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Citation: J. Chem. Phys. 74, 1166 (1981); doi: 10.1063/1.441224
View online: http://dx.doi.org/10.1063/1.441224
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v74/i2
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## ADVERTISEMENT



# Exciton-phonon coupling in a dimer: An analytic approximation for eigenvalues and eigenvectors ${ }^{\text {a) }}$ 

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#### Abstract

An analytic approximation method is introduced to study the eigenvalues and eigenvectors of the dimer exciton-phonon Hamiltonian with linear coupling. The transition from quasilocalized to quasidelocalized states as a function of $n$, the number of vibrational quanta, is discussed for various coupling strengths. A discussion of the applicability of this method to other problems is given.


## I. INTRODUCTION

Exciton-phonon interactions play a crucial role in determining static and dynamical processes in molecular aggregates. Therefore, many workers have studied aspects of exciton-phonon coupling in the context of various problems ${ }^{1-6}$ e.g., optical line shapes, excitation transport, electron transfer, and vibrational relaxation. Although many approximation techniques have been used, a common theme has been partial diagonalization of the exciton-phonon Hamiltonian to reduce the magnitude of the off-diagonal perturbations; despite the sophisticated methods available to the theoriest (projection operators, Green's function's, etc. ), it is still essential to find a suitable representation for the system under study.

The exciton dimer, the simplest of aggregates, is particularly amenable to investigation of the fundamental quantum mechanical features, eigenvalues, and eigenvectors. Several authors have diagonalized a model dimer Hamiltonian numerically, ${ }^{1}$ while others have studied this same Hamiltonian analytically. ${ }^{2}$ These efforts have produced qualitative insight into the nature of the low lying dimer vibronic states.

However, all of these methods have been very limited, both in their ability to treat more complex Hamiltonians qualitatively and in the physical picture they have provided. The numerical calculations provide no systematic understanding of the dependence of the dimer states on interaction parameters, while the analytical methods have usually been restricted to the lowest one-exciton state. Discussion of weak and strong coupling or localized and delocalized states have been somewhat confused in part because of a lack of a coherent picture of the entire vibronic manifold.

In this paper we introduce a new technique for approximate diagonalization of the dimer exciton-phonon Hamiltonian which yields accurate analytical solutions for the eigenvalues and eigenvectors for all values of the exchange interaction $J$, exciton-phonon coupling parameters $g$, and phonon number $n$. The method results in a comprehensive overview of the problem which clarifies the nature of dimer vibronic states, replacing the old weak/strong coupling localized/delocalized distinc-

[^0]tions by an alternate set of criteria. Furthermore, the method is quite general, and can be used to solve other vibronic coupling problems.

## II. THEORY

## A. Variational calculations of the ground state

We consider a system composed of two identical molecules, each with a ground state, one excited electronic state, and one vibrational mode. The orbital overlap is taken to be small enough so that the tight-binding approximation is valid; then, the Hamiltonian is in the linear exciton-phonon coupling model:

$$
\begin{equation*}
H=J\left(A_{1}^{*} A_{2}+A_{2}^{*} A_{1}\right)+\sum_{n=1}^{2}\left[B_{n}^{*} B_{n}-g\left(B_{n}+B_{n}^{*}\right)\right]\left(A_{n}^{*} A_{n}\right), \tag{1}
\end{equation*}
$$

where $A_{n}^{*}\left(A_{n}\right)$ creates (destroys) an exciton at site $n$, $B_{n}^{*}\left(B_{n}\right)$ creates (destroys) a phonon at site $n, J$ is the exchange interaction, and $g$ the exciton-phonon coupling parameter. We have expressed $J$ and $g$ in units of the vibrational spacing $\omega$ and set the zero of energy equal to $\frac{1}{2} \omega \hbar+\Delta E_{0}$, where $\Delta E_{0}$ is the separation of the electronic ground and excited states. It is well known that there is a smooth but relatively sharp transition in the nature of the vibronic one-exciton ground state as a function of $g$ and $J$. This transition is reflected in exciton-phonon correlation function $\delta$ :

$$
\begin{equation*}
\delta=\langle\psi|\left(A_{*}^{*} A_{-}+A_{-}^{*} A_{+}\right)\left(B_{-}+B_{-}^{*}\right)|\psi\rangle \times 1 / g, \tag{2}
\end{equation*}
$$

which varies from zero to one as $|g / J|$ varies from zero to infinity. It is also manifest in the behavior of the average number of phonons and the energy as functions of $g$ and $J$. This transition is the analogy of the delocalized to localized transition in the exciton states of solids. ${ }^{3}$

Recently, Allen and Silbey ${ }^{4}$ investigated this ground state transition by means of a modified variational calculation. They were able to derive expressions for the wave functions, energy, and exciton-phonon correlation function which reproduced the exact numerical results reasonably well in the transition region and in both asymptotic limits.

This variational procedure, however, is limited in its application to the ground one-exciton state. In order to calculate the excitation spectrum of the system the excited $n$-phonon vibronic states must also be determined. The existence of the ground state transition suggets
that a similar transition may occur for an arbitrary phonon number; however, the partitioning of ( $J, g$ ) space may be altered substantially as $n$ is varied.

Before proceeding further, however, we note that the transition we have been discussing is not one between a localized and delocalized state in the rigorous sense of these terms. We can represent the vibronic wave function as

$$
\psi=|1\rangle \chi_{1}(Q)+|2\rangle \chi_{2}(Q)
$$

where $|1\rangle=\phi_{1}^{e} \phi_{2}^{0}$ and $|2\rangle=\phi_{2}^{e} \phi_{1}^{0}$ are singly excited configurations, and $\chi_{1}$ and $\chi_{2}$ are vibrational wave functions. The excitation density on site $i$ is

$$
P_{i}=\int\left|\chi_{i}(Q)\right|^{2} d Q
$$

By the symmetry of the Hamiltonian $P_{1}=P_{2}$. Therefore, the excitation is completely delocalized according to this criterion and the transition must be characterized in some other manner. The formalism developed in this paper will provide a framework in which to do this.

We set $B_{+}=(1 / \sqrt{2})\left(B_{1}+B_{2}\right), \quad B_{-}=(1 / \sqrt{2})\left(B_{1}-B_{2}\right)$, $B_{+}^{*}=(1 / \sqrt{2})\left(B_{1}^{*}+B_{2}^{*}\right)$, and $B_{-}^{*}=(1 / \sqrt{2})\left(B_{1}^{*}-B_{2}^{*}\right)$.

Then, the Hamiltonian becomes

$$
\begin{align*}
H= & J\left(A_{1}^{*} A_{2}+A_{2}^{*} A_{1}\right)+B_{+}^{*} B_{+}+B_{-}^{*} B_{-} \\
& +(g / \sqrt{2})\left(A_{1}^{*} A_{1}-A_{2}^{*} A_{2}\right)\left(B_{-}^{*}+B_{-}\right) \\
& +(g / \sqrt{2})\left(A_{1}^{*} A_{1}+A_{2}^{*} A_{2}\right)\left(B_{+}^{*}+B_{+}\right) \tag{3}
\end{align*}
$$

In one-exciton space $A_{1}^{*} A_{1}+A_{2}^{*} A_{2}=1$, so that the $B_{+}$ vibration is equally coupled to both sites; we may then remove the $B_{+}$vibration in one-exciton space by simple unitary transformation. We then ignore the $B$, vibration and take

$$
\begin{align*}
H= & J\left(A_{1}^{*} A_{2}+A_{2}^{*} A_{1}\right)+B_{-}^{*} B_{-} \\
& +(g / \sqrt{2})\left(A_{1}^{*} A_{1}-A_{2}^{*} A_{2}\right)\left(B_{-}+B_{-}^{*}\right) \tag{3a}
\end{align*}
$$

If $\epsilon_{\alpha}$ is the eigenvalue of Eq. (3a), the excited energy levels of the dimer are given by

$$
\begin{equation*}
E_{\alpha, n_{+}}=\epsilon_{\alpha}-\frac{g^{2}}{2}+n_{+} \tag{4}
\end{equation*}
$$

where $n_{+}$is the number of $(+)$phonons in the state of interest.

