

Green's functions and optical line shapes of a general two-level system in the strong electronic coupling limit^{a)}

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An approximate analytic form for the time-dependent one-exciton Green's function of a system with two excited electronic states coupled to a single harmonic vibrational mode is derived. The Fourier transform of this is used to calculate optical line shapes; these are compared with results obtained from exact numerical methods and give excellent agreement. A discussion of the basic ideas of the formalism is given, and possible extensions of this work to more complicated systems (e.g., multimode vibronic coupling problems) are mentioned.

I. INTRODUCTION

In a series of previous papers¹ we introduced a new method for studying analytically the eigenvalues, eigenvectors, and optical line shapes of a system consisting of a ground state and two excited electronic states, linearly coupled to a single harmonic vibrational mode. The system is of interest both because it has direct applications (e.g., as a simple model for exciton-phonon interactions in a molecular dimer) and because insights can be obtained which are valuable in the solution of more complicated problems (e.g., coupling of electronic excitations to a phonon heat bath).

This paper is a logical continuation of the first three (hereafter designated papers I, II, and III) and completes our theoretical study of the optical properties of this simple Hamiltonian in the strong electronic coupling limit. Paper I considered only off-diagonal vibronic coupling (see Sec. II A for the representation to which this refers), determining the eigenvalue spectrum and some useful analytic properties of the eigenvectors. Paper II extended this work to include diagonal coupling as well. Paper III used the results from paper I to determine analytical formulas for optical spectra in the strong electronic coupling limit (only off-diagonal coupling was considered); this is the most difficult case to treat with standard perturbation techniques.

In this work we calculate the exciton Green's function matrix elements for both diagonal and off-diagonal coupling in the strong electronic coupling limit; the observable optical spectra of corresponding physical systems are easily determined from these quantities. The calculation in paper III is improved by using a second order (rather than first-order) cumulant expansion for certain matrix elements. A brief discussion of the weak electronic coupling region is given and some approximations are mentioned. Comparison is made with numerical calculations, and it is shown that the analytical results presented here are quantitatively accurate in all regions of interest.

In conclusion we contrast the underlying ideas of our

technique with standard perturbation theory and discuss future directions for research.

II. THEORY

A. Exciton-phonon Hamiltonian

We will consider an ensemble of exciton-phonon systems, the zeroth-order Hamiltonian of which is given by

$$\begin{aligned} \tilde{H} = & \Delta(A_a^*A_a - A_b^*A_b) + (B^*B + \frac{1}{2}) + \gamma(B + B^*)(A_a^*A_a - A_b^*A_b) \\ & + v(B + B^*)(A_a^*A_b + A_b^*A_a) + E_{ab}(A_a^*A_a + A_b^*A_b) + E_0A_0^*A_0. \end{aligned} \quad (1)$$

Here $|a\rangle$ and $|b\rangle$ are the excited electronic states with annihilation (creation) operators $A_a(A_a^*)$, $B(B^*)$ are the usual phonon annihilation (creation) operators (all energies are written in units of $\hbar\omega$), γ is the diagonal exciton-phonon coupling parameter, v the off-diagonal coupling parameter, E_{ab} the average energy of excitation $\frac{1}{2}(E_a + E_b)$, and E_0 the ground state energy. Derivation of this form of \tilde{H} from a more general two-level Hamiltonian is discussed in paper II.

We will set the zero of energy to $E_0 + \frac{1}{2}$, and consider only singly excited configurations such that

$$\langle \Psi | A_a^*A_a + A_b^*A_b | \Psi \rangle = 1. \quad (2)$$

In addition, we will introduce a term into the Hamiltonian to account for various perturbations and corrections to \tilde{H} ; e.g., inhomogeneous broadening with respect to E_{ab} , other vibrational modes equivalently coupled to $|a\rangle$ and $|b\rangle$, equivalent phonon fluctuations. The simplest approach is to define a term $H'(\delta)$ which leads to broadening of every vibronic transition from the ground state $|0m\rangle$ (m is a vibrational quantum number) to an excited vibronic state $|\Psi_n\rangle$

$$H'(\delta) = \delta(A_a^*A_a + A_b^*A_b). \quad (3)$$

Then

$$H(\delta) = \tilde{H} + H'(\delta), \quad (4)$$

and ensemble average quantities \bar{A} are computed by taking

$$\bar{A} = \int A(\delta)p(\delta)d\delta, \quad (5)$$

where $p(\delta)$ is a normalized distribution function. Further discussion of this idea can be found in paper III and Ref. 2.

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In paper II we showed that the parameter space (Δ , g , v) of H can be divided into two regions, each of which possess a specific type of approximate analytical solution. The first region, weak electronic coupling (in different language, the diabatic region) is approximately defined by

$$2\Delta < 1 \quad (6)$$

or

$$v < \gamma.$$

The second, strong electronic coupling (the adiabatic region) is roughly the complement of this;

$$2\Delta > 1 \quad \text{and} \quad v > \gamma. \quad (7)$$

In addition the diabatic region may again be entered for very large v ($\frac{1}{2}v^2 \gg \Delta$); we will not discuss this case here.

We will continue to use terms "strong" and "weak" electronic coupling in what follows, to retain continuity with previous work. However, the rigorous meaning of these terms is given by Eqs. (6) and (7) and the corresponding discussion in paper II, and they should be understood accordingly.

