

Linear vibronic coupling in a general two level system

Richard A. Friesner and Robert Silbey

Citation: *J. Chem. Phys.* **75**, 3925 (1981); doi: 10.1063/1.442549

View online: <http://dx.doi.org/10.1063/1.442549>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v75/i8>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Linear vibronic coupling in a general two level system^{a)}

Richard A. Friesner and Robert Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 22 April 1981; accepted 17 June 1981)

The energy levels and wave functions for the excited vibronic states of a dimer made up of inequivalent molecules which interact (linearly) with vibrations and are coupled together electronically are treated. Two approximate schemes whose ranges of validity are substantially different and whose results are shown to agree well with exact numerical calculations are given. A discussion of the effect of the vibronic coupling on localization of the wave functions is given.

I. INTRODUCTION

In a previous paper¹ (henceforth referred to as I), we found approximate analytic eigenvalues and eigenvectors of a simple vibronic Hamiltonian: two identical molecules each with a single vibrational mode linearly coupled to an excited electronic level, and coupled together by an electronic exchange interaction J .² The most interesting result of this investigation was an analysis of the change in the nature of the vibronic wave function as a function of J , the exciton-phonon coupling parameter g , phonon number n , and vibrational frequency.

In this paper, we extend our approach to a generalized system consisting of two electronic levels, each linearly coupled to one vibrational mode. The elimination of symmetry in the Hamiltonian (present in the identical dimer) has important effects on qualitative features of the eigenvectors; our analytic solutions provide insight into this process in all regions of parameter space. For many parameter values we obtain quantitatively accurate energies and wave functions.

In Sec. II the generalized Hamiltonian is constructed and certain basic features are analyzed. Then, two complementary approximation schemes are presented, which together span the entire parameter space in their regions of applicability. The wave functions which emerge from these methods are analyzed in terms of qualitative features like Born-Oppenheimer separability. Comparisons are made for various parameter values with exact numerical results, and the region of validity of each approximation scheme is discussed.

In Sec. III we consider a specific physical system, a dimer composed of two molecules with identical vibrational modes and exciton-phonon couplings but with different zeroth order electronic energies of their single excited state. Here, we use the results of Sec. II to determine the effect of the symmetry-breaking site-diagonal perturbation ϵ on the localization of excitation.

In conclusion, we discuss other possible applications of our formalism both in molecular two-level systems (e.g., Jahn-Teller systems, radiationless transitions) and in properties of molecular aggregates.

^{a)}Supported in part by a grant from the NSF (CHE 78-07515) and by a NIH postdoctoral fellowship to RAF.

II. GENERALIZED TWO LEVEL SYSTEM

A. Hamiltonian

We consider a system with an electronic ground state and two excited electronic states a and b separated by energy 2Δ . Each electronic level is coupled to a single harmonic vibrational mode of frequency ω . If the equilibrium position of the normal coordinate Q is taken to be zero in the ground state (energy E_g^0), the minima in states a and b (energies E_a^0 and E_b^0 at $Q=0$) are, respectively, g_a and g_b . These shifts arise from the linear term in the Taylor's expansion of the potential energy surfaces of a and b , i.e.,

$$\begin{aligned}g_a &= (\partial V_a / \partial Q)_0, \\g_b &= (\partial V_b / \partial Q)_0.\end{aligned}\quad (1)$$

The frequency ω is taken to be independent of electronic level. We also include a linear term which vibronically couples a and b ; the magnitude of this coupling is given by the parameter v . This term arises from that part of the Hamiltonian discarded in the Born-Oppenheimer (BO) approximation.

Taking the zero of energy to be $\frac{1}{2}(E_a^0 + E_b^0) - E_g^0 + \frac{1}{2}\omega$ ($\hbar=1$) and representing all parameters in units of the vibrational frequency ω , we write the Hamiltonian in second quantized form as

$$\begin{aligned}H &= \Delta(A_a^\dagger A_a - A_b^\dagger A_b) + B^\dagger B \\&+ (1/\sqrt{2})g_a A_a^\dagger A_a (B + B^\dagger) + (1/\sqrt{2})g_b A_b^\dagger A_b (B + B^\dagger) \\&+ (1/\sqrt{2})v(A_a^\dagger A_b + A_b^\dagger A_a)(B + B^\dagger),\end{aligned}\quad (2)$$

where B^\dagger and B create and destroy a vibrational quantum, respectively [and $Q = (1/\sqrt{2})(B + B^\dagger)$], and A_a^\dagger , A_a , A_b^\dagger , and A_b are creation and destruction operators for occupation of levels a and b . This Hamiltonian may arise from a variety of physical systems; in Sec. III we shall see that the dimer Hamiltonian with unequal monomer excited energy levels may be cast into this form.

We seek only singly (electronically) excited states as solutions, i.e., such that

$$\langle \psi | A_a^\dagger A_a + A_b^\dagger A_b | \psi \rangle = 1. \quad (3)$$

We first define

$$\gamma_\pm = \frac{1}{2}(g_a \pm g_b). \quad (4)$$

Then, using Eq. (2), we have

$$H = \Delta(A_a^*A_a - A_b^*A_b) + B^*B + \frac{1}{\sqrt{2}}\gamma_+(B + B^*) + \frac{1}{\sqrt{2}}\gamma_-(B + B^*)(A_a^*A_a - A_b^*A_b) + \frac{1}{\sqrt{2}}v(B + B^*)(A_a^*A_b + A_b^*A_a). \quad (5)$$

We will first remove the γ_+ term by defining new operators (equivalent to redefining the origin of the vibrational coordinate)

$$\tilde{B} = B + \frac{1}{\sqrt{2}}\gamma_+. \quad (6)$$

Then

$$H = -\frac{1}{2}\gamma_+^2 + \tilde{B}^*\tilde{B} + (\gamma_-/\sqrt{2})(\tilde{B} + \tilde{B}^*)(A_a^*A_a - A_b^*A_b) + (v/\sqrt{2})(\tilde{B} + \tilde{B}^*)(A_a^*A_b + A_b^*A_a) + (\Delta - \gamma_+\gamma_-)(A_a^*A_a - A_b^*A_b) - (A_a^*A_b + A_b^*A_a)(\gamma_+v). \quad (7)$$

We can now remove the static electronic coupling $(-\gamma_+v)$ by a unitary transformation of the electronic states

$$A_a = \cos\theta \tilde{A}_a + \sin\theta \tilde{A}_b, \quad (8) \\ A_b = -\sin\theta \tilde{A}_a + \cos\theta \tilde{A}_b,$$

so that in these new electronic states

$$H = \Delta'(\tilde{A}_a^*\tilde{A}_a - \tilde{A}_b^*\tilde{A}_b) - \frac{1}{2}\gamma_+^2 + \tilde{B}^*\tilde{B} + (1/\sqrt{2})\gamma'_+(\tilde{A}_a^*\tilde{A}_a - \tilde{A}_b^*\tilde{A}_b)(\tilde{B} + \tilde{B}^*) + (1/\sqrt{2})v'(\tilde{A}_a^*\tilde{A}_b + \tilde{A}_b^*\tilde{A}_a)(\tilde{B} + \tilde{B}^*), \quad (9)$$

where

$$\Delta' = [(\Delta - \gamma_+\gamma_-)^2 + \gamma_+^2v^2]^{1/2}, \quad (10) \\ \gamma'_+ = \gamma_- \cos\theta + v \sin\theta, \\ v' = -\gamma_- \sin\theta + v \cos\theta.$$

It is this Hamiltonian which we will deal with in the present paper. In order to make the notation simple, we will change the zero of energy by $\frac{1}{2}\gamma_+^2$, drop the primes and tildes, and let $\gamma_- = \gamma$ to obtain

$$H = \Delta(A_a^*A_a - A_b^*A_b) + B^*B + (1/\sqrt{2})\gamma(A_a^*A_a - A_b^*A_b)(B + B^*) + (1/\sqrt{2})v(A_a^*A_b + A_b^*A_a)(B + B^*). \quad (11)$$

Note that this is equivalent to Eq. (5) except that now $\gamma_+ = 0$.