If we set $J=0$, this Hamiltonian can be diagonalized by the transformation $H^{\prime}=e^{-S} H e^{-S}$, where

$$
\begin{equation*}
S=(g / \sqrt{2})\left(A_{1}^{*} A_{1}-A_{2}^{*} A_{2}\right)\left(B_{-}-B_{-}^{*}\right) \tag{5}
\end{equation*}
$$

The eigenstates of $H$, in coordinate space, are then

$$
\begin{equation*}
\psi_{n}^{ \pm}=\frac{1}{\sqrt{2}}\left(|1\rangle \phi_{n}^{\varepsilon} \pm|2\rangle \phi_{n}^{-\delta}\right) \tag{6}
\end{equation*}
$$

where $\phi_{n}^{z}$ is the $n$th harmonic oscillator eigenfunctions with argument $Q_{-}+g$. Note that the eigenvalues are $\epsilon_{n}^{ \pm}$ $=-g^{2} / 2+n$, so that $\psi_{n}^{\star}$ are degenerate.

One would expect that in some neighborhood of $J=0$ the functions $\psi_{n}^{ \pm}$constitute an approximate solution to the Hamiltonian. We investiage this further by writing $H$ in matrix form in the $\psi_{n}$ basis:

$$
\begin{align*}
& H_{n n}^{ \pm}=n-\frac{1}{2} g^{2} \pm J\left\langle\phi_{n}^{\xi} \mid \phi_{n}^{-g}\right\rangle \\
& \left\langle\psi_{n}^{ \pm}\right| H\left|\psi_{m}^{ \pm}\right\rangle= \pm(J / 2)\left(\left\langle\phi_{n}^{s} \mid \phi_{m}^{-g}\right\rangle+\left\langle\phi_{n}^{-\varepsilon} \mid \phi_{m}^{\boldsymbol{E}}\right\rangle\right)  \tag{7}\\
& \left\langle\psi_{n}^{ \pm}\right| H\left|\psi_{m}^{\mp}\right\rangle= \pm(J / 2)\left(-\left\langle\phi_{n}^{g} \mid \phi_{m}^{-g}\right\rangle+\left\langle\phi_{n}^{-g} \mid \phi_{m}^{s}\right\rangle\right)
\end{align*}
$$

Because of the parity of the harmonic oscillator functions, the Hamiltonian matrix splits into two blocks, with one state at each value of $n$ having total even parity and one having total odd parity.

The validity of this representation for further approximation will depend on the convergence of the per turbation series for the energy and wave function. Unfortunately, this is difficult to evaluate, since there are an infinite number of off-diagonal elements. As a first approximation we could look at

$$
\begin{equation*}
\Delta E^{(1)} \simeq \sum_{m} \frac{H_{n m}^{2}}{E_{m}-E_{m}} \cong \sum_{m} \frac{\left|J\left\langle\phi_{n}^{\varepsilon} \mid \phi_{m}^{-\varepsilon}\right\rangle\right|^{2}}{n-m} \tag{8}
\end{equation*}
$$

However, even this is hard to work with as the overlaps $\left\langle\phi_{n}^{\delta} \mid \phi_{m}^{-8}\right\rangle$ depend in a complex way on $g, n, m$.

It is clear, however, that for sufficiently large $J$ the perturbation series will not converge and the $\psi_{n}^{ \pm}$will be a poor representation. In fact, this condition corresponds to the transition discussed in Sec. II A. The problem is then to find a representation in which perturbation theory will be valid for large $J$.

The usual approach to this has been based on the vibrational calculation mentioned earlier. First, the exciton operators in Eq. (3) are converted to the $k$ representation i. e. , $\left[A_{*}=\frac{1}{2}\left(A_{1}+A_{2}\right), A_{*}^{*}=\frac{1}{2}\left(A_{1}^{*}+A_{2}^{*}\right), A_{-}\right.$ $=\frac{1}{2}\left(A_{1}-A_{2}\right) ; A_{-}^{*}=\frac{1}{2}\left(A_{1}^{*}-A_{2}^{*}\right)$,

$$
\begin{align*}
H= & J\left(A_{+}^{*} A_{+}-A_{-}^{*} A_{-}\right)+B_{-}^{*} B_{-} \\
& +\left(\frac{g}{\sqrt{2}}\right)\left(A_{*}^{*} A_{-}+A_{-}^{*} A_{+}\right)\left(B_{-}+B_{-}^{*}\right) \tag{9}
\end{align*}
$$

Then, a transformation $H^{\prime}=e^{+S} H e^{-S}$ is applied where

$$
\begin{equation*}
S=\tilde{g} / \sqrt{2}\left(A_{+}^{*} A_{-}+A_{-}^{*} A_{+}\right)\left(B_{-}-B_{-}^{*}\right) \tag{10}
\end{equation*}
$$

When $\tilde{g}=g$, we immediately obtain the earlier representation (5). When $\tilde{g}=0$, we remain in the $k$ space, which is diagonal when $g=0$. Thus, in some neighborhood of $g=0$ we expect this representation to be valid.

The trouble with this method is that no matter how small $g$ is, one eventually reaches a point in the matrix of $H$ where perturbation theory fails. The matrix in the $|+\rangle \phi_{n}^{0}, \quad|-\rangle \phi_{n}^{0}$ basis can be factored into two blocks

$$
\begin{align*}
& I=|+0\rangle|-1\rangle|+2\rangle \cdots \\
& I I=|-0\rangle|+1\rangle|-2\rangle \tag{11}
\end{align*}
$$

where $|+n\rangle=1+\rangle \phi_{n}^{0}$.
For one of these blocks (the other is found by changing the sign of $J$ ), we have

$$
\begin{align*}
& H_{n n}=n+J(-1)^{n} \\
& H_{n, n+1}=H_{n, n-1}=g \sqrt{n},  \tag{12}\\
& H_{n m}=0, \quad m \neq n, \quad n+1, \text { or } n-1
\end{align*}
$$

The criterion for perturbation theory to be valid is approximately

$$
\begin{equation*}
\left|\frac{H_{n m}}{E_{n}-E_{m}}\right|<1 \tag{13}
\end{equation*}
$$

or

$$
|g \sqrt{n} /(1-2 J)|<1 .
$$

Thus, when $n>(1-2 J)^{2} / g^{2}$, this representation no longer provides useful energies or wave functions.

If we set $\tilde{g}$ in Eq. (10) to some value $0<\bar{g}<g$, the same problem appears, although now the condition is $n>(1-2 J)^{2} /(g-\tilde{g})^{2}$. Furthermore, for $\tilde{g}>0$, off-diagonal terms of the form $J\left\langle\phi_{n}^{\tilde{\tilde{F}}} \mid \phi_{m}^{-\vec{\xi}}\right\rangle$ appear, and lead to the same sort of problems as the full site space representation.

We see then that the canonical transformation given by Eq. (10) is limited in its ability to generate useful approximate eigenstates. It is possible to show that a generalized form of Eq. (10) (using vibronic excitation operators rather than separate phonon and exciton operators) is also insufficient. ${ }^{7}$ We therefore formulate a new representation which in combination with the site space representation, completely spans the space of all values of $g, J$, and $n$. For the moment, we shall refer to that part of the ( $J, g$ ) plane in which the site space representation is a good approximation as region I, and the remainder as region II.

