$$

The square root must be taken with positive imaginary past (same sign as ImE, a positive infinitesimal) to secure the correct asymptotic behavior of $\underline{G}(E)$ as $E \rightarrow \pm\infty$.

Before we proceed further, two comments of the numerical method are pertinent. First, we find that $|E_m|$ and p_0 increase as S/B increases. Second, the iterative method developed above is not applicable to the finite-temperature case. From Eqs. (2.15)–(2.23) we see that $\underline{G}(E)$ is a function of $\underline{V}(E \pm p)$, $p=1,2,3,\ldots$. For the particular case $\beta^{-1}=0$, $\underline{G}(E)$ will depend on $\underline{V}(E-p)$, $p=1,2,3,\ldots$. Only for the latter can we start an iteration procedure, given the asymptotic behavior of $\underline{V}(E)$ for large negative energies. For the general case ($\beta^{-1}\neq 0$) a trial $\underline{V}(E)$ must be assumed throughout a whole range of energies. Furthermore, once an acceptable trial $\underline{V}(E)$ is assigned, upon one iteration we get $\underline{G}(E)$, from which by inversion via Eq. (3.5) we obtain a new $\underline{V}(E)$ in order to proceed to the next iteration step. This method and results will be analyzed in a planned subsequent paper.

Once $\underline{V}(E)$ is evaluated in a desired energy range we compute several quantities amenable to easy physical interpretation, comparison with other theoretical methods or experimental data. The energy spectrum E_k for the exciton phonon is given by the poles of $G_D(E)$ [Eq. (2.12)], i.e.,

$$E_k=\mathrm{Re}[\Sigma_D(E_k)+\Sigma_N(E_k)\Omega(\vec{k})] . \tag{3.6}$$

The density of states $n(E)$ is given by

$$n(E)=(-1/\pi)\mathrm{Im}G_D(E) . \tag{3.7}$$

The ground-state energy E_0 is given by the smallest root of Eq. (3.6) with $\Omega(\vec{k})=-1$ (bottom of the band). For E near E_0 both $\Sigma_D(E)$ and $\Sigma_N(E)$ are real numbers (provided, of course, Im$E \rightarrow 0$). Then, the equation for E_0 is the smallest root of

$$E_0=\Sigma_D(E_0)-\Sigma_N(E_0) . \tag{3.8}$$

The effective mass associated with this ground state is denoted by m_p and given by

$$\frac{m_p}{m^*}=\frac{\Sigma_N(E_0)}{B}\left[1-\frac{\partial\Sigma_D(E_0)}{\partial E}+\frac{\partial\Sigma_N(E_0)}{\partial E}\right] \tag{3.9}$$

with m^* the corresponding effective mass at $S=0$.

The absorption spectrum $I(E)$ is proportional to the imaginary part of the zero momentum component of $G_D(E)$ [Eq. (2.12)]. Thus

$$I(E)=\frac{-1}{\pi}\mathrm{Im}\frac{1}{E-\Sigma_D(E)+\Sigma_N(E)} , \tag{3.10}$$

where we have normalized $I(E)$ such that total absorption is unity. Equation (3.10) corresponds to the direct edge case; for the case of indirect edge $\Sigma_N(E)$ in Eq. (3.10) must be replaced by $-\Sigma_N(E)$. For $E \sim E_0$ it is easy to show

$$I(E)=I_0\delta(E-E_0) \tag{3.11}$$

with

$$I_0=\frac{\Sigma_N(E_0)}{B}\left[\frac{m_p}{m^*}\right]^{-1} . \tag{3.12}$$

We compute the ground-state energy E_0 and the 0-0 phonon line strength I_0 as functions of B and S, in the range $0.2 \leq B \leq 4.0$, $S \leq 5.5$ using both the 1- and 2-DCPA.

For $S \ll B$, perturbation theory is applicable and from Eq. (2.25) we obtain

$$\begin{aligned} (E_0)_{\mathrm{pert}} &= -B-SF_1 , \\ (I_0)_{\mathrm{pert}} &= 1-SF_2 , \end{aligned} \tag{3.13}$$

with both F_1 and F_2 positive functions of B only.

For $S \gg B$, the small polaron transformation is applicable;[11] then E_0 and I_0 (with superscript sp) are given by (to first order in the approximation)

$$\begin{aligned} E_0^{\mathrm{sp}} &= -S-B\exp(-S) , \\ I_0^{\mathrm{sp}} &= \exp-(S) . \end{aligned} \tag{3.14}$$

For a fixed value of B it is convenient to work with the quantity

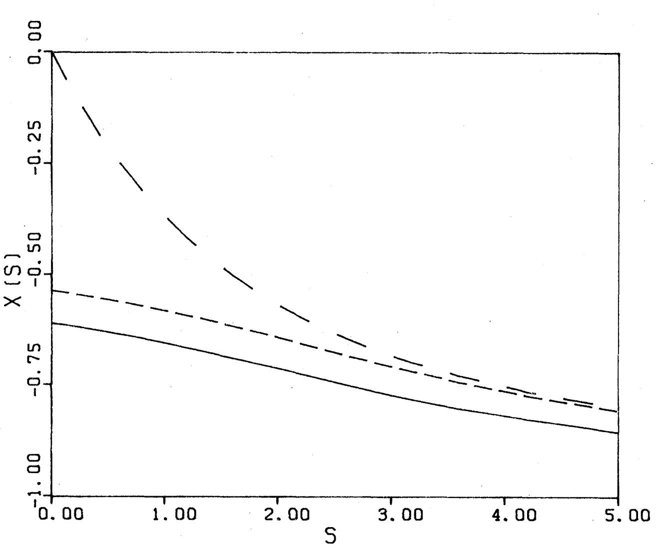

FIG. 1. $X(S)$ vs S for $B=1$. 2-DCPA (solid line), 1-DCPA (short-dashed line), and small polaron (long-dashed line).

