

CALCULATION OF THE EXCITON GREEN'S FUNCTION OF A MOLECULAR CRYSTAL FROM A TWO-SITE DYNAMICAL COHERENT POTENTIAL APPROXIMATION

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A new two-site dynamical coherent potential approximation for exciton-phonon interaction models corresponding to a homomorphic partition of the hamiltonian is described. The renormalization of both the site energy and the exciton bandwidth is accomplished in contrast to single-site CPA models.

The dynamical coherent potential approximation (CPA) was developed by Sumi [1] to treat exciton-phonon interactions in a simple model hamiltonian. The model arises from, e.g. a molecular crystal with one molecule per unit cell and one harmonic vibrational mode per molecule linearly coupled to a single excited state:

$$H = \sum_k \epsilon(k) A_k^\dagger A_k + h\omega \sum_n h_n + h\omega g \sum_n Q_n A_n^\dagger A_n. \quad (1)$$

Here $\epsilon(k)$ is the energy of an exciton with wave vector k , ω is the vibrational frequency (hereafter we set $h\omega = 1$ and express all energies in units of $h\omega$), g is the exciton-phonon coupling constant, $h_n = B_n^\dagger B_n$ is the phonon number operator for lattice site n , A_k^\dagger (A_k) are creation (destruction) operators for the Bloch states $|k\rangle$, and A_n^\dagger (A_n) are creation (destruction) operators for the Wannier states $|n\rangle$. We are interested only in one-exciton states, so that $\sum_k A_k^\dagger A_k = \sum_n A_n^\dagger A_n = 1$. The vibrational coordinates Q_1, \dots, Q_N are taken to be independent normal modes localized at site n .

In Sumi's original version of the dynamical CPA, the coherent potential $V(E)$ (the site diagonal self-consistent self-energy) is found by requiring that the averaged T -matrix for scattering by phonons at a single site in the effective medium vanish. The exci-

ton Green's function thermally averaged over the canonical ensemble of phonons is then

$$\langle \mathcal{G}(E) \rangle = \sum_k \frac{|k\rangle\langle k|}{\epsilon(k) - E - V(E)} \quad (2)$$

and the condition to determine $V(E)$ is

$$\langle \mathcal{G}(E) \rangle_{11} = \sum_k \frac{1}{\epsilon(k) - E - V(E)} = \langle \mathcal{G}'(E) \rangle_{11}, \quad (3)$$

where $\langle \mathcal{G}'(E) \rangle$ is the thermally averaged one-exciton Green's function of the hamiltonian

$$H_1 = H_0 + [gQ_1 - V(E)] A_1^\dagger A_1 + h_1 \quad (4)$$

and

$$H_0 = \sum_k [\epsilon(k) + V(E)] A_k^\dagger A_k. \quad (5)$$

We shall call this formulation the one-site dynamical CPA.

Physical insight into the validity of this approximation can be obtained by rewriting the effective hamiltonian H_0 in terms of site-diagonal exciton operators:

$$H_0 = V(E) \sum_n A_n^\dagger A_n + J \sum_n \sum_{m \neq n} A_n^\dagger A_m. \quad (6)$$

We will assume henceforth that the exchange integral J connects only nearest neighbors.

It is clear from this representation that the coherent potential $V(E)$ renormalizes the diagonal energy per

site but not the exciton bandwidth $B = 2J$. This is a reasonable approach for the disordered systems without phonons for which the CPA was originally developed [2,3]. However, in exciton-phonon problems it is well known that renormalization of the exciton bandwidth is quite important for a wide range of parameter values. For example, in a calculation utilizing a variational small polaron transformation [4], the hamiltonian is transformed to

$$\tilde{H} = e^S H e^{-S}, \quad (7)$$

where

$$S = \sum_n \tilde{g} (B_n - B_n^+) A_n^+ A_n,$$

so that to first order the site energies are renormalized by $-\frac{1}{2}\tilde{g}^2$ and the exchange term becomes

$$\begin{aligned} H_{ex} &= J \left\langle e^S \sum_n \sum_m A_n^+ A_m e^{-S} \right\rangle \\ &= \tilde{J} \sum_n \sum_m A_n^+ A_m, \end{aligned} \quad (8)$$

where the outer brackets in eq. (8) represent an average over the canonical ensemble.

The problem with the above technique is that to evaluate the Green's function in detail, it is necessary to use perturbation expansions in J or g .