## B. Schrödinger representation

In phonon coordinate space the dimer vibronic wave function is

$$
\begin{equation*}
\psi=|+\rangle \chi_{1}(Q)+|-\rangle \chi_{2}(Q) \tag{14}
\end{equation*}
$$

The Schrödinger equation for $\psi$ is

$$
\begin{align*}
\left\{-\frac{1}{2}\right. & \frac{d^{2}}{d Q^{2}}+\frac{1}{2} Q^{2}+J\left(A_{*}^{*} A_{+}-A_{*}^{*} A_{-}\right) \\
& \left.+g Q\left(A_{*}^{*} A_{-}+A_{*}^{*} A_{*}\right)\right\} \psi=E \psi . \tag{15}
\end{align*}
$$

Multiplying both sides by either $|+\rangle$ or $|-\rangle$ and integrating, we obtain two coupled differential equations:

$$
\begin{align*}
& (h+J-E) \chi_{1}(Q)=-g Q \chi_{2}(Q), \\
& (h-J-E) \chi_{2}(Q)=-g Q \chi_{1}(Q), \tag{16}
\end{align*}
$$

where $h=-\frac{1}{2}\left(d^{2} / d Q^{2}\right)+\frac{1}{2} Q^{2}$ is the zeroth-order phonon energy operator.

We now expand $\chi_{1}(Q)$ and $\chi_{2}(Q)$ in harmonic oscillator states centered at $Q=0$ :

$$
\begin{align*}
& \chi_{1}(Q)=\sum_{n} c_{n} \phi_{n}^{0}, \\
& \chi_{2}(Q)=\sum_{n} b_{n} \phi_{n}^{0} . \tag{17}
\end{align*}
$$

Substituting into Eq. (16) and integrating over $\phi_{n}^{0}$ yields a set of coefficient equations

$$
\begin{align*}
& c_{n}(n+J-E)=\left(\frac{g}{\sqrt{2}}\right)\left(b_{n-1} \sqrt{n}+b_{n+1} \sqrt{n+1}\right),  \tag{18a}\\
& b_{n}(n-J-E)=\frac{g}{\sqrt{2}}\left(c_{n-1} \sqrt{n}+c_{n+1} \sqrt{n+1}\right) \tag{18b}
\end{align*}
$$

Inserting Eq. (18b) into Eq. (18a) gives

$$
\begin{align*}
c_{n}(n+J-E)= & \left(\frac{g}{\sqrt{2}}\right)^{2}\left[\frac{c_{n-2} \sqrt{n(n-1)}}{(n-1-J-E)}+\frac{c_{n+2} \sqrt{(n+1)(n+2)}}{(n+1-J-E)}\right. \\
& \left.+\frac{c_{n} n}{n-1-J-E}+\frac{c_{n}(n+1)}{n+1-J-E}\right] . \tag{19}
\end{align*}
$$

If the energy is shifted from its zeroth order value by an amount large compared to unity, which we will show to be correct in region II, we can then make the approximation on the right-hand side ${ }^{8}$ :

$$
\begin{equation*}
n-1-J-E \approx n+1-J-E \approx n-J-E . \tag{20}
\end{equation*}
$$

Then, we obtain

$$
\begin{align*}
& c_{n}\left[(n+J-E)(n-J-E)-(2 n+1) g^{2} / 2\right]=c_{n+2} \frac{g^{2}}{2} \\
& \times \sqrt{(n+1)(n+2)}+c_{n-2} \frac{g^{2}}{2} \sqrt{n(n-1)} . \tag{21}
\end{align*}
$$

The entire set of these equations constitutes a matrix equation for the $c_{n}$ 's:

$$
\begin{equation*}
\mathbf{M} \cdot \mathbf{C}=0, \tag{22}
\end{equation*}
$$

where
$M_{n n}=(n-E)^{2}-\left[J^{2}+\frac{g^{2}}{2}(2 n+1)\right] \equiv\left(\mu_{n}+n-E\right)\left(-\mu_{n}+n-E\right)$,
$\mu_{n}=\left[J^{2}+g^{2}(2 n+1) / 2\right]^{1 / 2}$,
$M_{n, n+2}=M_{n+2, n}=\frac{g^{2}}{2} \sqrt{(n+1)(n+2)}$.
As there are no $c_{n+1}$ terms, $M$ can be divided into two unconnected blocks, one in which $n$ is even, the other in which $n$ is odd. The condition for the eigenvalues of $H$ are of course that the determinant of $M$ vanishes. Since $M$ factorizes, this occurs when the determinant of either the even block or the odd block vanishes. Since the diagonal elements of $M$ are quadratic in $E$, the number of eigenvalues of each block will be twice the order of the block. Thus, the entire eigenvalue spectrum is obtained in this way.

In order to find approximate values of the energies, we factor one of the blocks of $\boldsymbol{m}$ (say the even block for definiteness) by writing

$$
\begin{align*}
\mathbf{M}=\mathbf{M}^{(1)} & \cdot \mathbf{M}^{(2)}, \\
\left(\mathbf{M}^{(1)}\right)_{n m}= & \left(n+\mu_{n}-E\right) \delta_{n m},  \tag{24}\\
\left(\mathbf{M}^{(2)}\right)_{n m}= & \left(n-\mu_{n}-E\right) \delta_{n m}+\delta_{m, n+2} g^{2}[(n+1)(n+2)]^{1 / 2} \\
& \times\left(n+2+\mu_{n}-E\right)^{-1} \\
& +\delta_{m, n-2} g^{2}[(n-1) n]^{1 / 2}\left(n-2+\mu_{n}-E\right)^{-1}
\end{align*}
$$

Note that since $n$ and $m$ are both even numbers, $M^{(2)}$ is a tridiagonal matrix. (Also, this factorization could be done just as easily by dividing through by $n-\mu_{n}-E$ rather than $n+\mu_{n}-E$; this freedom can be considered by allowing $\mu_{n}$ to be either positive or negative in the above.) The eigenvalues are then given by the zeros of $\operatorname{det} \mathbf{M}^{(1)} \operatorname{ordet} \mathbf{M}^{(2)}$. The zeros of det $\mathbf{M}^{(1)}$, however, occur at $E=n+\mu_{n}$ at which value some off-diagonal elements of $\mathbf{M}^{(2)}$ blow up. The zeroth order approximation to an eigenvalue will be

$$
\begin{equation*}
E_{n}^{(0)}=n-\mu_{n}=n-\left[J^{2}+g^{2}(2 n+1) / 2\right]^{1 / 2} . \tag{25}
\end{equation*}
$$

Substituting this into the off-diagonal elements of $M^{(2)}$ results in

$$
\begin{equation*}
\left\{M^{(2)}\right\}_{p, p+2} \cong g^{2}[(p+1)(p+2)]^{1 / 2}\left(p+\mu_{p}+2-n+\mu_{n}\right)^{-1} . \tag{26}
\end{equation*}
$$

The first correction to $E_{n}^{(0)}$ will then be

$$
\begin{align*}
E_{n}^{(1)}= & g^{4}(n+1)(n+2) /\left[\left(2 \mu_{n}+2\right)\left(\mu_{n}-\mu_{n+2}\right)\right] \\
& +g^{4}(n-1) n /\left[\left(2 \mu_{n-2}+2\right)\left(\mu_{n}-\mu_{n-2}\right)\right] \tag{27}
\end{align*}
$$

which for large $J / g^{2}$ will be $O\left(g^{4} / J\right)$ and therefore small, and in addition for large $n$ will be small. We have thus taken as an approximate eigenvalue $E_{n}^{(0)}$ (as given above). Numerical calculations (see below) will show the accuracy of this expression in region II. A further justification for this approximation can be made by noting that $M_{\rho, p+2}^{(2)}$, in the region of the matrix near $p=n$, will for large $n$ look like

$$
\begin{equation*}
M_{n, n+2}^{(2)} \simeq g \sqrt{n} \quad(\text { large } n), \tag{28}
\end{equation*}
$$

while the separation between diagonal elements becomes

$$
\begin{equation*}
M_{n, n}^{(2)}-M_{n+2, n+2}^{(2)} \simeq-2, \tag{29}
\end{equation*}
$$

so that in this region the matrix resembles a displaced harmonic oscillator of frequency 2 . This leads to a correction in the energy of $-g^{2} / 2$, which is small relative to $\mu_{n}$. In order for our approximation (in region II) to be valid, $\left|\mu_{n}\right|>\frac{1}{2} g^{2}$. Numerical calculations confirm this in this region.