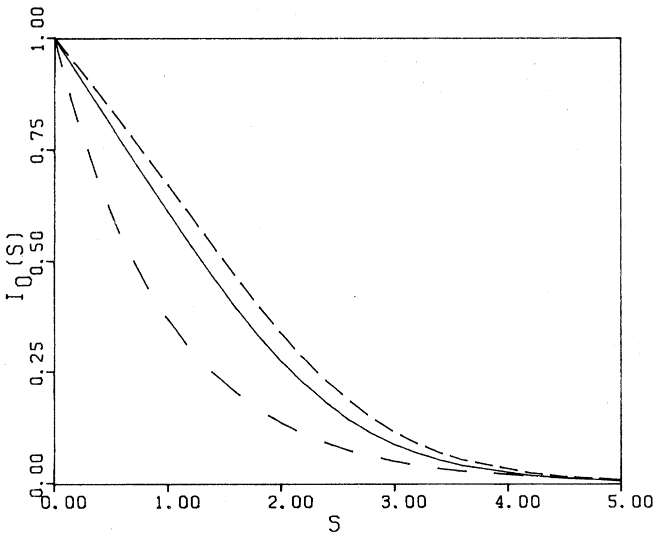

FIG. 2. $I_0(S)$ (0-0 phonon line strength) vs S for $B=1$. 2-DCPA (solid line), 1-DCPA (short-dashed line), and small polaron (long-dashed line).

$$X(S)=\frac{E_0(S)+B}{S} \tag{3.15}$$

rather than $E_0(S)$, since $X(S)$ is bounded between 0.0 and -1.0 and $X_{\text{pert}}(S)=\text{const}$.

In Figs. 1 and 2, we plot $X(S)$ and $I_0(S)$, respectively, for $B=1.0$. The 2-DCPA, 1-DCPA, and small-polaron results are plotted with a solid, short-dashed, and long-dashed line, respectively. This particular value of B is taken as a representative case, since for $0.2 \le B \le 4.0$ the qualitative features of the calculations remain unchanged, with the exception, of course, of the length and boundaries of the several coupling regimes: weak for $S \ll B$, intermediate for $S \sim B$, and strong for $S \gg B$.

Several features of Fig. 1 are noteworthy. First, the ground-state energy of the 2-DCPA is always lower than that of the 1-DCPA (which in turn is lower than the small-polaron energy). This suggests an analogy with variational calculations,[15,16] in which greater flexibility in parametrization of the effective Green's functions allows relaxation towards the true ground state [although, here the "parameters" $\Sigma_D(E),\Sigma_N(E)$ are adjusted by self-consistent equations and not from a variational principle]. It would be interesting to compare the present results with the variational small-polaron method of Ref. 16.

Second, the asymptotic values of $X(S)$ as $S \to 0$ are different for the 1- and 2-DCPA calculations. These quantities are the limiting slope with which the ground-state energy linearly approaches $-B$, the $S=0$ value. (Note that both DCPA calculations correctly approach this value.) The small correction of the 2-DCPA is due to band renormalization, and is reflected in a perturbation calculation which includes such terms.

In the large-S limit ($S \gg B$) $X(S)$ should converge to -1.0, the isolated molecule value. While this convergence is not completed in Fig. 1, calculations with other (smaller) values of B (for which the limiting value is reached more rapidly) show that this does indeed occur.

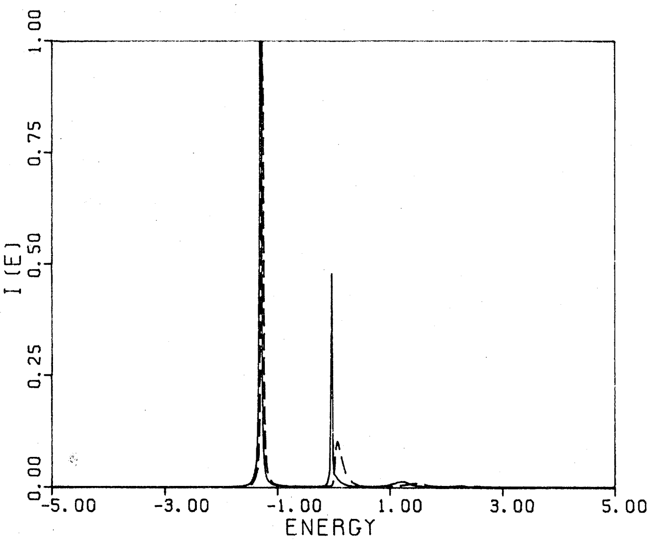

FIG. 3. Absorption spectrum $I(E)$, in arbitrary units, vs energy for $B=1.0$ and $S=0.5$. 2-DCPA (solid line) and 1-DCPA (dashed line). The heights of the peaks off scale (the 0-0 phonon line, almost identical for both DCPA's) have a ratio (2-DCPA)/(1-DCPA)=0.91.

In Fig. 2 we plot I_0, the 0-0 phonon line strength. As before both DCPA's reproduce the correct limits as $S \to 0$ and $S \gg B$. Band renormalization effects are manifested via the reduction of the line strength. Also as S is increased the small-polaron regime is approached more rapidly by the 2-DCPA calculation. With respect to the increase of the effective-mass ratio [Eq. (3.9)], $(m_p/m^*)^{-1}$ and I_0 are equivalent in the 1-DCPA and in the small-polaron regime (to lowest order in B/S). For the 2-DCPA $(m_p/m^*)^{-1}=I_0B/\Sigma_N(E_0)$. Since $B/\Sigma_N(E_0) \le 1$ and $(I_0)_{\text{2-DCPA}} < (I_0)_{\text{1-DCPA}}$ the effect of band renormalization is to increase the effective-mass ratio, i.e.,

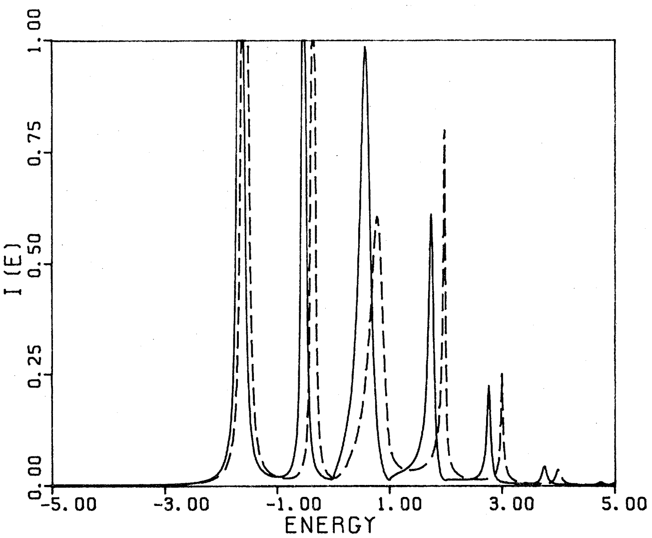

FIG. 4. Absorption spectrum $I(E)$ in arbitrary units vs energy for $B=1.0$ and $S=1.0$. 2-DCPA (solid line) and 1-DCPA (dashed line). The heights of the peaks off scale have ratios (2-DCPA/1-DCPA), from left to right, equal to 0.91 and 1.06, respectively.