There are certainly regions of parameter space in which this procedure is valid, but in general one has no guarantee that the expansions will converge. Recent studies on the analogous dimer problem [5,6] indicate that for $2J > \omega$, a temperature is invariably reached (for some values of g , this will be at $T = 0$) for which the variational small polaron treatment is incapable of generating accurate results.

In this letter, we introduce a modification of the dynamical CPA which overcomes the difficulties associated with each of the two approaches described above, i.e. both the site energies and the bandwidth are renormalized and self-consistent (rather than perturbative) methods are used to calculate the averaged diagonal and off-diagonal self-energies.

There have been self-consistent formulations of the CPA previously [7], as well as attempts to renormalize the off-diagonal self-energy [8]; we believe our work to be the first to attempt both. Detailed numerical calculations and comparison with previous

theories will be presented in a future publication.

The hamiltonian is rewritten as

$$\begin{aligned} H &= H_0 + H', \\ H_0 &= V(E) \sum_n A_n^+ A_n \\ &+ \sigma(E) \sum_n \sum_{m \neq n}' A_n^+ A_m + \sum_n h_n, \\ H' &= \sum_n [gQ_n - V(E)] A_n^+ A_n \\ &+ [J - \sigma(E)] \sum_n \sum_{m \neq n}' A_n^+ A_m. \end{aligned} \quad (9)$$

Here $V(E)$ is, as before, the site-diagonal averaged self-energy and $\sigma(E)$ is an off-diagonal averaged self-energy coupling nearest neighbors (the prime on the double sums restricts the terms to nearest neighbors). The symmetry of the hamiltonian ensures that

$$\sigma_{nm}(E) = \sigma(E) \quad \text{for all nearest neighbors } n, m. \quad (10)$$

We must find $V(E)$ and $\sigma(E)$ simultaneously for a given energy E . To do this we need two simultaneous equations which must be derived using the perturbation H' . The simplest approach is to define a two-site (nearest neighbor) scattering hamiltonian in the effective medium.

$$\begin{aligned} H_{12} &= H_0 + (1/2z) \{ [gQ_1 - V(E)] A_1^+ A_1 \\ &+ [gQ_2 - V(E)] A_2^+ A_2 \} + \frac{1}{2} [J - \sigma(E)] (A_1^+ A_2 + A_2^+ A_1) \\ &= H_0 + \tilde{H}_{12}, \end{aligned} \quad (11)$$

where z is the number of nearest neighbors. Note that we have defined \tilde{H}_{12} so that

$$\sum_{i,j \neq i} \tilde{H}_{ij} = H'. \quad (12)$$

Thus our two-site dynamical CPA is derived from a homomorphic partition of H and, as shown by Odagaki and Yonezawa [9,10] yields an averaged Green's function which is analytic off the real axis. We define the thermally averaged exciton Green's function matrix elements for H_{12} as

$$\langle \Gamma(E) \rangle_{\alpha\alpha'} = \frac{1}{Z} \sum_{n_1} \sum_{n_2} \exp[-\beta(n_1 + n_2)] \times D_{n_1 n_2}^{\alpha\alpha'}(E; n_1 n_2), \quad (13)$$

where

$$D_{n_1 n_2}^{\alpha\alpha'}(E; m_1 m_2) = \int \langle n_1 n_2 | e^{iH_{12}t} A_{\alpha}^+ \times e^{-iH_{12}t} A_{\alpha'}^+ | m_1 m_2 \rangle e^{iEt} dt$$

and $|n_1 n_2\rangle$ is a basis vector with n_1 phonons in oscillator 1, n_2 in oscillator 2, and contains the exciton vacuum. Z is the harmonic oscillator partition function;

$$Z = \sum_{n_1} \sum_{n_2} \exp[-\beta(n_1 + n_2)]$$

and $\beta = 1/kT$.

If G^0 is the Green's function associated with H_0 , we have

$$\langle \Gamma \rangle = G^0 + G^0 \langle T^{(12)} \rangle G^0, \quad (14)$$

where $T^{(12)}$ is the T -matrix associated with the perturbation part of H_{12}

The usual CPA condition then is to require that

$$\langle T^{(12)} \rangle = 0, \quad (15)$$

which is equivalent to

$$\langle \Gamma \rangle = G^0. \quad (16)$$

The symmetry of H_{12} and H_0 guarantees that

$$G_{11}^0 = G_{22}^0, \quad \langle \Gamma \rangle_{11} = \langle \Gamma \rangle_{22} \quad (17)$$

so that eq (16) leads to two relevant equations

$$\langle \Gamma \rangle_{11} = G_{11}^0, \quad \langle \Gamma \rangle_{12} = G_{12}^0. \quad (18)$$

These two simultaneous equations determine the self-consistent self-energies $V(E)$ and $\sigma(E)$.