This discussion suggest a mathematical model for the transition in the vibronic wave function. In region $I$ of ( $J, g$ ) space the matrix of Eq. (4) is close to a DHO so that the energy is within a neighborhood of the DHO energy [Eq. (5)] [equivalently, the matrix defined by Eq.
(6) is nearly diagonal]. In region II it is $M^{(2)}$ which approximates a DHO; the energy is then given by Eq.
(25). The criterion for "closeness" to a displaced oscillator for each matrix must be the inverse of the other, i. e., perturbation theory cannot be valid for both representations simultaneously.

This situation corresponds to a well-known mathematical behavior of the roots of polynomials. The determinantal equation for $E$ has an unstable region (as a function of parameters $g, J$ ) where the roots are transformed by a small change in the parameters from $n \pm \frac{1}{2} g^{2}$ to $n \pm\left[J^{2}+\left(g^{2} / 2\right)(2 n+1)\right]^{1 / 2}$. The characterization of the instability criteria is equivalent to evaluating the convergence criteria of the perturbation series for matrix (6) (or, alternately, for $M^{(2)}$ ). This is an interesting but difficult problem, and we shall not attempt its solution here formally. In the results section we do investigate several points in ( $g, J$ ) space, make some empirical observations about the $n$ dependence of the transition, and formulate an approximate analytical criterion which is valid in some parameter regions.

In the transition region itself the energy can be approximated by $E \approx n-\left[J^{2}+\left(g^{2}-s^{2}\right)(2 n+1) / 2\right]^{1 / 2}$, where $s$ is a parameter obtained by expanding $\chi_{1}, \chi_{2}$ in Eq. (11) in a basis $\left\{\phi_{n}^{s}, \phi_{n}^{-s}\right\}$ and evaluating the value of $s$ which leads to the best DHO approximation. We have not investigated this region in detail nor determined a practical procedure for finding $s$.

## C. Determination of the wave function for region II

While Eq. (19) yields the correct eigenvalues of $M$ as those of $\mathbf{M}^{(2)}$, the presence of $\mathbf{M}^{(1)}$ transforms the eigenvectors of $M$ away from the DHO solutions to the problem $\mathbf{M}^{(2)} \cdot \mathbf{C}^{\prime}=0$. Therefore, the coefficients have to be obtained in a different manner. Because of the displacement of $E$ from $n\left(\left\{J^{2}+\left(g^{2} / 2\right)[2(n+1)]\right\}^{1 / 2}\right)$, we can use the matrix equations from Eq. (4) and the energy expression to determine the eigenvectors directly. Note that the coefficients $c_{n}$ now refer to the original $\{1+n\rangle$, $|-, n+1\rangle, \ldots\}$ basis rather than the $|+, n\rangle, 1+, n+2\rangle$ basis, which spans the Hilbert space of $\chi_{1}$.

First, we determine the coefficient $c_{n+1}$ as a function of $c_{n}$ (if $-\mu \rightarrow+\mu$, we first determine $c_{n-1}$ ) as follows (note that we are performing this calculation for block 1 here): The relevant matrix equations are, for general $k$,

$$
\begin{equation*}
c_{k-2} g \sqrt{k-1}+c_{k-1}(k-1-E \pm J)+c_{k} g \sqrt{k}=0 \tag{30}
\end{equation*}
$$

where the $\pm J$ depends on $k$ and the block number.
We take, in a second order approximation (this procedure could clearly be extended to higher order), the two equations
$c_{n+2} g \sqrt{n+2}+c_{n+1}(n+1-E+J)+c_{n} g \sqrt{n+1}=0$,
$c_{n+3} g \sqrt{n+3}+c_{n+2}(n+2-E-J)+c_{n+1} g \sqrt{n+2}=0$.
Setting $c_{n+3}=0$, substituting $E=n-\mu$, eliminating $c_{n+2}$, and solving for $c_{n+1}$ yields
$c_{n+1}=\frac{-c_{n} g \sqrt{n+2}(2+\mu-J)}{(2+\mu-J)(1+\mu+J)-g^{2}\left[(n+1)^{1 / 2}(n+2)^{1 / 2}\right]}$.
This procedure converges effectively because of the relatively large value of $n-E+J$ (the displacement of the diagonal element multiplying $c_{n}$ ), i. e., $\mu<g \sqrt{n}$. The remaining coefficients can now be obtained exactly by iteration of the matrix equations, i. e.,

$$
\begin{equation*}
c_{n-k}=\frac{-c_{n-k+1}(\mu \pm J)-c_{n-k-1} g \sqrt{n+1}}{g \sqrt{n}} \tag{33}
\end{equation*}
$$

where, again, the $\pm J$ depends on $k$ and the block number

$$
\begin{equation*}
c_{n+k}=\frac{-c_{n+k-1}(\mu \pm J)-c_{n+k-2} g \sqrt{n-1}}{g \sqrt{n}} \tag{34}
\end{equation*}
$$

Finally, $c_{n}$ is determined from the normalization condition

$$
\begin{equation*}
\sum_{j} c_{j}^{2}=1 \tag{35}
\end{equation*}
$$

## III. RESULTS AND DISCUSSION

We present our results in the form of energies and eigenfunctions for various values of $n$ for fixed points in the ( $J, g$ ) plane. Viewing the transition as a function of $n$, there are three types of points:

## Case (1): All $n$ states are in region II.

Case (2): States of both types exist, but there is no configuration interaction between them (i. e., the sites of region I and region II states are well separated.)

Then, one can define a critical phonon level $n_{F}$ such that for $\left\langle n_{p}\right\rangle \leq n_{T}, \psi_{n_{p}}$ is in region I while for $\left.\left\langle n_{p}\right\rangle\right\rangle n_{T}, \psi_{n_{p}}$ is in region II. An approximate expression for $n_{T}$ is given by the breakdown of perturbation theory in the $k$ space representation when $2 J<1$ (see Sec. IIE for a more detailed discussion of this point), i. e.,

$$
\begin{equation*}
n_{T} \approx \frac{(1-2 J)^{2}}{g^{2}} . \tag{36}
\end{equation*}
$$

Case (3): Some $n$ states fall in region $I$ and others in region $I$, but extensive configuration interaction (CI) occurs. The approximate states described here are not exact and will have nonzero off-diagonal terms in the Hamiltonian; if these are large compared to the energy difference, CI will be important. This interaction will generally be relevant when it is between region $I$ and region II states which are nearly degenerate in energy.