B. Strong electronic coupling

From paper II, the eigenvalues of \tilde{H} in this limit are well represented by

$$\tilde{E}_{n\alpha} = E_{ab} + n \pm [\Delta^2 + (\gamma^2 + v^2 - s_n^2)(n + \frac{1}{2})]^{1/2} = n \pm \Gamma_n + E_{ab}, \quad (8)$$

where

$$s_n^2 = \frac{1}{2} \left(\frac{2\Delta^2}{2n+1} + \gamma^2 + v^2 \right) - \left[\left(\frac{2\Delta^2}{2n+1} + \gamma^2 + v^2 \right)^2 - \frac{8\Delta^2\gamma^2}{2n+1} \right]^{1/2},$$

and α is a quantum number referring to the symmetry of the eigenstate [$\alpha = +$ corresponds to the (+) sign in Eq. (8), while $\alpha = -$ corresponds to the (-) sign].

The eigenfunctions corresponding to $\tilde{E}_{n\alpha}$ are

$$\Psi_{n\alpha} = |a\rangle \chi_{n\alpha}^a(Q \pm s_n) + |b\rangle \chi_{n\alpha}^b(Q \pm s_n), \quad (9)$$

where $\chi_{n\alpha}^a(Q)$, $\chi_{n\alpha}^b(Q)$ are solutions to a Hamiltonian \hat{H} with $\gamma = 0$;

$$\hat{H} = \Delta(A_a^\dagger A_a - A_b^\dagger A_b) + B^\dagger B + \frac{\tilde{v}}{\sqrt{2}} (A_a^\dagger A_b + A_b^\dagger A_a)(B + B^*), \quad (10)$$

$$\tilde{v} = (\gamma^2 + v^2 - s_n^2)^{1/2}. \quad (11)$$

In Eq. (9) Q is the vibrational coordinate.

Each state $\Psi_{n\alpha}$ will have non-negligible configuration interaction with one state $\Psi_{n'\alpha'}$, where $E_{n'\alpha'} \approx E_{n\alpha}$ and $\Psi_{n'\alpha'}$ has the correct symmetry (see paper II for details). In the calculations which follow, we will ignore this interaction, and take the $\Psi_{n\alpha}$ to be the correct singly excited eigenstates. The justification for this approximation is as follows.

(1) Although configuration mixing is significant, the actual values of the interaction matrix elements are

small, i.e., the eigenvalues are displaced very little (a few percent maximum) from the values given by Eq. (8). The line broadening from $H'(\delta)$ will tend to smooth out the effects of such small displacements.

(2) The sign of the interaction is random (as a function of eigenstate quantum number) and so, over a large number of states, the effects will tend to cancel.

(3) The excellent agreement obtained with numerical calculations indicates that the approximation is a reasonable one.

We shall calculate the exciton Green's function matrix elements G_{ij} in the $\{|a\rangle, |b\rangle\}$ electronic basis. In paper II we gave symmetry arguments to show that

$$\langle \chi_{n\alpha}^a | \chi_{n\alpha}^b \rangle \approx 0. \quad (12)$$

Then, $G_{ab} \approx 0$, and we need only calculate G_{aa} and G_{bb} . Initially we fix δ and calculate the time Green's function's

$$G_{ii}(t, \delta) = \langle S_{ii}(t, \delta) \rangle. \quad (13)$$

The outer brackets represent an average over the canonical ensemble of the vibrational mode (this is effectively an average over the thermal distribution of the ground vibronic states), and

$$S_{ii}(t, \delta) = \exp[iH(\delta)t] A_i^\dagger \exp[-iH(\delta)t] A_i. \quad (14)$$

Notice that H' does not affect the eigenstates; it simply adds a displacement δ to the excited state energy. To proceed further, we substitute Eq. (14) into Eq. (13) and perform the canonical average to obtain

$$G_{ii}(t, \delta) = \sum_m \sum_{n\alpha} \langle 0m | \exp(iHt) | 0m \rangle \langle 0m | A_i^\dagger | \psi_{n\alpha} \rangle \times \langle \psi_{n\alpha} | \exp(-iHt) | \psi_{n\alpha} \rangle \langle \psi_{n\alpha} | A_i | 0m \rangle, \quad (15)$$

where $|0m\rangle$ is the electronic ground state with m phonons, and β is the inverse temperature $1/kT$. Defining the phonon number operator $h_0 = B^\dagger B$, and noting that $|0m\rangle$ is an eigenstate of h_0 we can rewrite Eq. (15) (see paper III) as

$$G_{ii}(t, \delta) = \sum_{n\alpha} \langle \chi_{n\alpha}^i | \exp(-iE_{n\alpha}t) \exp(ih_0t) \times \exp(-\beta h_0) | \chi_{n\alpha}^i \rangle, \quad (16)$$

where

$$E_{n\alpha} = \tilde{E}_{n\alpha} + \delta.$$

As in paper III, we define a normalized $\tilde{\chi}_{n\alpha}^i$ such that

$$\langle \tilde{\chi}_{n\alpha}^i | \tilde{\chi}_{n\alpha}^i \rangle = 1. \quad (17)$$

The relation between $\tilde{\chi}_{n\alpha}^i$ and $\chi_{n\alpha}^i$ is obtained from the equation

$$\begin{aligned} \langle \chi_{n\alpha}^a | \chi_{n\alpha}^a \rangle - \langle \chi_{n\alpha}^b | \chi_{n\alpha}^b \rangle &= \langle \Psi_{n\alpha} | A_a^\dagger A_a - A_b^\dagger A_b | \Psi_{n\alpha} \rangle = \partial E_{n\alpha} / \partial \Delta \\ &= \pm \left[\left(\Delta - \frac{\partial s_n^2(n + \frac{1}{2})}{\partial \Delta} \right) / \Gamma_n \right] \\ &= \nu_n, \end{aligned} \quad (18)$$

where $\partial s_n^2 / \partial \Delta$ can be evaluated from Eq. (8). Thus

$$| \tilde{\chi}_{n\alpha}^i \rangle = 1 / \sqrt{2} (1 \pm \nu_n)^{1/2} | \chi_{n\alpha}^i \rangle, \quad (19)$$

where the + or - signs in Eq. (19) depend upon both i

and α .