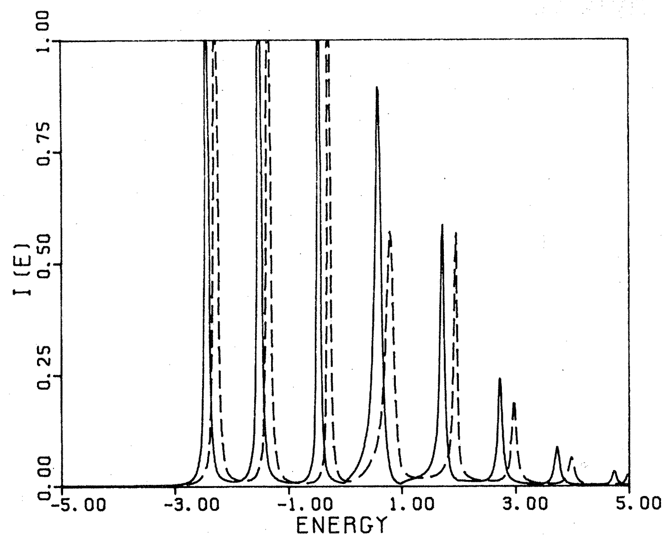

FIG. 5. Absorption spectrum $I(E)$ is arbitrary units, vs energy for $B=1.0$ and $S=2.0$. 2-CDPA (solid line) and 1-DCPA (dashed line). The heights of the peaks off scale have ratios (2-DCPA)/(1-DCPA) from left to right, equal to 0.81, 1.04, and 1.14, respectively.

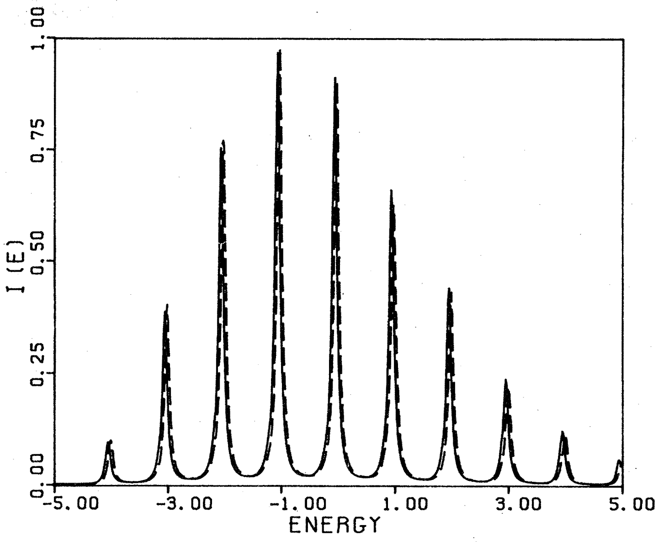

FIG. 7. Absorption spectrum $I(E)$ vs energy for $B=0.2$ and $S=4.0$ 2-DCPA (solid line) and 1-DCPA (dashed line). Both DCPA's in this case of strong coupling are almost identical and approaching the isolated molecule case. For this case we have used $\text{Im}E=0.05$. $X(S)$ for $S=4$ is equal to -0.95 for both the small-polaron case and the 1-DCPA. For the 2-DCPA, $X(4)=-.0.97$.

$(m_p/m^*)_{\text{2-DCPA}} > (m_p/m^*)_{\text{1-DCPA}}$ (we do not plot the effective-mass ratio versus S, since it will look exactly like I_0 vs S).

The integrated absorption spectrum $\int dE\, I(E)$ must equal 1 (in normalized units) for both DCPA's. Since I_0 is reduced in the 2-DCPA with respect to the 1-DCPA it is interesting to see the consequences of this reduction on the whole spectrum. In Figs. 3–7 we plot $I(E)$ vs E for several values of B and S. As before the 2-DCPA (1-DCPA) spectrum is given by the solid (dashed) line. We use for the spectra calculation a finite $\text{Im}E=0.007$ to broaden the δ functions and smear out small unimportant structures. The effects of band renormalization are evident. Besides a shift of the absorption peaks to lower energies, the width of such peaks are systematically reduced. Also the height of low-energy peaks is reduced (as suggested by the values of I_0) at the expense [since the sum rule $\int dE\, I(E)=1$ must be satisifed] of increasing the oscillator strength of high-energy peaks. In Fig. 3, $B=1.0$ and $S=0.5$, we see that we are approaching the weak coupling limit, a similar result is obtained from perturbation theory, from Eq. (2.25) displaying the 0-0 phonon line and the first vibronic level broadening in the crystal corresponding to the emission of one phonon [Eq. (2.25)]. Of course, on a full DCPA, higher-energy vibronic lines will appear, but are not visible in the scale used in Fig. 3. Figures 3 and 4–6 are characteristic of the intermediate coupling regime $S \sim B$, where the effects of band renormalization mentioned above are the most evident. Finally, in Fig. 7, with $B=0.2$ and $S=4.0$, a strong coupling case, the spectra begin to resemble that of an isolated molecule without molecular relaxation,[1,11] given by

$$I(E)=\exp(-S)\sum_{n=0}^{\infty}\frac{S^n}{n!}\delta(E-E_0-n)\ . \qquad (3.16)$$