The $n$ referred to above is not the rank of the energy level in the exact diagonalization but is instead the index of the diagonal element (minus one) used in the approximate calculation. Thus, in region I we define the states

$$
\begin{align*}
& \psi_{n}^{ \pm} \cong \frac{1}{\sqrt{2}}\left(|1\rangle \phi_{n}^{\varepsilon}+|2\rangle \phi_{n}^{-\varepsilon}\right),  \tag{37}\\
& E_{n} \cong n-\frac{1}{2} g^{2} \pm J\left\langle\phi_{n}^{g} \mid \phi_{n}^{-g}\right\rangle
\end{align*}
$$

and in region II, $\psi_{n}^{ \pm}$is given in Sec. II C, with

$$
\begin{equation*}
E_{n}=n \pm\left[J^{2}+\frac{g^{2}}{2}(2 n+1)\right]^{1 / 2} \tag{38}
\end{equation*}
$$

The corresponding state in the exact diagonalization can be found by computing the average phonon number

$$
\begin{equation*}
\left\langle n_{p}\right\rangle=\sum_{n} n\left|c_{n}\right|^{2} \tag{39}
\end{equation*}
$$

For $g<1$ this number will be reasonably constant for regions I and II [i. e., the state corresponding to the $n$th diagonal of the matrix of Eq. (7) will have an $\left\langle n_{p}\right\rangle$ close to the state corresponding to the $n$th diagonal element of the matrix of Eq. (23)]. For $g \gg 1$ one would have to renormalize for the region I states.

We examine examples of each of these kinds, making quantitative comparison with exact numerical results and providing a qualitative overview. Numerical results are in all cases obtained by diagonalizing a $75 \times 75$ matrix given by Eq. (4). We consider only $n \leq 50$ and $g<1.0$ as these limits are reasonable ranges of inter est for typical molecular systems. Also, all results here are for block I (cf. Sec. II B); block II gives analogous results.

## A. Case I

Table I compares numerical and approximate calculations of energies and coefficients at several points in ( $J, g$ ) space for which the states are in region II for all $n$. In the approximate calculations, Eq. (25) is used for the energy and Eq. (32) or its analog for either $c_{n+1}$ or $c_{n-1}$ (see the text of Sec. II C for a further explanation). Only the ratio $c_{n+1} / c_{n}$ is computed. Calculation of the remaining coefficients involves no further approximations, although of course the error in $c_{n} \pm 1$ will be propagated.

TABLE I. Energies and eigenfunctions in region II for various $J$ and $g$ values.

| $n_{\text {Dn }}[i]^{\text {a }}$ | $E$ (exact) | $E$ (approx) | $C_{n \pm 1}$ (exact) | $C_{n \pm 1}$ (approx) |
| :---: | :---: | :---: | :---: | :---: |
| (a) $J=0.5, \quad g / \sqrt{2}=0.5$ |  |  |  |  |
| $5[7]$ | 6.77 | 6.73 | 0.380 | 0.377 |
| 10[8\|) | 7.69 | 7.66 | $-0.577$ | -0.510 |
| 15 [18] | 17.80 | 17.83 | 0.585 | 0.545 |
| 20 [17] | 16.80 | 16.76 | -0.705 | -0.6200 |
| 25 [29] | 28.70 | 28.61 | 0.667 | 0.632 |
| $30[26]$ | 25.90 | 26.06 | -0.736 | -0.686 |
| 35 [39] | 38.80 | 39.20 | 0.925 | 0.6940 |
| 40[36] | 35.70 | 35.47 | $-1.02$ | $-0.734$ |
| 45 [50] | 49.70 | 49.80 | 0.886 | 0.734 |
| 50 [45] | 44.90 | 44.95 | $-0.923$ | -0.771 |
| (b) $J=1.0, \quad g / \sqrt{2}=0.5$ |  |  |  |  |
| $5[8]$ | 6.92 | 6.94 | 0.314 | 0.307 |
| 10 [9] | 7.54 | 7. 50 | $-0.415$ | $-0.430$ |
| 15 [19] | 17.8 | 17.96 | 0.529 | 0.471 |
| $20[18]$ | 16.7 | 16.65 | -0.267 | -0.542 |
| $25[30]$ | 28.6 | 28.71 | 0.618 | 0.561 |
| 30[27] | 25.9 | 25.97 | $-0.705$ | -0.613 |
| $35[40]$ | 38.9 | 39.33 | 0.811 | 0.622 |
| 40[37] | 35.6 | 35.40 | -0.899 | -0.664 |
| $45[51]$ | 49. 7 | 49.87 | +0.833 | 0.668 |
| $50[46]$ | 44.9 | 44.88 | -0.901 | $-0.704$ |
| (c) $J=2.0, \quad g / \sqrt{2}=0.5$ |  |  |  |  |
| $5[9]$ | 7.59 | 7.60 | 0.215 | 0.212 |
| 10[8] | 6.96 | 6.96 | $-0.340$ | -0.310 |
| 15 [20] | 18.40 | 18.43 | 0.372 | 0.356 |
| 20 [18] | 16.30 | 16.23 | -0.479 | -0.418 |
| $25[30]$ | 28.90 | 29.09 | 0.492 | 0.442 |
| 30 [27] | 25.70 | 25.61 | -0.581 | $-0.490$ |
| $35[41]$ | 39.50 | 39.66 | 0.580 | 0.504 |
| 40 [36] | 35.10 | 35.08 | -0.656 | -0.544 |
| $45[51]$ | 49.90 | 50.17 | 0.691 | 0.553 |
| 50[46] | 44.80 | 44.59 | -0.765 | $-0.587$ |
| (d) $J=0.5, \quad g / \sqrt{2}=0.2$ |  |  |  |  |
| $5[7]$ | 5.95 | 5.83 | 0.188 | 0.197 |
| 10 [10] | 8.89 | 8.96 | -0.274 | -0.268 |
| 15 [17] | 16.1 | 16.22 | 0.320 | 0.307 |
| 20 [20] | 18.80 | 18.63 | -0.383 | -0.347 |
| 25[26] | 26.10 | 26.51 | 0.447 | 0.370 |
| 30 [29] | 28.10 | 28.36 | -0.375 | $-0.400$ |
| 35 [38] | 36.90 | 36.76 | 0.401 | 0.415 |
| 40 [39] | 38.0 | 38.13 | -0.435 | -0.439 |
| 45 [48] | 47.0 | 46.97 | 0.458 | 0.452 |
| 50 [49] | 47.90 | 47.93 | -0.490 | -0.472 |

${ }^{\mathrm{a}}[i]=$ level index (see the text).

The agreement of the energies is excellent over a range of $J$ and $g$ values, while that for $c_{n \pm 1} / c_{n}$ is fair, worsening with increasing $g \sqrt{n}$. This latter effect is due to truncation of the matrix equations (30); precision could be improved by truncating at a further point. The necessity of such a procedure will be clearer when we have performed calcultions of optical or dynamic properties.