We now introduce two different but complementary approximation schemes to diagonalize Eq. (11). In Scheme 1, we canonically transform the electronic states $|a\rangle$ and $|b\rangle$ in an attempt to obtain a BO separable form for the wave function by eliminating the off-diagonal phonon coupling. In Scheme 2, we assume $|a\rangle$ and $|b\rangle$ to be the optimal electronic states and try to eliminate the site-diagonal phonon coupling by an expansion of the vibronic wave function in an appropriate set of displaced oscillators.

B. Electronic rotation to remove the off-diagonal phonon term

In this approximation scheme (scheme 1) we attempt to optimize the electronic basis functions by a canonical transformation given by

$$|\alpha\rangle = \cos\theta |a\rangle + \sin\theta |b\rangle, \quad (12) \\ |\beta\rangle = -\sin\theta |a\rangle + \cos\theta |b\rangle,$$

or, in operator space,

$$A_\alpha = A_a \cos\theta + A_b \sin\theta, \quad (13) \\ A_\beta = -\sin\theta A_a + \cos\theta A_b.$$

We shall choose θ so that the off-diagonal phonon term $(A_a^*A_b + A_b^*A_a)(B + B^*)$ vanishes; the correct θ is then given by

$$\tan 2\theta = v/\gamma. \quad (14)$$

The transformed Hamiltonian is then

$$\tilde{H} = \left[\Delta\gamma/(\gamma^2 + v^2)^{1/2} + \frac{1}{\sqrt{2}}(\gamma^2 + v^2)^{1/2}(B + B^*) \right] (A_\alpha^*A_\alpha - A_\beta^*A_\beta) + B^*B - \frac{\Delta v}{(\gamma^2 + v^2)^{1/2}}(A_\alpha^*A_\beta + A_\beta^*A_\alpha) = \tilde{H}_0 + H_{ph} + H'. \quad (15)$$

The perturbation $H' \propto \Delta v/(\gamma^2 + v^2)^{1/2}$ is now independent of vibrational operators and will be unimportant if $\Delta v/(\gamma^2 + v^2)^{1/2}$ is small compared to the difference in energies of the states mixed by H' . These are the solutions of the remainder of \tilde{H} , i. e., $\tilde{H}_0 + H_{ph}$, which are given by

$$\psi_n^\alpha = |\alpha\rangle \phi_n^\alpha, \quad \psi_n^\beta = |\beta\rangle \phi_n^\beta, \quad (16) \\ E_n^\alpha = n + \Delta' - \frac{1}{2}z^2, \quad E_n^\beta = n - \Delta' - \frac{1}{2}z^2,$$

where

$$\Delta' = \Delta\gamma/(\gamma^2 + v^2)^{1/2}, \\ z = [(\gamma^2 + v^2)]^{1/2},$$

and ϕ_n^α is a harmonic oscillator eigenfunction with n phonons and argument $Q' = Q + z$.

The matrix element of H' between ψ_n^α and ψ_m^β is

$$H'_{n\alpha m\beta} = \langle \psi_n^\alpha | H' | \psi_m^\beta \rangle = \frac{\Delta v}{(\gamma^2 + v^2)^{1/2}} \langle \phi_n^\alpha | \phi_m^\beta \rangle. \quad (17)$$

Note that $H'_{n\alpha m\beta} < \Delta$ for any γ and v . The diagonal energy separation is $E_{n\alpha m\beta} = E_n^\alpha - E_m^\beta = n - m + 2\Delta$.

When $\Delta \ll 1$ (remember that all energies are in units of ω so this condition corresponds to $\Delta' \ll \omega$) we have

$$E_n^\alpha - E_m^\beta \approx n - m, \quad \text{for } n \neq m, \quad (18)$$

and $H_{n\alpha m\beta} < \Delta \ll |n - m|$ for $n \neq m$. Thus, the only important interaction is for $n = m$, i. e.,

$$H'_{n\alpha n\beta} = \Delta v/(\gamma^2 + v^2)^{1/2} \langle \phi_n^\alpha | \phi_n^\beta \rangle, \\ E_n^\alpha - E_n^\beta = 2\Delta' = 2\Delta\gamma/(\gamma^2 + v^2)^{1/2}. \quad (19)$$

This interaction will be insignificant if

$$\mu_{n\alpha n\beta} = \left| \frac{H'_{n\alpha n\beta}}{E_n^\alpha - E_n^\beta} \right| = \left| \frac{v}{\gamma} \right| \left| \langle \phi_n^\alpha | \phi_n^\beta \rangle \right| \ll 1. \quad (20)$$

We immediately note two cases where this condition

holds:

$$(1) \gamma \gg v, \quad (21)$$

$$(2) \langle \phi_n^\alpha | \phi_n^{-\alpha} \rangle \ll 1.$$

For large n we have³

$$|\langle \phi_n^\alpha | \phi_n^{-\alpha} \rangle| \leq \frac{1}{[(2n+1)z/2]^{1/2}} \quad (22)$$

so that, as $n \rightarrow \infty$ condition (2) eventually is valid for any finite value of v/γ .

When $\mu_{n\alpha n\beta} \geq 1$ we have configuration interaction (CI) between ψ_n^α and ψ_n^β , the final wave functions will be

$$\psi_+ = c_1 \psi_n^\alpha + c_2 \psi_n^\beta, \quad E = E_{n\alpha n\beta}^+, \quad (23)$$

$$\psi_- = c_1 \psi_n^\beta - c_2 \psi_n^\alpha, \quad E = E_{n\alpha n\beta}^-,$$

where c_1 , c_2 , $E_{n\alpha n\beta}^+$ and $E_{n\alpha n\beta}^-$ are found by diagonalizing the 2×2 matrix

$$\mathbf{M}_{n\alpha n\beta} = \begin{bmatrix} E_n^\alpha & H_{n\alpha n\beta} \\ H_{n\alpha n\beta} & E_n^\beta \end{bmatrix}. \quad (24)$$

As $\gamma \rightarrow 0$, we obtain the limits

$$c_1 = c_2 = 1/\sqrt{2}, \quad (25)$$

which can be recognized as the solutions to the identical dimer problem of paper I in the limit as $J \rightarrow 0$.

We now turn to the case where $\Delta \geq 1$. First, we suppose that $\Delta v/(\gamma^2 + v^2)^{1/2} \ll 1$ (this clearly requires $\gamma \gg v$). Then, for each n , there will be only one m for which the condition

$$\mu_{n\alpha m\beta} \ll 1 \quad (26)$$

is possibly not satisfied, as $|E_{n\alpha m\beta}| > 1$ for all but the value of $n-m$ where $n-m \sim 2\Delta$. We therefore have to consider configuration interaction between ψ_n^α and one $\psi_{m^*}^\beta$, where $m^* \sim n + 2\Delta$. Then the analysis of eigenvectors, eigenvalues, and CI proceeds as before, except that the 2×2 matrix to be diagonalized is now

$$\mathbf{M}_{n\alpha m^*\beta} = \begin{bmatrix} E_{n\alpha} & H_{n\alpha m^*\beta} \\ H_{n\alpha m^*\beta} & E_{m^*\beta} \end{bmatrix}. \quad (27)$$

A systematic analysis of the CI is more difficult here as we need to know the separation of the *accidentally* degenerate levels $n = m^* + 2\Delta$ and the generalized overlap $\langle \phi_n^\alpha | \phi_{m^*}^\beta \rangle$. However, we note that, as $n \rightarrow \infty$, $\mu_{n\alpha m^*\beta} \rightarrow 0$ (so that CI becomes negligible for $n >$ some n_{\min}), and that the largest CI should occur when $2\Delta'$ is an integral multiple of ω (so that $n - m^* + 2\Delta \approx 0$).