For notational convenience we define

$$\hat{O}_{n\alpha} = \exp(-iE_{n\alpha}t) \exp(ih_0t) \exp(-\beta h_0). \quad (20)$$

We now rewrite Eq. (16) in terms of the $\tilde{\chi}_{n\alpha}^i$ and perform the sums over α explicitly

$$G_{ii}(t, \delta) = \frac{1}{2} \left[\sum_n \langle \tilde{\chi}_{n+}^i | \hat{O}_{n+} | \tilde{\chi}_{n+}^i \rangle (1 \pm \nu_n) + \sum_n \langle \tilde{\chi}_{n-}^i | \hat{O}_{n-} | \tilde{\chi}_{n-}^i \rangle (1 \mp \nu_n) \right]. \quad (21)$$

We finally obtain explicit expressions for G_{aa} and G_{bb} :

$$G_{aa}(t, \delta) = \frac{1}{2} \left[\sum_n [\langle \tilde{\chi}_{n+}^a | \hat{O}_{n+} | \tilde{\chi}_{n+}^a \rangle + \langle \tilde{\chi}_{n-}^a | \hat{O}_{n-} | \tilde{\chi}_{n-}^a \rangle] + \frac{1}{2} \sum_n [\langle \tilde{\chi}_{n+}^a | \hat{O}_{n+} | \tilde{\chi}_{n+}^a \rangle - \langle \tilde{\chi}_{n-}^a | \hat{O}_{n-} | \tilde{\chi}_{n-}^a \rangle] \nu_n \right]. \quad (22)$$

Define

$$\begin{aligned} \lambda_1^+ &= \sum_n \langle \tilde{\chi}_{n+}^a | \hat{O}_{n+} | \tilde{\chi}_{n+}^a \rangle, \\ \lambda_1^- &= \sum_n \langle \tilde{\chi}_{n-}^a | \hat{O}_{n-} | \tilde{\chi}_{n-}^a \rangle, \\ \lambda_2^+ &= \sum_n \langle \tilde{\chi}_{n+}^a | \hat{O}_{n+} | \tilde{\chi}_{n+}^a \rangle \nu_n, \\ \lambda_2^- &= \sum_n \langle \tilde{\chi}_{n-}^a | \hat{O}_{n-} | \tilde{\chi}_{n-}^a \rangle \nu_n. \end{aligned} \quad (23)$$

We have

$$G_{aa}(t, \delta) = \frac{1}{2} [\lambda_1^+ + \lambda_1^-] + \frac{1}{2} [\lambda_2^+ - \lambda_2^-]. \quad (24)$$

Analogously,

$$G_{bb}(t, \delta) = \frac{1}{2} [\lambda_1^+ + \lambda_1^-] - \frac{1}{2} [\lambda_2^+ - \lambda_2^-]. \quad (25)$$

In paper III we evaluated the λ_i^{\pm} by making a first order cumulant expansion of each term in the sum, converting the resulting sum into an integral, and analytically evaluating this integral. Here we have additional complications because of the presence of the s_n^2 term (s_n^2 is identically zero for all n in the limit $\gamma=0$). In fact, it is almost as convenient to evaluate the sums over n directly as it is to convert them to an integral. Furthermore, this procedure provides greater flexibility in the types of terms which can be included, and is somewhat more accurate. In what follows, we will define the λ_i^{\pm} as sums over n which must be evaluated numerically, truncating the summation at a point where the individual terms become sufficiently small.

A further improvement can be made in the results of paper III by considering higher order terms in the cumulant expansion. The details of this process are presented in Appendix A, where we evaluate the relevant matrix elements.

The inclusion of higher order terms from the cumulant expansion will improve the approximate expressions only if these terms are not cancelled by other, still higher order terms. We have investigated this point by comparing the results for the first and second order cumulants with numerical calculations (see the results sec-

tion). We find that for $\gamma=0$, the second order terms significantly improve the calculation of $[\lambda_1^+ + \lambda_1^-]$ but not of $[\lambda_2^+ - \lambda_2^-]$. While no rigorous justification for this can be offered, it is plausible that the weighting factors ν_n and the fact that a difference is being taken could lead to cancellation of the higher order terms in the expansion for $\lambda_2^+ - \lambda_2^-$, and that this cancellation could be less efficient when the second order terms are included explicitly. This point needs further study; in what follows, however, we will use the above scheme. For $\gamma \neq 0$, the second order correction $\rho_n^2(s) = [s_n^2(n + \frac{1}{2})]/2$ (see Eq. A14) should be made for both the $[\lambda_1^+ + \lambda_1^-]$ and $[\lambda_2^+ - \lambda_2^-]$ terms. The results from Appendix A can finally be combined with Eqs. (23), (8), and (16) to yield

$$\lambda_1^{\pm} = \frac{1}{z} \sum_n \exp(-\beta n) \exp[-it(E_{ab} + \delta \pm \Gamma_n)] \times \exp[-(\phi_n^2 + \rho_n^2)t^2], \quad (26)$$

where $z = \sum_n \exp(-\beta n)$ is the normalization of the harmonic oscillator and

$$\phi_n^2 = \frac{\tilde{\gamma}_n^4(n + \frac{1}{2})^2}{8\Gamma_n^2}, \quad (27)$$

while

$$\lambda_2^{\pm} = \frac{1}{z} \sum_n \exp(-\beta n) \exp[-it(E_{ab} + \delta \pm \Gamma_n)] \nu_n \exp(-\rho_n^2 t^2). \quad (28)$$