In Table I, we have also indicated the level index of the exact energies. This index is the number of levels of the same total symmetry below the one considered (so that the lowest level has index 0 ). Note that even when the energy is very close to the level index, the largest component of the vector $c_{n}$ has an index $n$ which may be far from the level index. Finally, we note that the approximate eigenvalues fround from Eq. (7) (by us-

TABLE II. Energies and eigenfunctions for various $J$ and $q$ values in region I and region II.

| $n$ | $E_{\text {ex }}$ | $E_{\text {app }}$ | $C_{\text {ex }}$ |  | $C_{\text {app }}$ |  | Disp. |  | Region |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $n-1$ | $n+1$ | $n-1$ | $n+1$ | Exact | App. |  |
| (a) $C=0.1, \quad g / \sqrt{2}=0.2$ |  |  |  |  |  |  |  |  |  |
| 0 | -0.134 | $-0.133$ |  | -0.168 |  | -0.167 | -0.134 | -0.133 | I |
| 2 | 1.90 | 1.90 | 0.364 | -0.309 | 0.353 | -0.289 | -0.1 | -0.1 | I |
| 4 | 3.92 | 3.93 | 0.526 | -0.425 | 0.500 | -0.373 | -0.08 | -0.07 | I |
| 6 | 5.94 | 5.966 | 0.662 | -0.537 | 0.612 | -0.441 | -0.06 | -0.034 | I |
| 8 | 7.96 | 7.974 | 0.791 | -0.652 | 0.707 | -0.5 | -0.04 | -0.026 | I |
| 10 | 9.97 | 10.633 | 0.922 | -0.774 | 0.790 | -0.552 | -0.03 | +0.033 | I |
| 12 | 10.9 | 11.0 | -0.995 | -0.369 |  | -0.361 | $-1.1$ | -1.0 | II |
| 15 | 16.0 | 16.12 | +0.410 | +0.720 | 0.380 |  | +1.0 | +1.12 | II |
| 18 | 16.9 | 16.78 | -0.675 | -0.462 |  | -0.410 | $-1.1$ | -1.22 | II |
| 20 | 18.9 | 18.72 | -0.589 | -0.493 |  | $-0.423$ | $-1.1$ | -1.28 | II |
| (b) $J=0.3 \quad g / \sqrt{2}=0.1$ |  |  |  |  |  |  |  |  |  |
| 0 | -0.306 | $-0.306$ |  | -0.0626 |  | -0.0625 | -0.306 | -0.306 | I |
| 5 | 5.20 | 5.18 | 0.151 | -0.530 | 0.140 | -0.612 | $+0.2$ | 0.18 | I |
| 10 | 9.83 | 9.89 | 0.652 | -0.0236 | 0.79 | -0.190 | -0.17 | -0.11 | I |
| 15 | 15.10 | 15.01 | 0.292 | -0.775 | 0.242 | -1.0 | +0.10 | +0.01 | I |
| 20 | 19.9 | 20.07 | 0.852 | -0.364 | 0.12 | -0.286 | -0.10 | +0.07 | I |
| 25 | 25.0 | 24.83 | 0.421 | -0.939 | 0.312 | -1.25 | 0 | -0.17 | I |
| 30 | 30.0 | 30.25 | 0.474 | -1.0 | 0.342 | -1.39 | 0 | +0.25 | I |
| 35 | 36.0 | 35.89 | 0.272 |  | 0.286 |  | 1.0 | 1.11 | II |
| 40 | 39.0 | 39.05 |  | -0.294 |  | $-0.302$ | $-1.0$ | -1.05 | II |
| 45 | 46.0 | 46.0 | 0.308 |  | 0.314 |  | 1.0 | 1.0 | II |
| 50 | 48.9 | 48.95 |  | -0.328 |  | -0.327 | $-1.1$ | -1.05 | II |

ing the diagonal elements $H_{n n}^{ \pm}$) often are close to the exact eigenvalues in region II (for small $J, g$ ); however, the exact eigenfunctions (and hence optical properties) are not given as accurately by this approximation as by the procedure of Sec. IIC.

## B. Case II

Here, we need to compute approximate solutions for both region I and region II states. The region II states are found as in case I, while the region I states are determined from second order perturbation theory applied to the matrix of Eq. (12), i.e.,

$$
\begin{align*}
& c_{n+1} \approx-\left(\frac{g \sqrt{n+1}}{1 \pm 2 J}\right) \\
& c_{n-1} \approx\left(\frac{g \sqrt{n}}{1 \mp 2 J}\right)  \tag{40}\\
& E_{n} \approx n \pm J+g \sqrt{n} c_{n-1}
\end{align*}
$$

When case II is valid [i. e., an $n_{T}$ given by Eq. (9) can be defined] these perturbation expressions give a reasonable approximation to the displaced oscillator transformation, as $g \sqrt{n}$ must be small in region I. One could alternately start from Eq. (6) and perform a perturbative calculation (indeed, this would give better results when $J$ is small relative to $g$ and $n$ is close to $n_{T}$ ) but this is complicated by the infinite set of off-diagonal elements in this basis.

In this paper we shall not be interested in the detailed form of the region I states as $J, g$, and $n$ are varied, and we thus will not investigate this question further. For the two points in $(J, g)$ space presented in Table II;
agreement is reasonable for both the region I and region II states for both energies and coefficients. For the region I states we compute both $c_{n+1}$ and $c_{n-1}$ as these are both subject to approximation, while for the region II states we continue to compute only one or the other as in case I.

The displacement of the energy from the unperturbed oscillator value $n-E$ is a more sensitive indicator of the adequacy of the model than the energy itself. Therefore, in Table II we calculate the exact and approximate displacements for both region I and region II states. We note that (1) as $n-n_{T}$, agreement for the region I states becomes worse; here use of the zeroth order displacement of the displaced oscillator [Eq. (6)] basis $D=-\frac{1}{2} g^{2} \pm J\left\langle\phi_{n}^{g} \mid \phi_{n}^{-g}\right\rangle$ would be more accurate.
Agreement is good for small $n$. (2) At $n=n_{T}$ there is a large discontinuous jump in the displacement. (3) The magnitude of the displacement is predicted accurately for the region II states.

Table III lists the exact and approximate values of $n_{T}$ for a region of ( $J, g$ ) space which falls into case II ( $J=0.1 \rightarrow 0.5, g=0.1 \rightarrow 0.3$ ). The approximate values are found from Eq. (36).

TABLE III. $n_{r}$ as a function of $J$ and $g$ (exact/approximate). a

| $J$ |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :--- |
| $g$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| 0.1 | $47 / 64$ | $40 / 36$ | $32 / 16$ | $16 / 4$ | $\cdots / \cdots$ |
| 0.2 | $12 / 16$ | $10 / 9$ | $8 / 4$ | $4 / 1$ | $\cdots / \cdots$ |
| 0.3 | $3 / 4$ | $3 / 2$ | $2 / 1$ | $1 / \cdots$ | $\cdots / \cdots$ |

${ }^{\text {a Approximate from }} n_{T}=(1-25)^{2} / g^{2}$.

TABLE IV. Sample exact eigenstate for $J=0.1, g / \sqrt{2}=0.5 ; E=45.73$.

| $n_{\text {ph }}$ | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $C_{n}$ | -0.08 | -0.17 | -0.18 | -0.38 | -0.26 | -0.065 | 0.32 | -0.18 | 0.36 | -0.34 | 0.23 |

The $g$ dependence is predicted very accurately ( $n_{T}$ $\propto 1 / g^{2}$ ) but the $J$ dependence is somewhat worse. This reflects the fact that Eq. (36) is only an approximate criterion.

## C. Case III

The results for this case are quite complicated and we have not sorted out the details. However, the general qualitative behavior can be discussed. We expect that initially each $n$ will yield a region I or region II state. Then, if a region I and region II state are close in energy, configuration interaction between these states (mixed by $\left\langle\psi_{\mathrm{I}}\right| H\left|\psi_{\mathrm{II}}\right\rangle$ ) would be expected. For a given energy $E$ a typical wave function in this region (we chose $g / \sqrt{2}=0.5, J=0.1$ ) has intensity both near $n=E$ (from the region I state) and near $n=E \pm\left[J^{2}+\left(g^{2} / 2\right)(2 n+1)\right]^{1 / 2}$ (from the region II state). Table IV presents a sample exact eigenstate from the diagonalization of $H$ for $g$ / $\sqrt{2}=0.5, J=0.1$.