The remaining case is $\Delta v/(\gamma^2 + v^2)^{1/2} > 1$. Here, there will be individual levels for which scheme 1 is a reasonable approximation but, in general, we expect it to be increasingly poor as $\Delta v/(\gamma^2 + v^2)^{1/2} \rightarrow \infty$. This is because H' will effectively couple more and more states, and so no simple representation in terms of the ψ_n^α and ψ_n^β will be possible. Fortunately, approximation scheme 2 is most useful in precisely this region of parameter space.

In Table I we compare approximate and exact wave functions for two typical examples of each of the three cases described above for which scheme 1 is valid:

$$(1) \Delta \ll 0.5, \quad v > g, \quad (28)$$

$$(2) \Delta \ll 0.5, \quad g > v,$$

$$(3) \Delta > 0.5, \quad g > v.$$

CI is calculated from Eqs. (24) and (27) when necessary, and from Eq. (14).

Final results are given in the electronic basis ($|a\rangle$, $|b\rangle$) of Eq. (11) with vibrational wave functions expanded in harmonic oscillator states centered at $Q=0$. Agreement between wave functions is estimated by the projection $\langle \psi_{\text{exact}} | \psi_{\text{approx}} \rangle / (\langle \psi_{\text{exact}} | \psi_{\text{exact}} \rangle \langle \psi_{\text{approx}} | \psi_{\text{approx}} \rangle)^{1/2}$. Exact numerical results were obtained by diagonalizing a 100×100 matrix (50 vibrational basis functions for each electronic state); however, for purposes of comparison with ψ_{approx} , we have truncated the basis sets used in Table I to include only the set of coefficients which contribute substantially to the amplitude.

The results indicate that, for $\Delta \ll 1$, CI is important only for $\gamma \ll v$ (this condition was not satisfied for any of our numerical examples). On the other hand, for $\Delta \geq 0.5$, substantial CI was necessary in both cases. However, the resulting wave functions, using 2×2 CI, agree quite well with the exact results, in accordance with the discussion above.

Finally, we discuss the BO separability of scheme 1 states. When there is negligible CI, we clearly have completely factorized states in the $\{\alpha, \beta\}$ basis. When CI is important, the $\{\alpha, \beta\}$ basis may no longer be the optimal one for BO separability. In Appendix B we calculate the maximum BO separability, defined by

$$B = \langle \psi | A_k^* A_k - A_l^* A_l | \psi \rangle, \quad (29)$$

where k and l are arbitrary orthogonal electronic states (linear combinations of $|a\rangle$ and $|b\rangle$) chosen to maximize B . B can be expressed in terms of the overlap parameters for a different electronic basis as

$$B = (U_{\alpha\beta}^2 + V_{\alpha\beta}^2)^{1/2}, \quad (30)$$

where

$$U_{\alpha\beta} = \langle \psi | A_\alpha^* A_\alpha - A_\beta^* A_\beta | \psi \rangle,$$

$$V_{\alpha\beta} = \langle \psi | A_\alpha^* A_\beta + A_\beta^* A_\alpha | \psi \rangle.$$

Using Eq. (23) for Ψ , we obtain

$$B = [(c_1^2 - c_2^2)^2 + (2c_1 c_2 \langle \phi_n^\alpha | \phi_{m^*}^\beta \rangle)^2]^{1/2}, \quad (31)$$

where $n=m$ for $\Delta \ll 1$ and $n-m \sim \Delta$ for $\Delta > 0.5$. In the limit as $n \rightarrow \infty$, we have in all cases $|c_1^2 - c_2^2| \rightarrow 1$, so that $B \rightarrow 1$ and all states become BO separable.

C. Expansion in displaced oscillator states (scheme 2)

When $v \gg \gamma$ and $2\Delta \gg 1$, we shall treat the diagonal phonon terms $\gamma(A_a^* A_a - A_b^* A_b)(B + B^*)$ in Eq. (11) as a perturbation. The Hamiltonian which remains when $\gamma=0$ is that for a dimer composed of identical monomers (i. e., the Hamiltonian of paper I) so it is natural to use the representations derived in paper I in a modified form to include the effects of the perturbation.

Following paper I, we represent H in phonon coordinate space and form the set of equations

TABLE I. Comparison of approximate and exact eigenstates for scheme 1. The index p denotes the phonon number of the harmonic oscillator basis function.

p	Coefficients			
	$ a\rangle$		$ b\rangle$	
	Approx	Exact	Approx	Exact
(a) $\Delta=0.1, v/\sqrt{2}=0.2, \gamma/\sqrt{2}=0.1,$ $E_{\text{exact}}=6.9047, E_{\text{approx}}=6.9053,$ $\psi_{\text{approx}}= \beta\rangle\phi_n^{-s},$ $z=0.223, n=7, \theta=0.55$				
5	-0.073	-0.072	0.121	0.126
6	0.270	0.293	-0.426	-0.399
7	-0.332	-0.362	0.551	0.544
8	-0.281	-0.220	0.443	0.471
9	-0.093	-0.107	0.154	0.150
$I_{\text{A.E.}}=0.99$				
(b) $\Delta=0.1, v/\sqrt{2}=0.3, \gamma/\sqrt{2}=0.1,$ $E_{\text{exact}}=2.869, E_{\text{approx}}=2.868,$ $\psi_{\text{approx}}= \beta\rangle\phi_n^{-s}, z=0.32, n=3, \theta=0.62$				
1	-0.063	-0.056	0.094	0.098
2	0.286	0.334	-0.373	-0.342
3	-0.381	-0.380	0.563	0.556
4	-0.312	-0.272	0.408	0.437
5	-0.108	-0.115	0.159	0.153
$I_{\text{A.E.}}=0.99$				
(c) $\Delta=0.1, v/\sqrt{2}=0.1, \gamma/\sqrt{2}=0.5,$ $E_{\text{exact}}=6.84, E_{\text{approx}}=6.84,$ $\psi_{\text{approx}}= \alpha\rangle\phi_n^s,$ $z=0.52, n=7, \theta=0.0987$				
3	0.061	0.061	0.066	0.005
4	0.213	0.212	0.021	0.023
5	0.456	0.457	0.045	0.038
6	0.439	0.442	0.044	0.047
7	-0.180	-0.180	-0.018	-0.019
8	-0.381	-0.381	-0.038	-0.038
9	0.484	0.483	0.048	0.054
10	-0.317	-0.317	-0.037	-0.209
11	0.149	0.149	0.015	0.017
12	-0.056	-0.056	-0.006	-0.005
$I_{\text{A.E.}}=1.00$				
(d) $\Delta=0.1, v/\sqrt{2}=0.2, \gamma/\sqrt{2}=0.5,$ $E_{\text{exact}}=6.803, E_{\text{approx}}=6.803,$ $\psi_{\text{approx}}= \alpha\rangle\phi_n^s,$ $z=0.58, n=7, \theta=0.19$				
4	0.235	0.234	0.045	0.053
5	0.465	0.470	0.089	0.067
6	0.388	0.385	0.075	0.088
7	-0.237	-0.238	-0.046	-0.043
8	-0.318	-0.316	-0.061	0.067
9	0.478	0.477	0.092	0.092
10	-0.341	-0.399	-0.066	-0.070
11	0.172	0.172	0.033	0.032
12	-0.069	-0.069	-0.013	-0.014
$I_{\text{A.E.}}=1.00$				