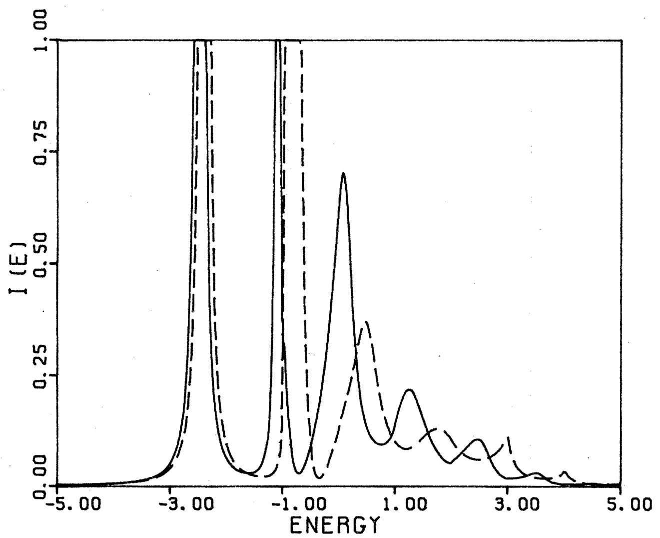

FIG. 6. Absorption spectrum $I(E)$ in arbitrary units, vs energy for $B=2.0$ and $S=1.0$. 2-DCPA (solid line) and 1-DCPA (dashed line). The heights of the peaks off scale have ratios (2-DCPA)/(1-DCPA), from left to right, equal to 0.92 and 2.18, respectively.

IV. CONCLUSION

The aim of the present work is to develop a two-site DCPA and establish this self-consistent calculation as the natural generalization of the single-site DCPA (Ref. 1) that will include both site energy and band renormalization, valid in a wide range of parameter space (B,S). The numerical calculations display no unphysical behavior and agree with perturbation theory in the limits $S/B \rightarrow 0$, $S/B \rightarrow \infty$. The effects of renormalizing the off-diagonal part of the exciton Hamiltonian are what one would expect, e.g., reduction of the linewidth of vibronic peaks in the optical spectrum.

A systematic study of the absorption regions and spectra, the finite-temperature case, and two moelcules per unit cell (and the isomorphic problem of several excited states per molecule) will be presented in planned subsequent papers. Future theoretical developments will include simultaneous treatment of static disorder, calculations of transport properties, and incorporation of a finite phonon bandwidth in the calculation.

Several direct applications of the 1-DCPA to experimental data have been attempted; analysis of optical data from mixed crystals,[17] anthracene crystals,[18] and surface excitons.[19,20] Our method will allow a more quantitative treatment of these (and other) systems; the present theory can already include several potentially important effects (bandwidth renormalization, several molecules per unit cell) which are completely absent from 1-DCPA. A study of the temperature dependence of the full vibronic line shapes would provide for the best comparison of theory and experiment.

ACKNOWLEDGMENTS

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APPENDIX A

We plan to obtain and solve an equation for the matrix elements $\langle n_1,n_2 | \underline{D}(E) | n_1,n_2 \rangle$, Eq. (2.15), and derive Eqs. (2.17), (2.20), and (2.21).

We start from Eqs. (2.4) and (2.6)–(2.8) for $H_{\text{eff}}(E)$, $H_{12}(E)$, $H_A(E)$, and H_B. If

$$H_0(E) = H_{\text{eff}}(E) + H_A(E) \;, \tag{A1}$$

then

$$H_{12}(E) = H_0(E) + H_B \;. \tag{A2}$$

If we Fourier transform the trivial identity

$$\begin{aligned}(E - H_{12})^{-1} &= (E - H_0)^{-1} \\ &\quad + (E - H_0)^{-1} H_B (E - H_{12})^{-1} \;, \end{aligned} \tag{A3}$$

we obtain another identity

$$\begin{aligned}\exp(-iH_{12}t) &= \exp(-iH_0 t) \\ &\quad - i \int_0^t d\tau \exp[-iH_0(t-\tau)] H_B \\ &\quad \times \exp(-iH_{12}\tau) \end{aligned} \tag{A4}$$

(note that the Fourier transforms of $H_{12}(E)$ and $H_0(E)$ depends on the real time t, so $\exp-[iH(t)t]$ should be understood as a shorthand notation for $\exp[-i\int_0^t d\tau H(\tau)]$).

We define the auxiliary Green's function $\underline{D}(E)$ with matrix elements

$$\begin{aligned} D_{\alpha\alpha'}(E) &= -i \int_0^\infty dt \exp(iEt) \exp(iH_{12}t) A_\alpha \\ &\quad \times \exp(-iH_{12}t) A^\dagger_{\alpha'}, \quad \alpha,\alpha' = 1,2 \;. \end{aligned} \tag{A5}$$

As in the main text we denote by $| n_1,n_2 \rangle$ the complete basis set with n_1 (n_2) phonons in site 1 (2) which contains the exciton vacuum.

If we use Eqs. (A1), (A2), the identity Eq. (A4) in Eq. (A5), and use the fact that $H_0(E)$ is diagonal on the phonons states, we obtain, for $\langle n_1,n_2 | D_{\alpha\alpha'}(E) | m_1,m_2 \rangle$, the following equation:

$$\begin{aligned} \langle n_1,n_2 | D_{\alpha\alpha'}(E) | m_1,m_2 \rangle &= F_{\alpha\alpha'}(E) \delta_{n_1,m_1} \delta_{n_2,m_2} \\ &\quad - \int_0^\infty dt \int_0^t d\tau \exp[iEt + i\tau(n_1+n_2-m_1'-m_2')] \\ &\quad \times P_\gamma(n_1',n_2',m_1',m_2') \langle n_1,n_2 | \exp[iH_0(t-\tau)] A_\alpha \exp[-iH_0(t-\tau)] A^\dagger_\gamma | n_1' n_2' \rangle \\ &\quad \times \langle m_1' m_2' | \exp(iH_{12}\tau) A_\gamma \exp(-iH_{12}\tau) A^\dagger_{\alpha'} | m_1,m_2 \rangle, \alpha,\alpha',\gamma = 1,2, \end{aligned} \tag{A6}$$