We analyze this state as follows:
(1) The amplitude of $\psi$ near $n_{\text {ph }}=45$ is contributed by a region I state $\psi_{\mathrm{I}}$ of energy $E \approx n_{\mathrm{ph}} \approx 45$.
(2) The amplitude near $n_{\mathrm{ph}}=40$ is contributed by a region II state $\psi_{\text {II }}$ of energy $E \approx n_{\text {ph }}+\left\{J^{2}+\left(g^{2} / 2\right)[2(n p h\right.$ $+1]\}^{1 / 2} \approx 44$. 7 .
(3) The wave function is thus approximately

$$
\psi_{\mathrm{CI}}=\frac{1}{\sqrt{2}}\left(\psi_{\mathrm{I}}+\psi_{\mathrm{II}}\right)
$$

and the energy

$$
E \approx \frac{1}{2}\left(E_{1}+E_{2}\right)+\Delta
$$

where

$$
\Delta=\left\langle\psi_{1}\right| H\left|\psi_{I I}\right\rangle
$$

## D. Phenomenological characterization of the wave function in regions I and II

In a qualitative examination of the localized and delocalized wave functions, we note two major differences:
(1) In region I the energy is $\approx n-\frac{1}{2} g^{2} \pm J\left\langle\phi_{n}^{\delta} \mid \phi_{n}^{-8}\right\rangle$; in region $\Pi$ it is displaced by $\left[J^{2}+g^{2} / 2(2 n+1)\right]^{1 / 2}$.
(2) In region I the coefficients $c_{n+1}$ and $c_{n-1}$ of $\psi_{n}$ are of approximately equal magnitude and opposite sign for small $g \sqrt{n}$ [this can trivially be derived from Eq. (5)]; increasing $J$ relative to $g$ perturbs the ratio $\left|c_{n+1}\right|$ / $\left|c_{n-1}\right|$ away from $\approx 1$. In the delocalized state $\left|c_{n+1}\right| /$ $\left|c_{n-1}\right|$ is again $\approx 1$ but the signs are now the same, and the opposite of $c_{n}$. Here, increasing $J$ causes $\left|c_{n+1}\right| \mid$ $\left|c_{n-1}\right|$ to approach 1 more closely.

## E. Analysis of the energy eigenvalues

We need to discuss the approximation made in Eq. (15) to obtain the approximate energy [Eq. (25)]. A rigorous justification of this step could be made only from a detailed analytical determination of the transition criteria, which, as mentioned above, we do not intend to undertake here. (It is plausible purely on the basis of the size of the terms involved. ) Instead, we appeal to the excellent quantitative agreement of the energy as given by Eq. (25) with the exact numerical results in region 11 of $(g, J, n)$ space. In all cases the displacements are given to $\pm 10 \%$ (in most cases more accurately), whereas perturbation theory from the matrices defined by either Eq. (7) or (12) would err by orders of magnitude of this region.

The reader may have some question as to whether Eq. (20) can be valid when $n-J-E \pm 1$ is small. However, as long as we are in region II, this will never be the case. Specifically, we really need to evaluate

$$
\frac{g \sqrt{n}}{n-J-E \pm 1}
$$

Taking $E=n+\left[J^{2}+g^{2}(2 n+1)\right]^{1 / 2}$, we have

$$
\frac{g / \sqrt{n}}{-J-\left[J^{2}+\frac{g^{2}}{2}(2 n+1)\right]^{1 / 2} \pm 1}
$$

If $J>0.5$,

$$
\left|-J-\left[J^{2}+\frac{g^{2}}{2}(2 n+1)\right]^{1 / 2} \pm 1\right|>\left[\frac{g^{2}}{2}(2 n+1)\right]^{1 / 2}
$$

so that

$$
\frac{g / \sqrt{n}}{\left[\frac{g^{2}}{2}(2 n+1)\right]^{1 / 2}}<1
$$

## F. Exciton-phonon correlation function

In Fig. 1, we plot the exciton-phonon correlation function $\delta$ [Eq. (2)] as a function of $J$ for a given value of $\left\langle N_{\phi}\right\rangle$ (i. e., the state containing $\sim\left\langle N_{p}\right\rangle$ phonons is "followed" across regions I and II). It is apparent that the behavior of the ground state is quite different from the remaining states. For the ground state, $\delta$ is a smooth function of $J$, reaching a maximum of -1 at $J$ $=0$ and tending to 0 as $J \rightarrow \infty$. For all other levels, how ever, $\delta$ reaches a maximum at some intermediate value of $J$ and discontinuously changes sign in this region, although the limiting values of -1 at $g=0$ and 0 at $J=\infty$ are still preserved.

This behavior can be understood by considering the nature of the transition between regions $I$ and II. The correlation function $\delta$ can be shown to be given by


FIG. 1. Exciton-phonon correlation function $\delta$ as a function of $J$ for $g / \sqrt{2}=0.2$ plotted for three values of $\left\langle n_{\mathrm{ph}}\right\rangle . J$ is in units of the vibrational frequency while $\delta$ is a unitless quantity.

$$
\delta=\frac{1}{g} \frac{\partial E}{\partial g}
$$

Thus, at $J=0, E=n-\frac{1}{2} g^{2}$, so $(1 / g)(\partial E / \partial g)=-1$ and as $J \rightarrow \infty, E \rightarrow n \pm J$, so $(1 / g)(\partial E / \partial g) \rightarrow 0$.

For region II we have $E \approx n \pm\left[J^{2}+\left(g^{2} / 2\right)(2 n+1)\right]^{1 / 2}$, so

$$
\begin{equation*}
\frac{1}{g} \frac{\partial E}{\partial g} \pm\left(\frac{2 n+1}{2}\right)\left[J^{2}+\frac{g^{2}}{2}(2 n+1)\right]^{-1 / 2} \tag{41}
\end{equation*}
$$

For $g^{2}(2 n+1) \gg J$ this reduces to

$$
\begin{equation*}
\delta \approx \pm(2 n+1)^{1 / 2} / g \sqrt{2} \tag{42}
\end{equation*}
$$

For $\sqrt{n}>g$ we thus obtain $|\delta|>1$; in fact, correlations orders of magnitude larger than that for $J=0$ are often found.

The ground state fails to exhibit the above behavior because of the following:
(i) The displacement is always negative ( $\sim-\frac{1}{2} g^{2}$
$\left.-J\left\langle\phi_{n}^{\delta} \mid \phi_{n}^{-\delta}\right\rangle\right)$ for region $\mathrm{I}, \sim-\left[J^{2}+\left(g^{2} / 2\right)\right]^{1 / 2}$ for region II, so there is no change of sign.
(ii) The correlation function for region II is $-\left[J^{2}\right.$ $\left.+\left(g^{2} / 2\right)\right]^{-1 / 2}$ but this formula is valid only if $\left[J^{2}\right.$ $\left.+\left(g^{2} / 2\right)\right]^{1-2}>1$. Thus, when Eq. (42) is applicable it always yields $|\delta|<1 / J<1$. Therefore, $|\delta|$ will always be between 0 and 1 for the ground state.

The behavior of $\delta$ in region I close to the transition will depend on terms like $(d / d g)\left\langle\phi_{n}^{\delta} \mid \phi_{n}^{-\delta}\right\rangle$. The complexity of this term and the existence of the infinite number of off-diagonal elements in the perturbation series make it difficult to pursue this calculation analytically; we merely note the dependences given in Fig. 1 and see that it confirms our qualitative picture, i. e., as $J \rightarrow J_{\text {Trans, }}|\delta|$ becomes larger and changes sign sharply somewhere in the transition region.