To calculate observable quantities, we must Fourier transform $G_{ii}(t, \delta)$ and average over the distribution in δ . The relevant functions are then

$$\bar{\lambda}_i^{\pm}(E) = \text{Im} \int \exp(iEt) dt \int p(\delta) d\delta \lambda_i^{\pm}(t, \delta), \quad (29)$$

so that

$$\begin{aligned} \text{Im} \bar{G}_{aa}(E) &= \frac{1}{2} [\bar{\lambda}_1^+(E) + \bar{\lambda}_1^-(E)] \\ &\quad + \frac{1}{2} [\bar{\lambda}_2^+(E) - \bar{\lambda}_2^-(E)] \\ \text{Im} \bar{G}_{bb}(E) &= \frac{1}{2} [\bar{\lambda}_1^+(E) + \bar{\lambda}_1^-(E)] - \frac{1}{2} [\bar{\lambda}_2^+(E) - \bar{\lambda}_2^-(E)]. \end{aligned} \quad (30)$$

These functions can, in principle, be evaluated for any distribution $p(\delta)$. If we take $p(\delta)$ to be a Gaussian

$$p(\delta) = \frac{1}{\sqrt{\pi}W} \exp(-\delta^2/W^2), \quad (31)$$

where W is the width of the distribution, we obtain

$$I(E) = \frac{1}{z} \sum_n \exp(-\beta n) \exp[-(E \pm \Gamma_n - E_{ab})^2/\xi_n^2] \times \frac{1}{\sqrt{\pi} \xi_n}, \quad (32)$$

where $\xi_n = (W^2 + 4\phi_n^2 + 4\rho_n^2)^{1/2}$.

Similarly

$$\begin{aligned} \bar{\lambda}_2^{\pm}(E) &= \frac{1}{z} \sum_n \exp(-\beta n) \exp[-(E \pm \Gamma_n - E_{ab})^2/\eta_n^2] \\ &\quad \times \frac{\nu_n}{\sqrt{\pi} \eta_n}; \\ \eta_n &= (W^2 + 4\phi_n^2 + 4\rho_n^2)^{1/2}. \end{aligned} \quad (33)$$

We will use Eqs. (32) and (33) in all calculations which follow.

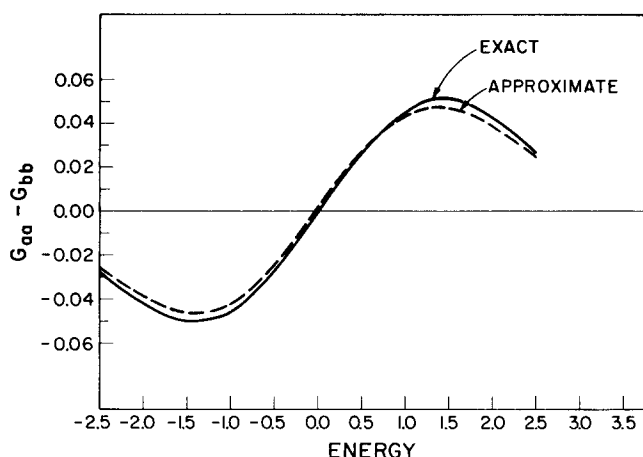


FIG. 1. Comparison of exact and approximate $G_{aa}-G_{bb}$ for weak electronic coupling; $\Delta=0.2$, $v/\sqrt{2}=0.5$, $\gamma=0.0$, $W=1.0$, $\beta=0.1$. Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

From Eq. (32), it is apparent that the effect of the second order corrections ϕ_n are to broaden the individual effective transitions at energy $E=E_{ab}\pm\Gamma_n$ by varying amounts for each n (ϕ_n increases as n increases) and thus represent a variable intrinsic vibronic lifetime. Allowing $\phi_n\rightarrow 0$ (this will occur as $\Delta\rightarrow\infty$) recovers the first order cumulant result of paper III for $\gamma=0$.

Note that we have here calculated the imaginary parts of the exciton Green's function matrix elements. The real parts could be obtained by taking the real part (principal part) of the Fourier integrals in Eq. (29) or, equivalently, by a Kronig-Kramers transform of the line shape functions in Eq. (30).

C. Weak electronic coupling

We will confine ourselves in this section to a few brief remarks concerning the relevance of our results to the weak electronic coupling region. For the most part, this region is best treated via standard perturbation theory techniques which have been discussed at length elsewhere.³

As shown in paper III, the absorption line shape (this was proportional to G_{aa}) as a whole is quite different in the weak couplings regime than the results obtained from Eq. (30). However, we note here that, at least for only off-diagonal coupling ($\gamma=0$), the calculation of part of the Green's function,

$$\text{Im}(\bar{G}_{aa}-\bar{G}_{bb})=\bar{\chi}_2^+-\bar{\chi}_2^- ,$$

gives correct results in the weak as well as strong coupling region. Our evidence is based entirely on comparison with numerical calculations. Figure 1 compares a typical calculation of $\text{Im}\bar{G}_{aa}-\bar{G}_{bb}$ for parameter values in the weak coupling region; agreement is excellent. The reason for this agreement still needs to be determined.

III. ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF A MOLECULAR DIMER

The Green's functions derived in Sec. II can be used to calculate a variety of observable quantities. To retain continuity with paper III, we choose as an explicit physical system a molecular dimer composed of two molecules, each with a single excited state coupled to a single vibrational mode. The vibrational frequencies and couplings are assumed to be identical, but the zeroth-order excited state electronic energies may be different.

The Hamiltonian is then

$$\begin{aligned} \tilde{H}_{\text{dimer}} = & J(A_1^\dagger A_2 + A_2^\dagger A_1) + (B_1^\dagger B_1 + B_2^\dagger B_2) \\ & + \Delta E + g[A_1^\dagger A_1(B_1 + B_1^\dagger) + A_2^\dagger A_2(B_2^\dagger + B_2)] \\ & + \epsilon(A_1^\dagger A_1 - A_2^\dagger A_2) . \end{aligned} \quad (34)$$

Here the labels 1 and 2 refer to molecules 1 and 2; all operators are as in the previous section; ΔE is the average separation from the ground state; J is the electronic exchange integral; and ϵ is the separation between the excited states of molecules 1 and 2. All energies are in units of $\hbar\omega$.

As in paper I, we can remove one vibrational mode by a canonical transformation; in addition, we transform the electronic states to the $|a\rangle$, $|b\rangle$ basis so as to produce a Hamiltonian isomorphic to Eq. (1). We set $\Delta E=0$ [this is equivalent to setting $E_{ab}=0$ in Eq. (1)] so that $E=0$ will be the average energy of the monomer spectra. When all of this is completed, we can use the results of Sec. II by setting

$$\begin{aligned} \Delta &= (J^2 + \epsilon^2)^{1/2} , \\ v &= gJ/(J^2 + \epsilon^2)^{1/2} , \\ \gamma &= g\epsilon/(J^2 + \epsilon^2)^{1/2} . \end{aligned} \quad (35)$$

We continue to define H' as in Sec. II.

The absorption and circular dichroism (CD) spectra can be calculated from the Green's functions (in the strong electronic coupling limit) as

$$\begin{aligned} I(E) = & \text{Im} [|\mu_{11}|^2 \bar{G}_{11} + |\mu_{22}|^2 \bar{G}_{22} + 2\mu_1 \cdot \mu_2 \bar{G}_{12}] \\ = & \text{Im} [|\mu_{aa}|^2 \bar{G}_{aa} + |\mu_{bb}|^2 \bar{G}_{bb}] , \end{aligned} \quad (36)$$

$$\begin{aligned} \theta(E) &= K \text{Im} \bar{G}_{12}(E) \\ &= K \sigma_{ab} \text{Im}(\bar{G}_{aa} - \bar{G}_{bb}) . \end{aligned} \quad (37)$$

Here

$$\begin{aligned} \mu_a &= c_1 \mu_1 + c_2 \mu_2 , \\ \mu_b &= c_1 \mu_2 - c_2 \mu_1 , \end{aligned} \quad (38)$$

are the transition dipole moments of the electronic states $|a\rangle$, $|b\rangle$. The coefficients c_1 , c_2 are those of the canonical transformation from $|1\rangle$, $|2\rangle$ to $|a\rangle$, $|b\rangle$. In Eq. (37) K is a constant which depends on the dimer geometry and monomer absorption band (see paper III) and σ_{ab} again accounts for the electronic rotation to the $|a\rangle$, $|b\rangle$ basis and is given by

$$\sigma_{ab} = J/(J^2 + \epsilon^2)^{1/2} . \quad (39)$$

In all of the above calculations, we have used the result that $\bar{G}_{ab}=0$.

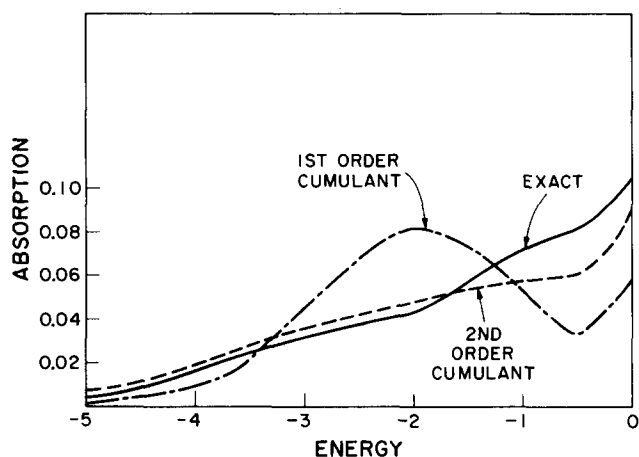


FIG. 2. Comparison of exact and approximate (both first- and second order cumulant expansions) low energy absorption line shape for the dimer parameter values $J=1.0$, $g/\sqrt{2}=0.5$, $\epsilon=0.0$, $W=1.0$, $\beta=0.2$. Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