$G_{\alpha\alpha}^0$ is easily computed once a dispersion relation $\epsilon(k)$ is chosen for the exciton band. Evaluation of $\langle \Gamma \rangle_{\alpha\alpha'}$ (which requires evaluation of $\langle T \rangle$) is more complicated and must be done numerically. In what follows we give a brief outline of a practical procedure for doing this.

We rewrite H_{12} as

$$H_{12} = H_A + H_B,$$

$$H_A = H_0 + [J - \sigma(E)](A_1^+ A_2 + A_2^+ A_1)$$

$$- V(E)(A_1^+ A_1 + A_2^+ A_2),$$

$$H_B = (\xi Q_1 A_1^+ A_1 + \xi Q_2 A_2^+ A_2). \quad (19)$$

The Green's function $G^A(E)$ associated with H_A is just that of a dimer embedded in the effective medium and can be found using standard impurity scattering techniques [11].

We can now obtain, in a manner analogous to Sumi, a matrix equation for the vibronic Green's function matrix elements $D_{n_1 n_2}^{\alpha\alpha'}(E; m_1 m_2)$

$$M D = \Psi \quad \text{or} \quad D = M^{-1} \Psi, \quad (20)$$

from which the required diagonal elements of D , $D_{n_1 n_2}^{\alpha\alpha}$, can be determined.

The matrices M and Ψ are defined from the set of equations

$$D_{n_1 n_2}^{\alpha\alpha'}(E; m_1 m_2) = \delta_{n_1 m_1} \delta_{n_2 m_2} G_{\alpha\alpha}^A(E) + 2^{-1/2} g \sum_{\gamma=1}^2 G_{\alpha\gamma}^A(E + n_1 + n_2 - m_1 - m_2) \times [(n_1 + 1)^{1/2} D_{n_1+1, n_2}^{\alpha\alpha'}(E; m_1 m_2) + n_1^{1/2} D_{n_1-1, n_2}^{\alpha\alpha'}(E; m_1 m_2) + (n_2 + 1)^{1/2} D_{n_1, n_2+1}^{\alpha\alpha'}(E; m_1 m_2) + n_2^{1/2} D_{n_1, n_2-1}^{\alpha\alpha'}(E; m_1 m_2)]. \quad (21)$$

The equations can be simplified by using the symmetry relations

$$D_{n_1 n_2}^{11}(E; m_1 m_2) = D_{n_1 n_2}^{22}(E; m_1 m_2), \quad D_{n_1 n_2}^{12}(E; m_1 m_2) = D_{n_1 n_2}^{21}(E; m_1 m_2). \quad (22)$$

The matrix elements $\langle \Gamma(E) \rangle_{\alpha\alpha'}$ will be dependent upon coherent potentials $V(E \pm p)$, $\sigma(E \pm p)$, $p = 1, 2, \dots$. Thus, self-consistent solutions must be found for all values of p simultaneously. This process is facilitated by noting that for p greater than some p_{max} , we can set $V(E - p)$, $\sigma(E - p) = 0$. The remaining coherent potentials can be determined iteratively.

The validity of n -site generalizations of the CPA has been established by Odagaki and Yonezawa, as

long as the partition of the hamiltonian is homomorphic. We therefore expect no non-physical singularities to arise in this approximate calculation of the exciton Green's function.

The present theory should agree with that of Sumi when bandwidth renormalization is unimportant ($J \rightarrow \infty$ or $g \rightarrow 0$) and with the variational small polaron treatment when site energy renormalization is adequately described by a variational polaron binding energy ($\omega > 2J$ or $g \rightarrow \infty$). In the intermediate coupling regime, or at high temperature in the strong electronic coupling limit, the two-site CPA will be valid as well. It can thus be used in the entire parameter space of (J, g, ω, β, E) .

Our approach combines, for the first time, a self-consistent calculation of the averaged Green's function with a renormalization of all of the physically relevant parameters in the system. The application of these methods to more complicated vibronic coupling hamiltonians is a difficult but worthwhile objective.

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