TABLE I (Continued)

p	Coefficients			
	$ a\rangle$		$ b\rangle$	
	Approx	Exact	Approx	Exact
(e) $\Delta=1.0, v/\sqrt{2}=0.2, \gamma/\sqrt{2}=0.5,$ $E_{\text{exact}}=10.59, E_{\text{approx}}=10.59,$ $\psi_{\text{approx}}=c_\alpha \alpha\rangle\phi_{n_1}^s+c_\beta \beta\rangle\phi_{n_2}^{-s},$ $c_\alpha=0.889, c_\beta=-0.459, z=0.54, n_1=10, n_2=12, \theta=0.19$				
6	0.132	0.147	0.018	0.010
7	0.296	0.319	0.090	0.094
8	0.434	0.471	-0.014	-0.070
9	0.122	0.071	0.208	0.227
10	-0.292	-0.295	-0.261	-0.245
11	-0.099	-0.086	0.001	0.011
12	0.347	0.345	0.255	0.256
13	-0.361	-0.335	-0.061	-0.120
14	0.251	0.225	-0.127	-0.114
$I_{\text{A.E.}}=0.99$				
(f) $\Delta=1.0, v/\sqrt{2}=0.3, \gamma/\sqrt{2}=0.5,$ $E_{\text{exact}}=10.51, E_{\text{approx}}=10.50,$ $\psi_{\text{approx}}=c_\alpha \alpha\rangle\phi_{n_1}^s+c_\beta \beta\rangle\phi_{n_2}^{-s},$ $c_\alpha=0.974, c_\beta=0.228, z=0.58, n_1=10, n_2=12, \theta=0.27$				
6	0.176	0.195	0.054	0.024
7	0.357	0.370	0.121	0.137
8	0.435	0.493	-0.062	-0.055
9	-0.031	-0.039	0.109	0.185
10	-0.355	-0.348	-0.188	-0.169
11	0.017	0.044	-0.014	-0.017
12	0.331	0.303	0.183	0.149
13	-0.414	-0.368	-0.082	-0.138
14	0.297	0.260	0.014	0.078
$I_{\text{A.E.}}=0.99$				

$$\begin{aligned} \langle a|H-E|\psi\rangle &= 0, \\ \langle b|H-E|\psi\rangle &= 0, \end{aligned} \quad (32)$$

where $\psi=|a\rangle\chi_a+|b\rangle\chi_b$ [note here that $|a\rangle$ and $|b\rangle$ are the original electronic states of Eq. (11)]. Thus, we have

$$(h+\Delta+\gamma Q-E)\chi_a=-vQ\chi_b, \quad (33a)$$

$$(h-\Delta-\gamma Q-E)\chi_b=-vQ\chi_a, \quad (33b)$$

where $h=-\frac{1}{2}(d^2/dQ^2)+\frac{1}{2}Q^2$ is the phonon number operator.

We expand χ_a and χ_b in harmonic oscillator states centered at $Q+s$, where s is a parameter to be determined:

$$\chi_a=\sum c_n\phi_n^s, \quad (34)$$

$$\chi_b=\sum b_n\phi_n^s.$$

We substitute Eqs. (34) into Eq. (33) and, in Appendix A, derive an approximate set of equations for the coefficients c_n :

$$c_n \{ (n + \Delta - E)(n - \Delta - E) + [(\gamma^2 + v^2) - s^2](2n + 1)/2 \} + \frac{1}{\sqrt{2}}(\gamma - s)[c_{n+1}(n + 1)^{1/2} + c_{n-1}(\sqrt{n})]^{1/2}(n - \Delta - E) \\ = \frac{1}{2} [(\gamma^2 + v^2) - s^2] \{ c_{n-2}[n(n - 1)]^{1/2} + c_{n+2}[(n + 1)(n + 2)]^{1/2} \} + \frac{1}{\sqrt{2}}(\gamma + 2)(n + \Delta - E)[c_{n+1}(n + 1)^{1/2} + c_{n-1}(n)^{1/2}]. \quad (35)$$

We attempt to eliminate the terms in c_{n+1} and c_{n-1} by solving for s , i. e.,

$$(\gamma - s)(n - \Delta - E) = (\gamma + s)(n + \Delta - E). \quad (36)$$

Suppose we want the eigenvector and eigenvalue corresponding to n . We set

$$s_n = \frac{(\Delta\gamma)}{n - E_n}. \quad (37)$$

Then, the n th coefficient equation can be written

$$c_n \left[(n + \Delta - E)(n - \Delta - E) + \frac{g_n^2}{2}(2n + 1) \right] \\ = (g_n^2/2) \{ c_{n-2}[n(n - 1)]^{1/2} + c_{n+2}[(n + 1)(n + 2)]^{1/2} \}, \quad (38)$$

where $g_n^2 = (\gamma^2 + v^2) - s_n^2$.

The remaining coefficient equations will still have terms in c_{n+1} and c_{n-1} , but we neglect these expecting that their effect will be small. Then, this equation is isomorphic to Eq. (21) in paper I. The eigenvalues are, for $\Delta > 0.5$,

$$E_n^* \approx n \pm \left[\Delta^2 + \frac{g_n^2}{2}(2n + 1) \right]^{1/2}. \quad (39)$$

Substituting Eq. (39) into Eq. (37), we can solve for s_n to obtain

$$s_n^2 = \frac{1}{2} \left\{ \left(\frac{2\Delta^2}{2n + 1} + \gamma^2 + v^2 \right) \pm \left[\left(\frac{2\Delta^2}{2n + 1} + \gamma^2 + v^2 \right)^2 - \frac{8\Delta^2\gamma^2}{2n + 1} \right]^{1/2} \right\}. \quad (40)$$

In order to justify the approximations $|n - E^* \pm \Delta| \gg 1$ in Appendix A, we require that this is facilitated by making g_n^2 as large as possible, and thus s_n^2 as small as possible. We therefore choose the (-) sign in Eq. (40). The sign of s_n is determined by the sign of $n - E$ because of Eq. (37), i. e., s_n is positive for states where $E_n = E_n^*$, and negative for $E_n = E_n^-$.

The analytic behavior of s_n in various limits is easily determined from Eq. (40). As $n \rightarrow \infty$, $|s_n| \rightarrow 0$. However, the important quantity for determining the magnitude of the expansion coefficients of a displaced oscillator of quantum number n is

$$y_n = (s_n/\sqrt{2})(\sqrt{2n + 1}). \quad (41)$$

The limit of y_n as $n \rightarrow \infty$ is

$$\lim_{n \rightarrow \infty} y_n = \frac{\Delta\gamma}{(\gamma^2 + v^2)^{1/2}}, \quad (42)$$

so that for large Δ this quantity will be nonnegligible. (As a rough estimate, the magnitude of y_n is comparable to the coefficient separation $|m - n|$ for which the coefficients c_m in the displaced oscillator expansion will have substantial amplitude.)

For $n \rightarrow 0$ or $\Delta \rightarrow \infty$, we have $s_n \rightarrow \gamma$. This leads to

eigenstates $\phi_n^* \approx |a\rangle \phi_n^\gamma$, $\phi_n^- \approx |b\rangle \phi_n^{-\gamma}$, and corresponds to neglect of the v term in the Hamiltonian. This approximation is valid when the separation between $|a\rangle$ and $|b\rangle$ is sufficiently large so that the perturbation vQ mixes them inefficiently (more likely for low n states because $\langle Q \rangle_{n,n+1}$ is smaller in these states).

The vibronic parts of the approximate wave functions ψ_n^+ and ψ_n^- are of the form

$$\chi_a^{n\pm} = \sum \bar{c}_m^{n\pm} \phi_m^{\pm |s_n|}, \quad (43) \\ \chi_b^{n\pm} = \sum \bar{b}_m^{n\pm} \phi_m^{\pm |s_n|},$$

where \bar{c}_m^n and \bar{b}_m^n are found by diagonalizing the identical dimer Hamiltonian

$$\tilde{H} = \Delta(A_a^* A_a - A_b^* A_b) \\ + B^* B + g_n(A_a^* A_b + A_b^* A_a)(B + B^*), \quad (44)$$

which has solutions

$$\tilde{\chi}_a^n = \sum \tilde{c}_m^n \phi_m^0, \quad (45) \\ \tilde{\chi}_b^n = \sum \tilde{b}_m^n \phi_m^0.$$

The symmetry of the identical dimer Hamiltonian leads to the condition that $\langle \tilde{\chi}_a^n | \tilde{\chi}_b^n \rangle = \sum_m \tilde{c}_m^n \tilde{b}_m^n = 0$, because these two functions are expanded in orthogonal basis sets, one with $\{\tilde{c}_m^n = 0\}$, n even and the other with $\{\tilde{b}_m^n = 0\}$, n odd (or *vice versa*). This condition is equally valid for the functions in Eq. (43), i. e., $\langle \chi_a^n | \chi_b^n \rangle = 0$.