For absorption we obtain finally

$$I(E) = \frac{1}{2} (|\mu_{aa}|^2 + |\mu_{bb}|^2) (\bar{\chi}_1^* + \bar{\chi}_1) + \frac{1}{2} (|\mu_{aa}|^2 - |\mu_{bb}|^2) (\bar{\chi}_2^* - \bar{\chi}_2) \\ = \frac{1}{2} |\mu|^2 [\bar{\chi}_1^* + \bar{\chi}_1] + \frac{1}{2} \frac{J}{(J^2 + \epsilon^2)^{1/2}} (\mu_1 \cdot \mu_2) (\bar{\chi}_2^* - \bar{\chi}_2), \quad (40)$$

where we have taken $|\mu_1|^2 = |\mu_2|^2 = |\mu|^2$ and evaluated c_1 , c_2 explicitly. For the calculations which follow, we set $|\mu|^2 = 1$ and take μ_1 and μ_2 to be parallel; then

$$I(E) = \frac{1}{2} [\bar{\chi}_1^* + \bar{\chi}_1] + \frac{1}{2} \left[\frac{J}{(J^2 + \epsilon^2)^{1/2}} (\bar{\chi}_2^* - \bar{\chi}_2) \right]. \quad (41)$$

For the circular dichroism, we set $K=1$ so that

$$\theta(E) = \frac{J}{(J^2 + \epsilon^2)^{1/2}} (\bar{\chi}_2^* - \bar{\chi}_2). \quad (42)$$

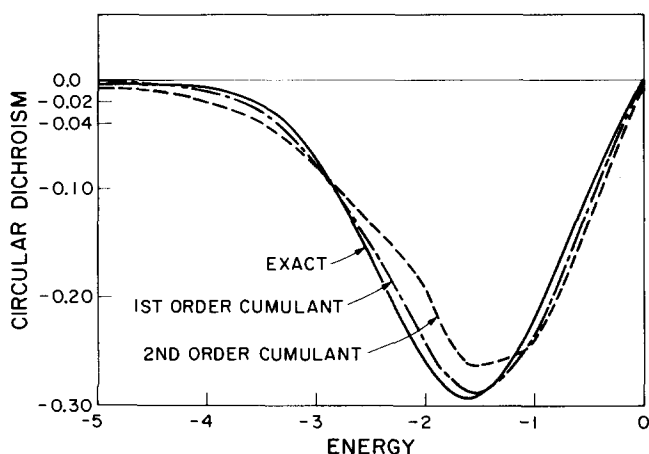


FIG. 3. Comparison of exact and approximate (both first- and second order cumulant expansions) low energy circular dichroism for the dimer parameter values $J=1.0$, $g/\sqrt{2}=0.5$, $\epsilon=0.0$, $W=1.0$, $\beta=0.2$. Ellipticity is in arbitrary units of K (see text and paper III); energy is in units of $\hbar\omega$.

IV. RESULTS

We present here calculations of the absorption and circular dichroism expressions derived in the previous section and compare them to numerical results obtained by direct diagonalization of H using a truncated basis set. (The latter calculations are performed as described in paper III.) This is equivalent, as a test of the theory, to comparing individual Green's functions and at the same time allows a simple physical interpretation of the quantities which are evaluated.

We first show that for $\epsilon=0$ ($\gamma=0$ in the $|a\rangle$, $|b\rangle$ representation) the second order cumulant expansion produces substantial improvement over the first order truncation used in paper III. Figure 2 compares the first and second order approximations for the absorption line shape with numerical results for the low energy region ($E < 0$) for a typical set of parameters; agreement is improved significantly for the second order expansion (agreement is excellent in the high energy region for both methods. To show that the second order terms do *not* improve the calculation of $\bar{\chi}_2^* - \bar{\chi}_2$, we compare the CD (proportional to this quantity) for this case with numerical results in

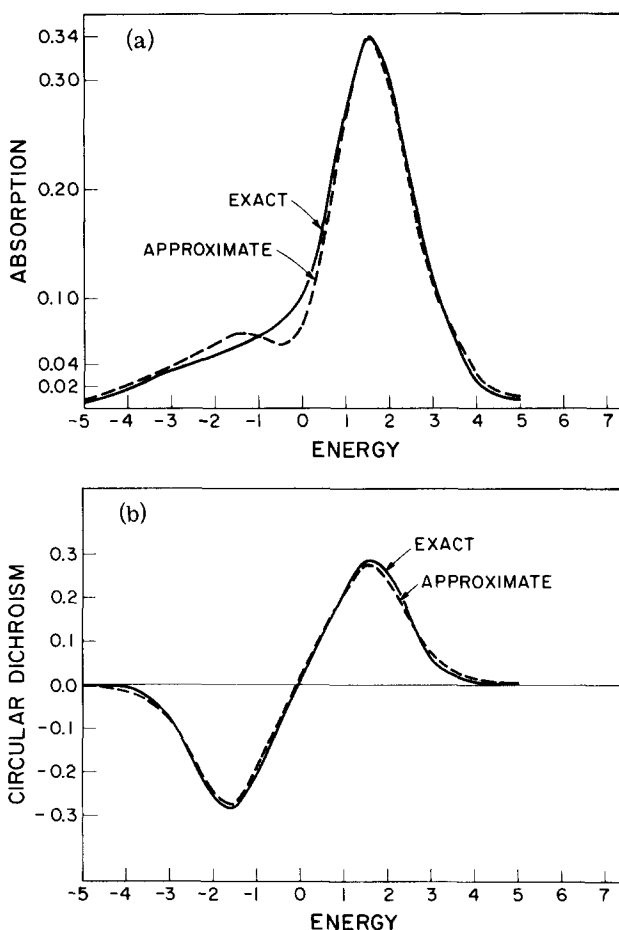


FIG. 4. (a) Comparison of exact and approximate absorption for dimer parameters $J=1.0$, $g/\sqrt{2}=0.5$, $\epsilon=0.5$, $W=1.0$, $\beta=0.2$. Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$. (b) Comparison of exact and approximate circular dichroism for dimer parameters $J=1.0$, $g/\sqrt{2}=0.5$, $\epsilon=0.5$, $W=1.0$, $\beta=0.2$. Ellipticity is in arbitrary units of K (see text); energy is in units of $\hbar\omega$.