where we have inserted a complete set of intermediate states (and use the summation convention for repeated indices). P_γ is given by

$$P_\gamma(n_1',n_2',m_1',,m_2') = \langle n_1',n_2' | A_\gamma H_B A^\dagger_\gamma | m_1',m_2' \rangle \tag{A7}$$

where $\gamma = 1,2$ with no summation over γ. From Eq. (2.8), using some harmonic-oscillator algebra, we find that, with $\lambda = (S)^{1/2}$

$$\begin{aligned} P_\gamma(n_1' n_2',m_1',m_2') &= \lambda \delta_{\gamma,1} \delta_{n_2',m_2'} [\delta_{n_1',m_1'+1}(m_1'+1)^{1/2} + \delta_{n_1',m_1'-1}(m_1')^{1/2}] \\ &\quad + \lambda \delta_{\gamma,2} \delta_{n_1' m_1'} [\delta_{n_2',m_2'+1}(m_2'+1)^{1/2} + \delta_{n_2',m_2'-1}(m_2')^{1/2}] \\ &\quad + \Delta\omega \delta_{n_1' m_1'} \delta_{n_2' m_2'} [\delta_{\gamma,1} m_1' + \delta_{\gamma,2} m_2'] \;. \end{aligned} \tag{A8}$$

By using the definition of $\underline{F}(E)$, $\underline{D}(E)$, and the convolution theorem, we obtain

$$\langle n_1,n_2 | D_{\alpha\alpha'}(E) | m_1,m_2 \rangle = F_{\alpha\alpha'}(E) \delta_{n_1 m_1} \delta_{n_2 m_2} + F_{\alpha\gamma}(E) \langle p_1,p_2 | D_{\gamma\alpha'}(E + n_1 + n_2 - p_1 - p_2) | m_1,m_2 \rangle P_\gamma(n_1,n_{2,}p_1,p_2) \;. \tag{A9}$$

We define the operator $\hat{\underline{B}}$,

$$\hat{\underline{B}}=\begin{bmatrix} b_1 & 0 \\ 0 & b_2 \end{bmatrix} . \tag{A10}$$

b_1 (b_2) annihilates a phonon in site 1 (2). Similarly we define $\hat{\underline{B}}^{\dagger}$. Equation (A9) can be regarded, after using Eq. (A8), as the matrix elements of the operator equation

$$\underline{D}(E)=\underline{R}(E)[1+\lambda\hat{\underline{B}}^{\dagger}\underline{D}(E+1)+\lambda\hat{\underline{B}}\,\underline{D}(E-1)] \tag{A11}$$

with

$$\underline{R}(E)=\underline{F}(E)[\mathbb{1}-\Delta\omega\,\hat{\underline{B}}^{\dagger}\hat{\underline{B}}\,\underline{F}(E)]^{-1} . \tag{A12}$$

We condense in one index the pair $(n_1,n_2)=N$ and define the following matrices:

$$||\underline{N}\rangle=\begin{bmatrix} |n_1,n_2\rangle & 0 \\ 0 & |n_1,n_2\rangle \end{bmatrix} ,$$

$$\underline{X}(N)=\begin{bmatrix} n_1\Theta(n_1) & 0 \\ 0 & n_2\Theta(n_2) \end{bmatrix} , \tag{A13}$$

and the associated matrices $||\underline{N}^{\pm}\rangle, \underline{W}(N)$,

$$||\underline{N}^{\pm}\rangle=\begin{bmatrix} |n_1\pm1,n_2\rangle & 0 \\ 0 & |n_1,n_2\pm1\rangle \end{bmatrix} ,$$

$$\underline{W}(N)=[\underline{X}(N)]^{1/2} . \tag{A14}$$

It follows that

$$\hat{\underline{B}}||\underline{N}\rangle=\underline{W}(N)||\underline{N}^{-}\rangle ,$$

$$\underline{B}^{\dagger}||\underline{N}\rangle=\underline{W}(N+1)||\underline{N}^{+}\rangle , \tag{A15}$$

$$\hat{\underline{B}}^{\dagger}\underline{B}||\underline{N}\rangle=\underline{X}(N)||\underline{N}\rangle .$$

By calculating $\langle\underline{N}||\underline{D}(E)||\underline{M}\rangle$ from Eq. (A11) we obtain

$$\langle\underline{N}||\underline{D}(E)||\underline{M}\rangle=\underline{R}_N(E)\underline{\delta}_{NM}+\lambda\underline{R}_N(E)\underline{W}(N)\langle\underline{N}^{-}||\underline{D}(E+1)||\underline{M}\rangle+\lambda\underline{R}_N(E)\underline{W}(N+1)\langle\underline{N}^{+}||\underline{D}(E-1)||\underline{M}\rangle \tag{A16}$$

with

$$\underline{\delta}_{NM}=\langle\underline{N}||\underline{M}\rangle=\begin{bmatrix} \delta_{n_1m_1}\delta_{n_2m_2} & 0 \\ 0 & \delta_{n_1m_1}\delta_{n_2m_2} \end{bmatrix} \tag{A17}$$

and

$$\underline{R}_N(E)=\langle\underline{N}||\underline{R}(E)||\underline{N}\rangle=\underline{F}(E)[\mathbb{1}-\Delta\omega\,\underline{X}(N)\underline{F}(E)]^{-1} . \tag{A18}$$

We define $\underline{H}(E)=\underline{F}^{-1}(E)$, $\underline{K}_N(E)=\underline{R}_N^{-1}(E)$, and $\underline{D}_N(E)=\langle\underline{N}||\underline{D}(E)||\underline{N}\rangle$.