Although we have minimized the $c_{n\pm 1}$ terms in the region of the matrix equations near n , we will still have coupling between the approximate states ψ_n^+ and ψ_m^- by the operator

$$H' = \frac{\gamma}{\sqrt{2}}(A_a^* A_a - A_b^* A_b)(B + B^*), \quad (46)$$

which will be important if $E_n^* \sim E_m^-$. In fact, we know that this configuration interaction must take place to break the symmetry of the solutions of Eq. (38), which have the symmetry appropriate for solutions to the identical dimer problem.

In cases where this approximation scheme is useful, a 2×2 CI will be sufficient to produce a good approximate wave function. It is difficult to calculate the CI analytically as it depends on the energy difference between accidentally degenerate wave functions whose eigenvalues are not known with sufficient precision and the perturbation matrix elements are hard to determine in closed form. We therefore investigate the CI qualitatively.

The matrix element between ψ_n^+ and ψ_m^- is

$$H'_{nm} = \frac{\gamma}{\sqrt{2}} [\langle \chi_a^n | (B + B^*) | \chi_a^m \rangle - \langle \chi_b^n | (B + B^*) | \chi_b^m \rangle]. \quad (47)$$

For a given ψ_n^* there are two possible ψ_m^- which may lie close in energy, i. e., such that $|E_n^* - E_m^-| < 1$; the approximate condition is

$$|n - m| \sim [\Delta^2 + g_n^2(2n + 1)]^{1/2} + [\Delta^2 + g_m^2(2m + 1)]^{1/2}. \quad (48)$$

In the small n limit [$g_n^2(2n + 1) \ll \Delta$], the wave functions are nearly $\psi_n^* \sim |a\rangle \phi_n^{s_n}$ and $\psi_m^- \sim |b\rangle \phi_m^{-s_n}$. This means that $H'_{nm} \sim 0$ because of the small amplitudes of χ_b^n and χ_a^m . In the large n limit, $s \rightarrow 0$ and we can approximate H'_{nm} by

$$H'_{nm} \approx \frac{\gamma}{\sqrt{2}} [\langle \bar{\chi}_a^n | (B + B^*) | \bar{\chi}_a^m \rangle - \langle \bar{\chi}_b^n | (B + B^*) | \bar{\chi}_b^m \rangle]. \quad (49)$$

Then, H' mixes only states where $\bar{\chi}_a^n$ and $\bar{\chi}_a^m$ are expanded in complementary basis sets, e. g., $\bar{\chi}_a^n = \sum c_n \phi_{2n}^0$ and $\bar{\chi}_a^m = \sum c_{2n+1} \phi_{2n+1}^0$, so that $\langle \bar{\chi}_a^n | \bar{\chi}_a^m \rangle = 0$. This rough criterion permits us to choose only the ψ_m^- with this symmetry for the 2×2 CI calculation.

The final CI wave functions are

$$\begin{aligned} \Psi_{nm}^+ &= \alpha_n \psi_n^+ + \alpha_m \psi_m^-, \\ \Psi_{nm}^- &= \alpha_n \psi_m^- - \alpha_m \psi_n^+, \end{aligned} \quad (50)$$

$$\begin{aligned} E_{nm}^\pm &= \frac{1}{2}(E_n + E_m) \pm \Gamma, \\ \Gamma &= [(H'_{nm})^2 + (\Delta E)^2]^{1/2}, \quad \Delta E = \frac{1}{2}(E_n - E_m), \end{aligned} \quad (51)$$

and

$$\alpha_n = \left(\frac{\Gamma + \Delta E}{2\Gamma} \right)^{1/2}, \quad \alpha_m = \left(\frac{\Gamma - \Delta E}{2\Gamma} \right)^{1/2}.$$

For small n , $H'_{nm} \ll \Delta E$ so that $2\alpha_n \alpha_m \ll 1$, while, as $n \rightarrow \infty$, H'_{nm} increases (because $\langle Q \rangle$ increases and the relative amplitudes of χ_a^n and χ_b^n become more equal) and so $2\alpha_n \alpha_m \rightarrow 1$; also, as γ increase, H'_{nm} increases and, for a given pair (n, m) , the CI should increase.

In Table II, we compare approximate scheme 2 wave functions with exact numerical results for several values of (Δ, v, g) . The CI is obtained by varying α_n until the best fit is obtained. Accuracy could be improved by mixing in additional basis functions, but this was judged not to be worthwhile.

The second example ($\Delta = 1.0$, $v/\sqrt{2} = 0.5$, and $g/\sqrt{2} = 0.3$) is in a region where scheme 2 is beginning to break down. The overlap of exact and approximate states (0.92) is reasonable but care must be taken in using the approximate wave function to predict observable properties which depend on off-diagonal matrix elements. For example, $\langle \chi_a^n | \chi_b^n \rangle = -0.14$ for the approximate calculation and -0.02 for the exact; this is due to the increasing importance of additional states as γ/v increases.

We have found the region of validity of scheme 2 to be approximately $\Delta > 0.5$, $v/\gamma > 1$, which is roughly the complement of the region of parameter space in which scheme 1 is valid ($\Delta < 0.5$, or $\Delta > 0.5$, $\gamma/v > 1$). For intermediate regions ($\Delta \sim 0.5$, $v/\gamma \sim 1$) both methods are problematic, although neither fails completely.

The Born-Oppenheimer separability can be evaluated

TABLE II. Comparison of approximate and exact eigenstates for scheme 2. The index p denotes the phonon number of the harmonic oscillator basis function.

p	Coefficients			
	a>		b>	
	Approx	Exact	Approx	Exact
(a) $\Delta = 1.0$, $v/\sqrt{2} = 0.5$, $\gamma/\sqrt{2} = 0.2$, $E_{\text{exact}} = 10.37$, $E_{\text{approx}} = 10.40$, $\psi_{\text{approx}} = c_+ \psi_n^+ + c_- \psi_m^-$, $n = 8$, $m = 14$, $c_+ = 0.89$, $c_- = 0.45$				
6	0.123	0.130	0.033	-0.001
7	0.064	0.095	0.248	0.264
8	0.596	0.637	-0.055	-0.142
9	-0.316	-0.164	0.306	0.363
10	-0.104	-0.148	-0.179	-0.086
11	0.142	0.114	-0.247	-0.273
12	0.034	0.054	0.110	0.010
13	-0.193	-0.140	0.211	0.196
14	-0.203	-0.105	0.236	0.283
$I_{\text{A.E.}} = 0.96$				
(b) $\Delta = 1.0$, $v/\sqrt{2} = 0.5$, $\gamma/\sqrt{2} = 0.3$, $E_{\text{exact}} = 10.368$, $E_{\text{approx}} = 10.545$, $\Psi = c_+ \psi_n^+ + c_- \psi_m^-$, $n = 8$, $m = 14$, $c_+ = 0.78$, $c_- = -0.63$				
6	-0.150	-0.168	-0.040	-0.013
7	-0.063	-0.197	-0.257	-0.260
8	-0.533	-0.579	0.086	0.124
9	0.386	0.158	-0.216	-0.266
10	0.173	0.272	0.172	0.085
11	-0.219	-0.144	0.124	0.147
12	-0.129	-0.177	-0.049	0.005
13	0.244	0.252	0.033	0.050
14	0.113	-0.077	-0.361	-0.345
$I_{\text{A.E.}} = 0.92$				