TABLE I. Comparison of exact and approximate calculations of various characteristic parameters of the absorption and circular dichroism as a function of ϵ . The meanings of the table headings are as follows: LET (low energy tail) $= \sum_{-\infty}^0 I(E)dE$; ROT STR (rotational strength) $= \sum_{-\infty}^0 \theta(E)dE$; A_{MAX} is the amplitude of the absorption maximum, and $E(A_{\text{MAX}})$ is the energy at which the absorption maximum occurs. The remaining dimer parameters are $J=2.0$, $g/\sqrt{2}=0.5$, $W=1.0$.

(A) $\beta = 0.2$								
ϵ	LET		ROT STR		A_{MAX}		$E(A_{\text{MAX}})$	
	Exact	Approximate	Exact	Approximate	Exact	Approximate	Exact	Approximate
0.0	0.089	0.083	-0.808	-0.814	0.442	0.427	2.4	2.4
0.5	0.093	0.092	-0.799	-0.796	0.433	0.420	2.4	2.4
1.0	0.102	0.114	-0.770	-0.746	0.408	0.402	2.5	2.5
2.0	0.131	0.169	-0.664	-0.613	0.329	0.358	2.8	3.0
(B) $\beta = 0.5$								
0.0	0.055	0.049	-0.895	-0.901	0.511	0.506	2.2	2.2
0.5	0.062	0.060	-0.881	-0.879	0.500	0.496	2.3	2.2
1.0	0.081	0.088	-0.839	-0.821	0.471	0.473	2.4	2.4
2.0	0.139	0.162	-0.701	-0.666	0.389	0.418	2.8	2.9
(C) $\beta = 1.0$								
0.0	0.037	0.020	-0.935	-0.939	0.535	0.537	2.1	2.1
0.5	0.046	0.042	-0.916	-0.914	0.525	0.527	2.2	2.2
1.0	0.071	0.074	-0.864	-0.851	0.499	0.502	2.3	2.3
2.0	0.143	0.156	-0.708	-0.684	0.425	0.445	2.8	2.9

Fig. 3. Agreement is excellent for the first order cumulant and not as good for the modified line shape.

In Fig. 4 we examine a nonzero value of ϵ , comparing the analytic and numerical results for $\theta(E)$ and $I(E)$. Agreement for both line shapes is quite good in all energy regions.

Table I shows the effect of variation of ϵ on characteristic parameters (low energy absorption, rotational strength of the CD, amplitude and position of the absorption maximum) of the optical line shapes. Increasing ϵ leads to a decreasing rotational strength and greater low energy absorption. This is consistent with the intuitive picture that separating the excited energy levels of the dimer drives the spectrum towards that of two isolated molecules. Of course, in these calculations we do not see the completion of this process, since before this occurs we pass into the weak coupling regime.

The value $\epsilon=2.0$ in Table I (i.e., $\epsilon=J$ or, in the language of Sec. II, $\gamma=v$) is at a point where the strong electronic coupling scheme is beginning to break down. Thus, agreement is not as good for this value as it is for the smaller values of ϵ .

V. CONCLUSION

Application of our formalism to other physical systems or other types of experiments than those discussed in Sec. III is straightforward, as long as the system can be represented by Hamiltonian (1). In addition our theory allows calculation of ensemble averages over other parameters of the Hamiltonian, e.g., a distribution of exchange interactions J or energy splittings ϵ for the molecular dimer. In this case the terms in the sums can be integrated over these distributions term by

term, perhaps analytically but numerically if necessary.

Although the system we have studied is extremely simple, the methodology which has emerged is nontrivial and may be valuable in analyzing more complicated problems. The essential feature of our approach is that calculations are done in the excited eigenstate representation; the matrix elements of the ground state vibrational Hamiltonian h_0 are evaluated via perturbation theory. All that is necessary to carry out this procedure is an analytic representation of the excited state eigenvalue spectrum and determination of the above matrix elements.

This can be contrasted to the usual techniques in which the ground state vibrational eigenvalues are used as a basis set and the exciton-phonon coupling term is treated via perturbation theory. The approximations made in this approach are quite different from the ones made here; in particular, our method is valid for strong electronic and moderate excitation-phonon coupling at high temperatures. In this limit, the expansion in powers of Δ (or in renormalized $\tilde{\Delta}$ after a small polaron transformation) does not converge rapidly (see paper I for a more concrete discussion), while our eigenstate representation is quite accurate.

In forthcoming papers, this approach will be extended to calculate the Green's functions and density matrix evolution of a two-level system coupled to an arbitrary set of phonon modes. Application of these ideas to generalized multilevel exciton systems would be quite interesting but presents great difficulties.

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APPENDIX A: CUMULANT EXPANSIONS OF THE ZERO-TH-ORDER PHONON OPERATOR

We have to evaluate

$$f(t) = \langle \tilde{\chi}_{n\alpha}^i | \exp(ih_0 t) | \tilde{\chi}_{n\alpha}^i \rangle, \quad (\text{A1})$$

where $i = a$ or b .