From Eqs. (A16) and (A18) it follows that

$$\begin{aligned}\underline{K}_N(E)=\underline{\delta}_{NM}\underline{D}_N^{-1}(E)&+\lambda\underline{W}(N)\langle\underline{N}^{-}||\underline{D}(E+1)||\underline{M}\rangle[\langle\underline{N}||\underline{D}(E)||\underline{M}\rangle]^{-1}\\&+\lambda\underline{W}(N+i)\langle\underline{N}^{+}||\underline{D}(E-1)||\underline{M}\rangle[\langle\underline{N}||\underline{D}(\underline{E})||\underline{M}\rangle]^{-1}\end{aligned} \tag{A19}$$

and

$$\underline{K}_N(E)=\underline{H}(E)-\Delta\omega\,\underline{X}(N) . \tag{A20}$$

Define $\underline{\Gamma}_{N,M}(E)$ as

$$\underline{\Gamma}_{N,M}(E)=\langle\underline{N}^{+}||\underline{D}(E-1)||\underline{M}\rangle[\langle\underline{N}||D(E)||\underline{M}\rangle]^{-1} . \tag{A21}$$

Then Eq. (A19) reads

$$\begin{aligned}\underline{K}_N(E)=\underline{\delta}_{NM}\underline{D}_N^{-1}(E)&+\lambda\underline{W}(N+1)\underline{\Gamma}_{NM}(E)\\&+\lambda\underline{W}(N)\underline{\Gamma}_{N^{-}M}^{-1}(E+1) .\end{aligned} \tag{A22}$$

If $N=M$ from Eq. (A22) we obtain

$$\begin{aligned}\underline{D}_N^{-1}(E)=\underline{K}_N(E)&-\lambda\underline{W}(N+1)\underline{\Gamma}_{NN}(E)\\&-\lambda\underline{W}(N)\underline{\Gamma}_{N^{-}N}^{-1}(E+1) .\end{aligned} \tag{A23}$$

For $N\neq M$ from Eq. (A22) we have either

$$\underline{\Gamma}_{N^{-}M}(E+1)=\lambda\underline{W}(N)[\underline{K}_N(E)-\lambda\underline{W}(N+1)\underline{\Gamma}_{NM}(E)]^{-1} \tag{A24}$$

or

$$\underline{\Gamma}_{NM}^{-1}(E)=\lambda\underline{W}(N+1)[\underline{K}_N(E)-\lambda\underline{W}(N)\underline{\Gamma}_{N^{-}M}^{-1}(E+1)]^{-1} . \tag{A25}$$

By iterating both Eqs. (A24) and (A25) we obtain

$$\underline{\Gamma}_{NN}(E)=\cfrac{S\underline{W}(N+1)}{\underline{K}_{N+1}(E-1)-\cfrac{S\underline{X}(N+2)}{\underline{K}_{N+2}(E-2)-\cfrac{S\underline{X}(N+3)}{\underline{K}_{N+3}(E-3)-\cdots}}} \tag{A26}$$

and

$$\Gamma^{-1}_{N-N}(E+1)=\cfrac{S\underline{W}(N)}{\underline{K}_{N-1}(E+1)-\cfrac{S\underline{X}(N-1)}{\underline{K}_{N-2}(E+2)-\cfrac{S\underline{X}(N-2)}{\underline{K}_{N-3}(E+3)-\cdots}}} . \tag{A27}$$

Finally we define

$$\begin{aligned}\underline{\Gamma}_1(E,n_1,n_2)&=\lambda\underline{W}(N)\underline{\Gamma}^{-1}_{N-N}(E+1) ,\\ \underline{\Gamma}_2(E,n_1,n_2)&=\lambda\underline{W}(N+1)\underline{\Gamma}_{NN}(E) .\end{aligned} \tag{A28}$$

From Eqs. (A14), (A20), (A23), and (A26)—(A28) we obtain

$$\langle n_1,n_2\,|\,\underline{D}(E)\,|\,n_1,n_2\rangle^{-i}=\underline{H}(E)-\Delta\omega\,\underline{X}(n_1,n_2)-\underline{\Gamma}_1(E,n_1,n_2)-\underline{\Gamma}_2(E,n_1,n_2) , \tag{A29}$$

where

$$\underline{\Gamma}_1(E,n_1,n_2)=\cfrac{S\underline{X}(n_1,n_2)}{\underline{H}(E+1)-\Delta\omega\underline{X}(n_1-1,n_2-1)-\cfrac{S\underline{X}(n_1-1,n_2-1)}{\underline{H}(E+2)-\cdots}} \tag{A30}$$

and

$$\underline{\Gamma}_2(E,n_1,n_2)=\cfrac{S\underline{X}(n_1+1,n_2+1)}{\underline{H}(E-1)-\Delta\omega\underline{X}(n_1+1,n_2+1)-\cfrac{S\underline{X}(n_1+2,n_2+2)}{\underline{H}(E-2)-\cdots}} \tag{A31}$$

are the desired continued fractions expansions for the matrix elements of $\underline{D}(E)$.

APPENDIX B

We generalize results of Sec. II for the case of more than one molecule per unit cell. We consider explicitly two molecules per unit cell; extension to a large number is straightforward and can be accomplished by replacing the 2×2 submatrices in what follows by $M\times M$ submatrices.

Let n label the position of the nth cell ($n=1,\ldots,N$) and $\alpha(\beta)=1,2$ label each molecule within the unit cell. We write the unperturbed exciton Hamiltonian H as (see, for example, Ref. 14)

$$H=\sum_{n,\alpha,\beta}\epsilon_{n,\alpha\beta}A^{\dagger}_{n\alpha}A_{n\beta}+\sum_{n\neq m}J_{n\alpha,m\beta}A^{\dagger}_{n\alpha}A_{m\beta} , \tag{B1}$$

where as usual $A_{n\alpha}$ ($A^{\dagger}_{n\alpha}$) annihilates (creates) an exciton at site (n,α).

The lattice is regarded as the superposition of two sublattices. Sublattice i ($i=1,2$) is composed of N molecules (n,α), $n=1,\ldots,N$, $\alpha=i$. Let us consider only nearest-neighbor (NN) interactions, but noticing that a molecule (n,α) has two sets of NN's, namely Z_α NN's of type α and $Z_{\alpha\beta}$ NN's of type $\beta\neq\alpha$. Translational invariance implies

$$\begin{aligned}&\epsilon_{n\alpha\beta}=\epsilon_{\alpha\beta} ,\\ &J_{n\alpha,m\beta}=\begin{cases}J_{\alpha\beta} & \text{if } n,m \text{ a NN cell}\\ 0 & \text{otherwise,}\end{cases}\\ &\alpha,\beta=1,2 .\end{aligned} \tag{B2}$$

We define

$$\begin{aligned}\underline{\epsilon}&=\begin{bmatrix}\epsilon_1 & \epsilon_{12}\\ \epsilon_{12} & \epsilon_2\end{bmatrix} ,\\ \underline{J}&=\begin{bmatrix}J_1 & J_{12}\\ J_{12} & J_2\end{bmatrix} ,\\ \vec{\mathrm{A}}_n&=\begin{bmatrix}A_{n1}\\ A_{n2}\end{bmatrix} ,\end{aligned} \tag{B3}$$

where we have supressed the double index for the diagonal terms and incorporated the symmetric character of the off-diagonal terms.