using the results of Appendix B and Appendix C. Defining

$$\begin{aligned} U_{mn} &= \langle \Psi_{mn} | A_a^* A_a - A_b^* A_b | \Psi_{mn} \rangle, \\ V_{mn} &= \langle \Psi_{mn} | A_a^* A_b + A_b^* A_a | \Psi_{mn} \rangle, \end{aligned} \quad (52)$$

and ignoring the small fluctuating terms, we have

$$B = (U_{mn}^2 + V_{mn}^2)^{1/2} \quad (53)$$

$$U_{mn} = \alpha_n^2 \left\{ \frac{\Delta}{[\Delta^2 + g_n^2(2n + 1)]^{1/2}} \right\} - \alpha_m^2 \left\{ \frac{\Delta}{[\Delta^2 + g_m^2(2m + 1)]^{1/2}} \right\}, \quad (54)$$

$$V_{nm} = k \left\{ 1 - \frac{\Delta}{[\Delta^2 + g_n^2(2n + 1)]^{1/2}} \right\} \left\{ 1 - \frac{\Delta}{[\Delta^2 + g_m^2(2m + 1)]^{1/2}} \right\}.$$

If we assume that $k \approx 1$ (which appears to be the case from numerical calculations; see Appendix C), then we have $V_{mn} \rightarrow 1$ as $n \rightarrow \infty$, so that $B \rightarrow 1$. This result is in sharp contrast to the identical dimer $\gamma = 0$, where $B \rightarrow 0$ as $n \rightarrow \infty$, and shows that the breaking of symmetry produces BO separable states in the limit of large phonon number.

III. DIMER WITH UNEQUAL ENERGY LEVELS

A. Transformation of the Hamiltonian

We consider a molecular dimer composed of two monomers 1 and 2. Each monomer has a ground state, a single excited state, and a single vibrational mode of frequency ω which is linearly coupled to the excited state via the exciton-phonon coupling parameter g .

The electronic energy of the excited state of monomer 1 is $+\epsilon$, while that of monomer 2 is $-\epsilon$ [we have taken the zero of electronic energy to be $\bar{E}_e - E_g$, where $\bar{E}_e = \frac{1}{2}(E_e^{(1)} + E_e^{(2)})$]; the monomers are electronically coupled by the exchange integral J which we shall take to be positive.

The second quantized Hamiltonian for this system is

$$H = \epsilon(A_1^\dagger A_1 - A_2^\dagger A_2) + J(A_1^\dagger A_2 + A_2^\dagger A_1) + B_1^\dagger B_1 + B_2^\dagger B_2 + gA_1^\dagger A_1(B_1 + B_1^\dagger) + gA_2^\dagger A_2(B_2 + B_2^\dagger), \quad (55)$$

where we have shifted the zero of energy by ω , and expressed all parameters in units of ω . We take g and $J > 0$. A_i^\dagger and A_i are creation and destruction operators for an electronic excitation on molecule i , respectively, and B_i^\dagger and B_i create and destroy a phonon on monomer i , respectively.

We now transform the phonon operators in the same manner as in paper I, setting

$$B_1 = \frac{1}{\sqrt{2}}(B_+ + B_-), \quad (56)$$

$$B_2 = \frac{1}{\sqrt{2}}(B_+ - B_-).$$

This permits decoupling of the B_+ vibration as in paper I; the resultant Hamiltonian is

$$H = \epsilon(A_1^\dagger A_1 - A_2^\dagger A_2) + J(A_1^\dagger A_2 + A_2^\dagger A_1) + B_+^\dagger B_+ + (g/\sqrt{2})(A_1^\dagger A_1 - A_2^\dagger A_2)(B_+ + B_+^\dagger). \quad (57)$$

If E_n is an eigenvalue of Eq. (57), the total energy [eigenvalue of Eq. (55)] will be given by $E_{n,m} = \epsilon_n + m - (g^2/2)$, where m is the number of quanta in the (+) vibrational mode.

B. Scheme 1

We first investigate the dimer in the region of parameter space where scheme 1 is valid. Then, we note that Eq. (57) is already in the required form (15), so no rotation of the electronic states is necessary. The basis solutions are then

$$\psi_n^1 = |1\rangle \phi_n^\epsilon, \quad E_n^1 = n + \epsilon - (g^2/2),$$

$$\psi_n^2 = |2\rangle \phi_n^{-\epsilon}, \quad E_n^2 = n - \epsilon - (g^2/2). \quad (58)$$

Thus, in the region where no CI is required, we have localized states. This clearly corresponds, as expected, to $\epsilon \gg J$, i.e., the diagonal energy separation is much larger than the exchange interaction. In this case the "dimer" behaves like two isolated molecules.

Now, suppose both ϵ , $J \ll 1$ (this corresponds to $\Delta \ll 1$ in Sec. II B); then

$$\psi_n^+ = c_1 \psi_n^1 + c_2 \psi_n^2,$$

$$\psi_n^- = c_2 \psi_n^1 - c_1 \psi_n^2. \quad (59)$$

We define the localization as

$$L = \langle \Psi | A_1^\dagger A_1 - A_2^\dagger A_2 | \Psi \rangle, \quad (60)$$

so

$$L_x^n = \pm (|c_1|^2 - |c_2|^2). \quad (61)$$

Now

$$H_{1n2n} = J \langle \phi_n^\epsilon | \phi_n^{-\epsilon} \rangle,$$

$$E_{1n2n} = 2\epsilon, \quad (62)$$

so

$$|c_1|^2 = (\lambda + \epsilon)/2\lambda,$$

$$|c_2|^2 = (\lambda - \epsilon)/2\lambda, \quad (63)$$

$$|L^n| = \epsilon/\lambda,$$

where $\lambda = (J^2 \langle \phi_n^\epsilon | \phi_n^{-\epsilon} \rangle^2 + \epsilon^2)^{1/2}$. For large $g(2n+1)^{1/2}$ we have³

$$\langle \phi_n^\epsilon | \phi_n^{-\epsilon} \rangle \approx \left[\frac{2}{\pi(2n+1)g^2} \right]^{1/2} \cos[(2n+1)^{1/2}g - (\pi/4)] \quad (64)$$

so, by substituting Eq. (64) into Eq. (63), we have an approximate analytical expression for the localization:

$$|L| \approx \epsilon \{ \epsilon^2 + J^2 \cos^2[(2n+1)^{1/2}g - (\pi/4)] \cdot [2/\pi(2n+1)g^2]^{-1/2} \}. \quad (65)$$

A similar expression would be obtained for the case where ψ_n^1 interacts with ψ_m^2 :

$$|L| = \frac{\frac{1}{2}(n-m) + \epsilon}{\{[(n-m) + \epsilon]^2 + J^2 \langle \phi_n^\epsilon | \phi_m^{-\epsilon} \rangle^2\}^{1/2}}. \quad (66)$$

In Fig. 1, we plot the absolute value of the localization versus eigenstate energy for several sets of parameters; in Figs. 1(a) and 1(b) the approximate curve is calculated using Eq. (63), while in Fig. 1(c), Eq. (66) is utilized. In Fig. 1(a) the CI matrix element is small enough, so that the localization undergoes no oscillations. In Figs. 1(b) and 1(c) oscillations occur; agreement is worst at low energy because the matrix element is sufficiently large so that other configurations than the one included in Eq. (59) are mixed. This defect would be more pronounced for larger J , reflecting a breakdown of the approximation scheme.