We are therefore led, for $n>0$, to define three re-
gions of $(J, g)$ space with regard to the exciton-phonon correlation. The first region. of low correlation, corresponds to $J \gg \sqrt{n}$ so that $\sqrt{n} /\left[J^{2}+\left(g^{2} / 2\right)(2 n+1)\right]^{1 / 2}$ $\ll 1$ is a subset of region II. The second, of high cor relation, is a subset of region $I$ in which $\delta \sim-1$. The third region is some neighborhood of the transition region and contains points in both regions I and II; we call this the region of anomalous correlation where, typical$l y,|\delta| \gg 1$.

The physical interpretation of these regions is as follows:
(1) We write the vibronic wave function as

$$
\begin{equation*}
\psi_{n}=|1\rangle \alpha_{1}\left(Q_{-}\right)+|2\rangle \alpha_{2}\left(Q_{-}\right) \tag{43}
\end{equation*}
$$

and $\delta$ as
$\frac{1}{g}\langle\bar{\Psi}|\left(A_{1}^{*} A_{1}-A_{2}^{*} A_{2}\right)\left(B_{-}+B_{-}^{*}\right)|\bar{\Psi}\rangle$

$$
\begin{equation*}
=\frac{1}{g}\left\langle\alpha_{1}\right| Q_{-}\left|\alpha_{1}\right\rangle-\frac{1}{g}\left\langle\alpha_{2}\right| Q_{-}\left|\alpha_{2}\right\rangle \tag{44}
\end{equation*}
$$

This is easily understood as the difference in the aver age position of $Q$. for the configurations $\phi_{1}^{e} \phi_{2}^{0}$ and $\phi_{1}^{0} \phi_{2}^{e}$.
(2) In the region of low correlation, $\left\langle Q_{-}\right\rangle_{1} \approx\left\langle Q_{-}\right\rangle_{2}$, i. e. , the average position of $Q_{\text {. }}$ is nearly equal whether molecule 1 or molecule 2 is excited.
(3) In the region of high correlation, the average value of $Q_{\text {_ }}$ on site 1 is close to $-g / 2$, while on site 2 it is close to $+g / 2$; thus, $\delta \approx 1 / g(-g / 2-g / 2) \approx-1$.
(4) In the region of anomalous correlation, $\left\langle Q_{-}\right\rangle_{1}$ $\approx \pm \sqrt{n} / 2$ while $\left\langle Q_{-}\right\rangle_{2} \approx \mp \sqrt{n} / 2$; thus, $\delta \approx \sqrt{n} / g$.

Thus, in the anomalous region extraordinarily large displacements of the coordinate may result. The precise physical reason for this and its consequences for other calculations (e.g., electron transfer) need to be investigated.

## G. Localization and delocalization

We showed earlier that for the Hamiltonian (1) all eigenstates are rigorously delocalized, i. e. , $P_{1}=P_{2}$. This result has been known for some time, of course, and is a consequence of the symmetry of the Hamiltonian. What has normally been meant by localization for such a Hamiltonian is an instability with respect to breaking this symmetry, i. e., for certain states the addition of a small perturbation of the appropriate symmetry to the Hamiltonian will convert this state to a truly localized one (i. e. , $\left.\left|\chi_{1}(Q)^{2}\right| \gg\left|\chi_{2}(Q)\right|^{2}\right)$.

For example, suppose $J$ is very small compared to $g$; the solutions of Eq. (1) are then $\psi_{n} \sim|1\rangle \phi_{n}^{\boldsymbol{g}} \pm|2\rangle \phi_{n}^{-g}$. However, a small diagonal site perturbation [i. e., a term like $\left.\Delta\left(A_{1}^{*} A_{1}-A_{2}^{*} A_{2}\right)\right]$ will, if $|\Delta|>|J|$, produce eigenstates $\psi_{n} \approx|1\rangle \phi_{n}^{g}$ or $\psi_{n} \approx|2\rangle \phi_{n}^{-g}$, which are quite localized.

It is tempting to identify our regions I and II as quasilocalized and quasidelocalized, respectively, the idea being that states in region I are unstable as described above, while those in region II are not. However, there is no need to do this speculatively; the effect of pertur -
bations described above can be examined analytically using the methods developed in this paper. We plan to do this in our next publication, where we shall delineate the precise criteria for the actual degree of localization as a function of the symmetry-breaking perturbation $\Delta, J$, and $g$. For the moment, we introduce these terms as having less explicit meaning, i. e., they categorize states only as belonging to region I or region II.

Finally, we note that as $n \rightarrow \infty$ we will reach a point in $n$ (or energy) where all states become quasidelocalized (region II states) regardless of the value of $g$ and $J$. Thus, for any two-level system represented by Eq. (1), the Born-Oppenheimer approximation will eventually fail, no matter how small the exciton-phonon coupling. This result is consistent with nonadiabatic theories of radiationless transition which rely on a similar mechanism to generate relaxation (5). In addition, this means that the standard theories of weak and strong vibronic coupling (6) apply only to certain values of $n$.

## IV. CONCLUSION

The method which we have used to obtain the region II states is quite unusual and needs to be further characterized. It may also prove to be applicable to other types of problems.

The analytical theory presented here spans the entire range of parameters $g, J$, and $n$; it thus suffices for calculation of optical properties. We plan to pursue these calculations in future publications, where quantitative discussions of dimer line shape as a function of homogeneous ( $g, J$ ) and inhomogeneous parameters will be given. One point can be made immediately, however. It seems clear that knowledge of $g$ and $w$ is critical to interpreting the apparent exciton splitting in a dimer absorption band. If one is in region II, the displacement of energy is $\left[J^{2}+\left(g^{2} / 2\right)(2 n+1)\right]^{1 / 2}$ rather than $J$. Thus, if large $n$ states contribute substantially to the spectrum, $J$ can be relatively small and one can still observe a large splitting in the dimer. To estimate $J$ directly from the apparent splitting is therefore an unacceptable procedure.

The theory presented here can be extended to more complicated dimer Hamiltonians: different diagonal site energies, coupling of phonons to the exchange and site energies, additional molecular and/or lattice vibrations, etc. Some of these Hamiltonians can
be solved analytically to the same level of approximation as the problem treated here, while others require additional approximations. All solutions are elegant, compact, and easily evaluated relative to the difficulty of the problem. These results will appear in forthcoming publications in this series.

Thus, our initial effort to solve Hamiltonian (1) has led to a generalized procedure for attacking vibronic coupling problems. Many Jahn-Teller problems, for example, are isomorphic to the problems listed above and so can be solved at once. Application of our technique to polymers and crystals is also a promising possibility. Finally, the ability to analytically transform a wide variety of exciton-phonon coupled Hamiltonian to a nearly diagonal basis should have important consequencies for calculation of dynamical properties (e.g., energy transfer, charge transfer).
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${ }^{8}$ This approximation may be derived in another way beginning from Eqs. (16). Multiply the second of Eqs. (16) by ( $h-J-E)^{-1}$, solve for $\chi_{2}(Q)$, and substitute into the first equation to get

$$
\left[(h+J-E)-g^{2} Q(h-J-E)^{-1} Q\right] \chi_{1}=0 .
$$

This corresponds to Eq. (19). The approximate result [Eq. (21)] corresponds to the neglect of the commutator $\left[Q,(h-J-E)^{-1}\right]$ and then multiplying through by $(h-J-E)$. The approximation in operator form is that $\mid(h-J-\epsilon)$ $\times Q(h-J-\epsilon)^{-1}-Q \mid$ is small in the sense that its matrix elements divided by energy differences is much less than 1. Equivalently, it corresponds to replacing the exact energy dependent "potential" by a simple approximate form. In region II, where the shift of the energies from $n \neq J$ is large compared to 1 , this is a good approximation correct to the inverse of the square of that shift.


[^0]:    ${ }^{\text {a }}$ Supported in part by the National Science Foundation (grant CHE-7807515).