Then Eq. (B1) reads

$$H=\sum_n\vec{\mathrm{A}}^{\dagger}_n\bar{\epsilon}\vec{\mathrm{A}}_n+\sum_{n\neq m}{}'\,\vec{\mathrm{A}}^{\dagger}_n\underline{J}\vec{\mathrm{A}}_m , \tag{B4}$$

where the prime stands for summation over NN cells. We also define $A_{k\alpha}$ ($A^{\dagger}_{k\alpha}$) as the annihilation (creation) of an exciton with momentum k at site α, given by

$$\vec{A}_{\vec{k}}=\begin{bmatrix} A_{\vec{k}_1} \\ A_{\vec{k}_2} \end{bmatrix}=(N)^{1/2}\sum_n \vec{A}_n \exp(i\vec{k}\cdot\vec{R}_n) , \tag{B5}$$

where $\vec{R}_n$ is the vector position of the nth cell ($n=1,\ldots,N$).

Define the matrix $\underline{B}$ as

$$\underline{B}=\begin{bmatrix} Z_1J_1 & Z_{12}J_{12} \\ Z_{12}J_{12} & Z_2J_2 \end{bmatrix} . \tag{B6}$$

H in Eq. (B4) can be written as

$$H=\sum_{\vec{k}} \vec{A}^{\dagger}_{\vec{k}}\underline{H}(\vec{k})\vec{A}_{\vec{k}} , \tag{B7}$$

where

$$\begin{aligned} &\underline{H}(\vec{k})=\underline{\epsilon}+\underline{B}\Omega(\vec{k}) , \\ &\underline{B}\Omega(\vec{k})=\sum_m{}' \underline{J}\exp(i\vec{k}\cdot\vec{B}_m) . \end{aligned} \tag{B8}$$

We have assumed identical sublattices, so $\Omega(\vec{k})$ is a scalar. Notice that for a fixed wave vector $\vec{k}$ we have two single-exciton states, associated with the bands $\alpha=1,2$, respectively. Band α ($\alpha=1,2$) is centered at ϵ_α, has a bandwidth $2B_\alpha$, and is described by the dispersion relation $E^0_\alpha(\vec{k})=\epsilon_\alpha+B_\alpha\Omega(\vec{k})$. The eigenvectors for $\underline{H}(\vec{k})$ are two single-exciton states given by a linear combination of exciton states of type 1 and 2. The mixture occurs via the off-diagonal elements of $\underline{\epsilon}$ and $\underline{B}$. Let us define $\xi(\vec{k})=\epsilon_{12}+B_{12}\Omega(\vec{k})$. The eigenvalues of H in Eq. (B7) are

$$E_{\pm}(\vec{k})=\tfrac{1}{2}(E^0_1(\vec{k})+E^0_2(\vec{k})\pm\{[E^0_1(\vec{k})-E^0_2(\vec{k})]^2 +4\xi^2(\vec{k})\}^{1/2}) . \tag{B9}$$

We define the Green's function operator $\hat{\underline{G}}(E)$ as

$$\hat{\underline{G}}(E)=\sum_k |k\rangle\langle k|\underline{G}(\vec{k},E) , \tag{B10}$$

where

$$\underline{G}(\vec{k},E)=[E-\underline{H}(\vec{k})]^{-1} \tag{B11}$$

and

$$|k\rangle=(N)^{-1/2}\sum_n \exp(i\vec{k}\cdot\vec{R}_n)|n\rangle \tag{B12}$$

with $|k\rangle$ and $|n\rangle$ single-exciton states with momentum $\vec{k}$ and at site $|n\rangle$, respectively.

Recalling that there is one unit cell per site and two molecules per site, in the two-site calculation, relevant functions are going to be 4×4 matrices, decomposed into 2×2 blocks according to site labeling, each block being a 2×2 matrix. For example, the Green's function $G(E)$ is (as in Sec. II)

$$\underline{G}(E)=\begin{bmatrix} \underline{G}^D(E) & \underline{G}^N(E) \\ \underline{G}^N(E) & \underline{G}^D(E) \end{bmatrix} . \tag{B13}$$

Translational invariance again imposes the equivalence of the diagonal (off-diagonal) labeled now with superscript $D(N)$. For two molecules per site $\underline{G}^D(E)$ and $\underline{D}^N(E)$ are themselves 2×2 matrices and given by

$$\begin{aligned} &\underline{G}^D(E)=\langle n|\hat{\underline{G}}(E)|n\rangle=N^{-1}\sum_{\vec{k}}\underline{G}(\vec{k},E) , \\ &\underline{G}^N(E)=\langle n|\hat{\underline{G}}(E)|m\rangle=N^{-1}\sum\underline{G}(\vec{k},E)\Omega(\vec{k}) , \end{aligned} \tag{B14}$$

where n,m are NN cells.

Let us define the function $g(E)$ as

$$g(E)=N^{-1}\sum_{\vec{k}}[E-\Omega(\vec{k})]^{-1} . \tag{B15}$$

$g(E)$ is the diagonal Green's function (scalar) for the case of unperturbed bands ($\epsilon_{12}=B_{12}=0$) for bands centered at $\epsilon_1=\epsilon_2=0$ with unit half-bandwidth, $B_1=B_2=1$. For a one-dimensional crystal there is an exact analytic expression for $g(E)$, and for dimension three we can use the Hubbard density of states model as pointed out in Sec. III.