C. Localization for scheme 2

We now examine the dimer system for parameter values in which scheme 2 is the appropriate approximation. We first transform Eq. (57) to remove the ϵ term; this yields an equation of the form of Eq. (11) with

$$|a\rangle = c_1 |1\rangle + c_2 |2\rangle,$$

$$|b\rangle = c_2 |1\rangle - c_1 |2\rangle, \quad (67)$$

where

$$c_1 = \left(\frac{\epsilon + \lambda}{2\lambda} \right)^{1/2},$$

$$c_2 = \left(\frac{\lambda - \epsilon}{2\lambda} \right)^{1/2}, \quad \lambda = (J^2 + g^2)^{1/2}.$$

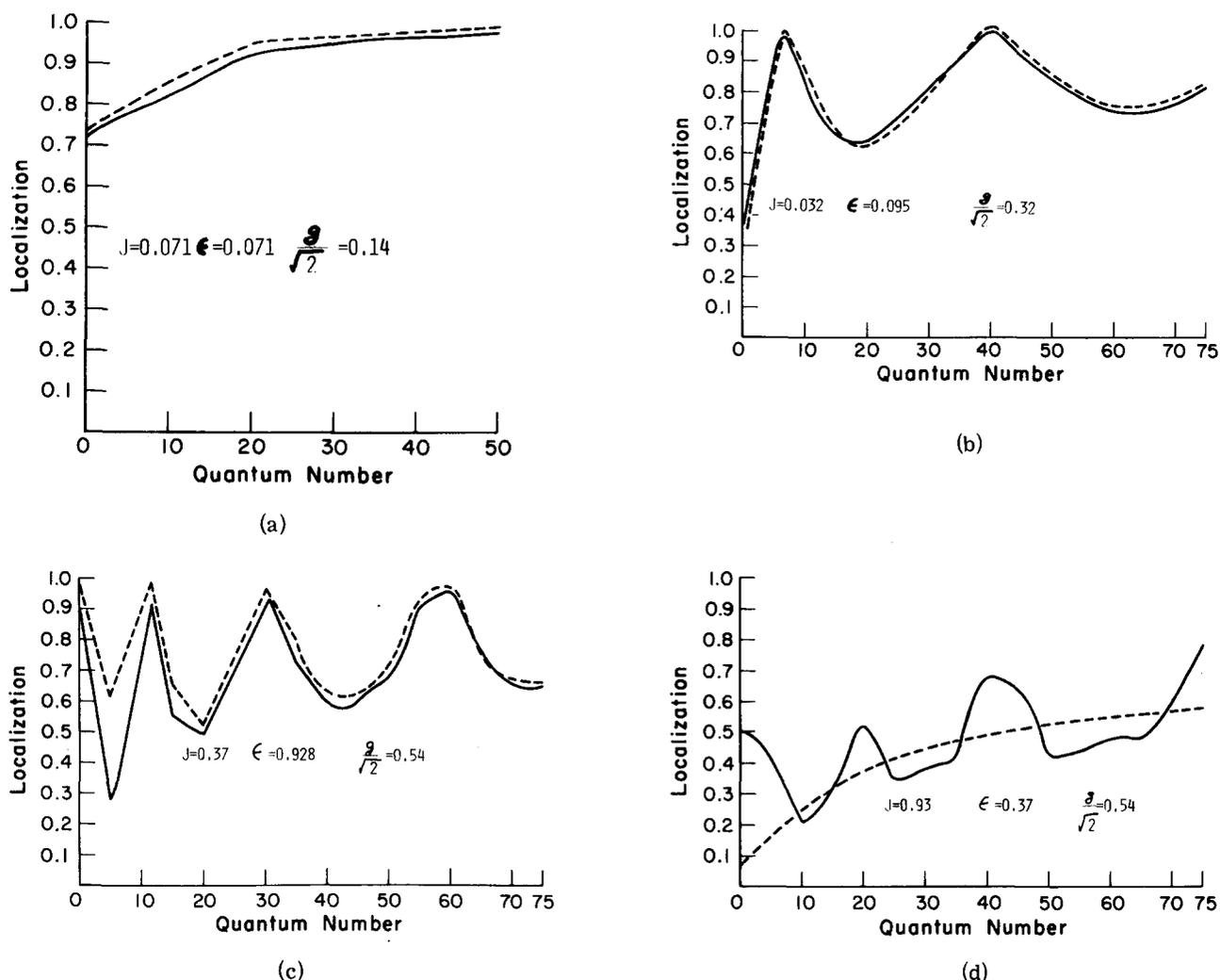


FIG. 1. Plots of localization versus eigenstate energy. In all cases the ordinate is the absolute value of the localization [defined in Eq. (60)], a dimensionless number. The abscissa is plotted as the index of the exact eigenstate (there are \sim two eigenstates per phonon energy, so a separation of one unit on the graph corresponds to $\sim \omega/2$ in energy.) Approximate localization is determined by finding the approximate state (or combination of states) which corresponds to the exact state and using the appropriate equation in the text for the localization.

The parameters in Eq. (11) take on the values

$$\begin{aligned} \Delta &= \lambda, \\ v/\sqrt{2} &= 2c_1c_2(g/\sqrt{2}), \\ \gamma/\sqrt{2} &= (c_1^2 - c_2^2)g/\sqrt{2}, \end{aligned} \quad (68)$$

and

$$(\gamma^2 + v^2) = g^2.$$

The localization can be expressed in terms of the integrals U_{nm} and V_{nm} as

$$L_{nm}^* = \frac{\epsilon}{\lambda} U_{nm} \pm \frac{J}{\lambda} V_{nm}, \quad (69)$$

where U_{nm} and V_{nm} are evaluated using Eq. (68) for Δ , V , and γ . For small n , both terms can be important, and $|L|$ may fluctuate considerably as a function of n . For large n , we expect $\langle U_{nm} \rangle \approx 0$, so that

$$|L_{nm}| \rightarrow (J/\lambda) V_{nm}. \quad (70)$$

Thus, the maximum value of L is limited to J/λ . Of

course, this expression is only valid for small ϵ (if $g > J$, for example, $\gamma > v$ and we are out of the region of validity of scheme 2).

In Fig. 1(d) we plot the absolute value of the localization versus eigenstate energy for a typical set of parameters. We approximate the average localization as

$$\begin{aligned} |L_{nm}| &= \frac{J}{\lambda} \left\{ 1 - \frac{\lambda}{\left[\lambda^2 + \frac{g^2}{2}(2n+1)^{1/2} \right]} \right\} \\ &\times \left\{ 1 - \frac{\lambda}{\left[\lambda^2 + \frac{g^2}{2}(2m+1)^{1/2} \right]} \right\}; \end{aligned} \quad (71)$$

we have neglected the U_{nm} term and used Eq. (C23) for V_{nm} with $\delta=0$, $k=1$.

The oscillations are either contained within $(\bar{\chi}_n | \bar{\chi}_m)$ or in the additional CI, and so cannot be predicted by Eq. (71). The average localization, however, does agree reasonably well with the exact results for high energy.

For low energy, $\alpha_n \alpha_m$ deviates significantly from 0.5 and the U_{nm} term becomes important.

D. Weak and strong coupling

We can now make a comparison of the effectiveness of the perturbation in driving the dimer into localized states for weak ($2J \ll 1$) and strong ($2J \gg 1$) coupling. We study localization as a function of the variable $\bar{\epsilon} = \epsilon/J$.