The first order cumulant approximation is⁴

$$f^{(1)}(t) \approx \exp \langle \tilde{\chi}_{n\alpha}^i | ih_0 t | \tilde{\chi}_{n\alpha}^i \rangle, \quad (\text{A2})$$

while the second is

$$f^{(2)}(t) = \exp \{ \langle \tilde{\chi}_{n\alpha}^i | ih_0 t | \tilde{\chi}_{n\alpha}^i \rangle + \frac{1}{2} [\langle \tilde{\chi}_{n\alpha}^i | (ih_0 t)^2 | \tilde{\chi}_{n\alpha}^i \rangle - \langle \tilde{\chi}_{n\alpha}^i | ih_0 t | \tilde{\chi}_{n\alpha}^i \rangle^2] \}. \quad (\text{A3})$$

We first consider the $\gamma = 0$ case. The first order term has been evaluated in paper III and yields

$$\langle \tilde{\chi}_{n\alpha}^i | ih_0 | \tilde{\chi}_{n\alpha}^i \rangle = itn \quad \text{for all } i, \alpha. \quad (\text{A4})$$

The second order term is more difficult; we make here what is essentially a reasonable guess which is justified by success in comparison with numerical results. Examination of paper I shows that the matrix equation for $\chi_{n\alpha}^i$ resembles that of a displaced oscillator of frequency 2ω with off-diagonal element

$$M_{n,n+2} \approx \frac{\tilde{v}^2 [(n+1)(n+2)]^{1/2}}{4\Gamma_n}. \quad (\text{A5})$$

Now the second cumulant of h_0 for a displaced oscillator with linear displacement gQ is

$$\frac{1}{2} [\langle \phi_n^i | (h_0)^2 | \phi_n^i \rangle - \langle \phi_n^i | h_0 | \phi_n^i \rangle^2] = g^2/2(n + \frac{1}{2}) \quad (\text{A6})$$

which is approximately the square of the off-diagonal matrix element

$$M_{n,n+1} = \frac{g}{\sqrt{2}} \sqrt{n+1}. \quad (\text{A7})$$

This suggests that we can approximate

$$\begin{aligned} \frac{1}{2} [\langle \tilde{\chi}_{n\alpha}^i | (it h_0)^2 | \tilde{\chi}_{n\alpha}^i \rangle - \langle \tilde{\chi}_{n\alpha}^i | it h_0 | \tilde{\chi}_{n\alpha}^i \rangle^2] \\ \approx 2(M_{n,n+2})^2 \\ \approx t^2 v^4 (n + \frac{1}{2})^2 / 8\Gamma_n^2 = \phi_n^2 t^2, \end{aligned} \quad (\text{A8})$$

where the factor of 2 multiplying $M_{n,n+2}$ arises because the frequency separation of the diagonal elements is 2ω , and we have used $(n + \frac{1}{2})^2$ so that in the limit as $n \rightarrow \infty$ the second cumulant will be proportional to that of

a displaced oscillator with displacement v .

Thus for $J \gg v^2(n + \frac{1}{2})$, ϕ_n^2 is small, while for $n \rightarrow \infty$, $\phi_n^2 \approx (v^2/8)(n + \frac{1}{2})$; this is qualitatively what one would expect.

Substitution of Eqs. (A4) into (A2) yields

$$f^{(1)}(t) = e^{itn}, \quad (\text{A9})$$

while from Eqs. (A3) and (A8)

$$f^{(2)}(t) = \exp(int - \phi_n^2 t^2),$$

where

$$\phi_n^2 = \frac{1}{8} \left[\frac{v^4 (n + \frac{1}{2})^2}{\Gamma_n^2} \right]. \quad (\text{A10})$$

We can now derive expressions for the general case.

We replace v by \tilde{v}_n and $\tilde{\chi}_{n\alpha}^i(Q)$ by $\tilde{\chi}_{n\alpha}^i(Q + s_n)$.

Defining

$$\hat{Q} = Q + s_n, \quad (\text{A11})$$

we have

$$h_0(Q) = h_0(\hat{Q}) - s_n \hat{Q} - \frac{1}{2} s_n^2, \quad (\text{A12})$$

so that, for the first cumulant we have

$$\begin{aligned} \langle \tilde{\chi}_{n\alpha}^i(\hat{Q}) | it [h_0(\hat{Q}) - s_n \hat{Q} - \frac{1}{2} s_n^2] | \tilde{\chi}_{n\alpha}^i(\hat{Q}) \rangle \\ = it(n + \frac{1}{2} s_n^2). \end{aligned} \quad (\text{A13})$$

If $\frac{1}{2} s_n^2 \ll n$ we can neglect this term in Eq. (A13). This is done in the text; however, if $\frac{1}{2} s_n^2$ is large, this term should be included.

For the second cumulant, a similar analysis yields

$$\begin{aligned} \frac{1}{2} \{ \langle \tilde{\chi}_{n\alpha}^i(Q + s) | h_0^2 | \tilde{\chi}_{n\alpha}^i(Q + s) \rangle - [\langle \tilde{\chi}_{n\alpha}^i(Q + s) | h_0 | \tilde{\chi}_{n\alpha}^i(Q + s) \rangle]^2 \} \\ \approx \phi_n^2 + \rho_n^2(s), \end{aligned} \quad (\text{A14})$$

where

$$\rho_n^2(s) = s_n^2/2(n + \frac{1}{2}).$$

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