After some lengthy but straightforward algebra, we obtain, for $\underline{G}^{D,N}(E)$, in terms of $g(E)$,

$$\begin{aligned} &\underline{G}^D(E)=\underline{A}_0(E)+\sum_{i=1}^{2}\underline{A}_i(E)g(X_i(E)) , \\ &\underline{G}^N(E)=\sum_{i=1}^{2}\underline{A}_i(E)[X_i(E)g(X_i(E))-1] . \end{aligned} \tag{B16}$$

Here we distinguish two cases: (i) $\det\underline{B}=b_0\neq0$ and (ii) $\det\underline{B}=0$. For case (i),

$$\begin{aligned} &\underline{A}_0(E)=\underline{0} , \\ &\underline{A}_i(E)=(-1)^{i+1}[2b_0\Delta(E)]^{-1}\underline{A}'_1(E) , \\ &A'_i(E)=\begin{bmatrix} E-\epsilon_2-B_2X_i(E) & \epsilon_{12}+B_{12}X_i(E) \\ \epsilon_{12}+B_{12}X_i(E) & E-\epsilon_1-B_1X_i(E) \end{bmatrix} , \end{aligned} \tag{B17}$$

with

$$\begin{aligned} &\Delta(E)=[b^2(E)-C(E)]^{1/2} , \\ &b(E)=(2b_0)^{-1}[B_1(E-\epsilon_2)+B_2(E-\epsilon_1) +2\epsilon_{12}B_{12}] , \\ &C(E)=b_0^{-1}[(E-\epsilon_1)(E-\epsilon_2)-\epsilon_{12}^2] , \\ &X_1(E)=b(E)-\Delta(E) , \\ &X_2(E)=b(E)+\Delta(E) . \end{aligned} \tag{B18}$$

For case (ii),

$$\begin{aligned} &\underline{A}_0(E)=K(E)\begin{bmatrix} B_2 & B_{12} \\ B_{12} & B_1 \end{bmatrix} , \\ &\underline{A}_1(E)=K(E)\begin{bmatrix} E-\epsilon_2-B_2X_1(E) & \epsilon_{12}+B_{12}X_1(E) \\ \epsilon_{12}+B_{12}X_1(E) & E-\epsilon_1-B_1X_1(E) \end{bmatrix} , \\ &\underline{A}_2(E)=\underline{0} , \end{aligned} \tag{B19}$$

with

$$K^{-1}(E)=B_1(E-\epsilon_2)+B_2(E-\epsilon_1)+2\epsilon_{12}B_{12}$$

and

$$X_1(E)=K(E)[(E-\epsilon_1)(E-\epsilon_2)-\epsilon_{12}^2]\ . \tag{B20}$$

For the case of unperturbed bands, we obtain the expected result

$$\begin{aligned}G^D_{\alpha\beta}(E)&=\delta_{\alpha\beta}B_\alpha^{-1}g(X_\alpha)\ ,\\ G^N_{\alpha\beta}(E)&=\delta_{\alpha\beta}B_\alpha^{-1}[X_\alpha g(X_\alpha)-1]\ ,\end{aligned} \tag{B21}$$

with

$$X_\alpha=B_\alpha^{-1}(E-\epsilon_\alpha)\ . \tag{B22}$$

Results from Sec. II can be readily applied for the case of a two-site two molecules per unit cell DCPA with the following provisions: n_1 (n_2), [Eq. (2.15)] should be understood as the pair n_{11},n_{12} (n_{21},n_{22}). $\underline{G}(E)$ [Eq. (2.12)] should be replaced by Eq. (B16), provided we substitute in Eq. (B16) $\underline{\epsilon}$ and $\underline{B}$ [Eq. (B3)] by $\underline{\Sigma}^D(E)$ and $\underline{\Sigma}^N(E)$, respectively, where

$$\underline{\Sigma}^{D,N}(E)=\begin{bmatrix}\Sigma_{11}^{D,N}(E) & \Sigma_{12}^{D,N}(E)\\ \Sigma_{12}^{D,N}(E) & \Sigma_{22}^{D,N}(E)\end{bmatrix}\ . \tag{B23}$$

$\underline{F}(E)$ is given by Eq. (2.14) provided we replace $\underline{G}(E)$ as stated above and $\underline{V}(E)$ by

$$\underline{V}(E)=\begin{bmatrix}\underline{\Sigma}^D(E)-\underline{\epsilon} & \underline{\Sigma}^N(E)-\underline{B}\\ \underline{\Sigma}^N(E)-\underline{B} & \underline{\Sigma}^D(E)-\underline{\epsilon}\end{bmatrix}\ . \tag{B24}$$

$\underline{\epsilon}$, $\underline{B}$, and $\underline{\Sigma}^{D,N}(E)$ are given by Eqs. (B3) and (B23), respectively. $\underline{X}(n_1,n_2)$ [Eq. (2.19)] should be replaced by

$$\underline{X}(n_{11},n_{12},n_{21},n_{22})=\begin{bmatrix}n_{11}\Theta(n_{11}) & 0 & 0 & 0\\ 0 & n_{12}\Theta(n_{12}) & 0 & 0\\ 0 & 0 & n_{21}\Theta(n_{21}) & 0\\ 0 & 0 & 0 & n_{22}\Theta(n_{22})\end{bmatrix}\ . \tag{B25}$$

Similarly if the linear and quadratic exciton-phonon coupling constants are different for each molecule in the unit cell, then S and $\Delta\omega$ should be replaced by

$$\underline{S}=\begin{bmatrix}S_1 & 0 & 0 & 0\\ 0 & S_2 & 0 & 0\\ 0 & 0 & S_1 & 0\\ 0 & 0 & 0 & S_2\end{bmatrix}$$

and

$$\underline{\Delta\omega}=\begin{bmatrix}\Delta\omega_1 & 0 & 0 & 0\\ 0 & \Delta\omega_2 & 0 & 0\\ 0 & 0 & \Delta\omega_1 & 0\\ 0 & 0 & 0 & \Delta\omega_2\end{bmatrix}\ . \tag{B26}$$

We have assumed throughout, that there is only one vibrational mode per moelcule with *identical* frequency for both molecules in the unit cell.

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