We will always be in scheme 1 for weak coupling; if $\epsilon < J$, $\Delta = (\epsilon^2 + J^2)^{1/2} < 0.5$, while if $\epsilon > J$, $\gamma > \nu$. For the first case, small $\bar{\epsilon}$, we have

$$|L|_{\text{weak}} = \frac{\bar{\epsilon}}{(\bar{\epsilon}^2 + \langle \phi_n^s | \phi_n^{-s} \rangle^2)^{1/2}}. \quad (72)$$

For strong coupling we will use scheme 2 for $\bar{\epsilon} < 1$; then, setting $\delta = 0$ in Eq. (C23), we have

$$|L|_{\text{strong}} = \frac{k}{(1 + \bar{\epsilon})^{1/2}} \left\{ 1 - \frac{1}{\left[1 + \bar{\epsilon}^2 + \left(\frac{g}{J} \right)^2 (2n + 1) \right]^{1/2}} \right\} \\ \times \left\{ 1 - \frac{1}{\left[1 + \bar{\epsilon}^2 + \left(\frac{g}{J} \right)^2 (2m + 1) \right]^{1/2}} \right\}. \quad (73)$$

It is apparent that there is an enormous difference in the effect of $\bar{\epsilon}$ in the two above cases. For weak coupling, for each n there is an $\bar{\epsilon}_0 < 1$ such that, for $\bar{\epsilon} > \bar{\epsilon}_0$, $|L_{\text{weak}}| \sim 1$. As $n \rightarrow \infty$, $\bar{\epsilon}_0 \rightarrow 0$. For strong coupling, on the other hand, the maximum value of L is limited, and increasing $\bar{\epsilon}$ to 1 has, in most cases, a minimal effect. Thus, for strong coupling, there is a persistence of delocalization which eventually is eliminated when $\bar{\epsilon} > 1$, so that we pass from scheme 2 to scheme 1.

For $\bar{\epsilon} > 1$, we are in scheme 1 for both weak and strong coupling, and the localization has the same functional form in both cases. This limit thus represents a dissolution of the weak/strong coupling distinction.

IV. CONCLUSIONS

In the present paper, we have constructed two schemes for approximating the energy levels and wave functions for a general two electronic state system coupled linearly to a vibrational mode. These two approaches are largely nonoverlapping in their range of validity and so allow the entire range of coupling to be considered. The agreement with exact numerical calculations is quite good, so that we are optimistic about applying these methods to the analysis of experimental spectra. Of course, in real systems, more than one vibrational mode has to be considered. In another publication, we will discuss a "mean-field" or Hartree-like theory for treating many vibrational modes.

The present schemes may be useful in treating other vibronic problems such as Jahn-Teller, pseudo-Jahn-Teller, or radiationless transition models. In these, there are often only two relevant electronic states and a small number of important vibrational modes, so that a suitable choice of zeroth order states may make the subsequent perturbation analyses easier.

APPENDIX A: DERIVATION OF APPROXIMATE HAMILTONIAN FOR STRONG COUPLING (SCHEME 2)

We will use the relation

$$Q \phi_n^s = (Q + s) \phi_n^s - s \phi_n^s \\ = \left(\frac{n}{2} \right)^{1/2} \phi_{n-1}^s + \left(\frac{n+1}{2} \right)^{1/2} \phi_{n+1}^s - s \phi_n^s. \quad (A1)$$

Substituting this into Eq. (33a) and integrating over ϕ_n^s yields

$$c_n [n + \Delta \frac{1}{2} s^2 - E - s(\gamma - s) + (\gamma - s)] \left[(n/2)^{1/2} c_{n-1} + \left(\frac{n+1}{2} \right) c_{n+1} \right] \\ = -v \left[(n/2)^{1/2} b_{n-1} + \left(\frac{n+1}{2} \right)^{1/2} b_{n+1} \right]. \quad (A2)$$

To obtain a useful equation for b_n , we multiply Eq. (33a) by $(\gamma + s)/v$ and add the result to Eq. (33b); integrating once again over ϕ_n^s gives

$$b_n (n - \Delta - E - \frac{1}{2} s^2) = - \left(\frac{\gamma + s}{v} \right) c_n (n + \Delta - E - \frac{1}{2} s^2) - (\gamma^2 + v^2 - s^2) v^{-1} \left[\left(\frac{n+1}{2} \right)^{1/2} c_{n+1} + \left(\frac{n}{2} \right)^{1/2} c_{n-1} - s c_n \right]. \quad (A3)$$

For the case of interest (strong coupling) we will have $n + \Delta - E \gg v^2$ as discussed in paper I; in addition, $|\gamma| < |v|$ by hypothesis (see Sec. III) and $|s| < |\gamma|$ (see below). We make the following approximations (shown to be self-consistent later):

$$\gamma_s \ll n + \Delta - E, \quad s^2 \ll n + \Delta - E < n - \Delta - E, \quad (\gamma^2 + v^2 - s^2) s \ll (\gamma + s)(n + \Delta - E).$$

Substituting these approximations into Eqs. (A2) and (A3), we find

$$c_n (n + \Delta - E) + (\gamma - s) \left[(n/2)^{1/2} c_n + \left(\frac{n+1}{2} \right)^{1/2} c_{n+1} \right] = -v \left[(n/2)^{1/2} b_{n-1} + \left(\frac{n+1}{2} \right)^{1/2} b_{n+1} \right] \quad (A4)$$

$$b_n (n - \Delta - E) = -(\gamma + s) v^{-1} c_n (n + \Delta - E) - (\gamma^2 + v^2 - s^2) v^{-1} \left[\left(\frac{n+1}{2} \right)^{1/2} c_{n+1} + \left(\frac{n}{2} \right)^{1/2} c_n \right]. \quad (A5)$$

Solving Eq. (A5) for b_n and substituting into Eq. (A4) gives

$$c_n (n + \Delta - E) + (\gamma - s) \left[\left(\frac{n+1}{2} \right)^{1/2} c_{n+1} + \left(\frac{n}{2} \right)^{1/2} c_{n-1} \right]$$

$$\begin{aligned}
&= (\gamma^2 + v^2 - s^2) \left\{ \frac{\left[\frac{n(n-1)}{4} \right]^{1/2} c_{n-2}}{n-1-\Delta-E} + \frac{(n/2)c_n}{n-1-\Delta-E} + \frac{c_n \left(\frac{n+1}{2} \right)}{n+1-\Delta-E} + \frac{c_{n+2} \left[\frac{(n+1)(n+2)}{4} \right]}{n+1-\Delta-E} \right\} \\
&+ (\gamma + s) \left[\frac{(n+1+\Delta-E)}{(n+1-\Delta-E)} \right] \left(\frac{n+1}{2} \right)^{1/2} c_{n+1} + \frac{(n-1+\Delta-E)}{(n-1-\Delta-E)} \left(\frac{n}{2} \right)^{1/2} c_{n-1} \\
&- s(\gamma + s) \left(\frac{n+\Delta-E}{n-\Delta-E} \right) c_n - \frac{s(\gamma^2 + v^2 - s^2)}{(n-\Delta-E)} \left[c_{n+1} \left(\frac{n+1}{2} \right)^{1/2} + c_{n-1} \left(\frac{n}{2} \right)^{1/2} \right]. \tag{A6}
\end{aligned}$$

For strong coupling, we assume that $n \pm 1 - \Delta - E \approx n - \Delta - E$, as in paper I. In addition, since s will be small, the last two terms on the right side of Eq. (A6) will be neglected. Also, we have that

$$s(\gamma + s)(n + \Delta - E) \ll (\gamma^2 + v^2 - s^2)(2n + 1), \quad s(\gamma^2 + v^2 - s^2) \ll n + \Delta - E,$$

because s is small; so that these two terms will be much smaller than the other terms multiplying c_n , c_{n+1} , and c_{n-1} on the rhs.

We arrive finally at the equation

$$\begin{aligned}
c_n &\left\{ [(n+\Delta-E)(n-\Delta-E) + \frac{1}{2}(2n+1)(\gamma^2 + v^2 - s^2)] + (\gamma - s) \left[c_{n+1} \left(\frac{n+1}{2} \right)^{1/2} + c_{n-1} \left(\frac{n}{2} \right)^{1/2} \right] \right\} \\
&= \frac{1}{2}(\gamma^2 + v^2 - s^2) \{ c_{n-2} [n(n-1)]^{1/2} + c_{n+2} [(n+1)(n+2)]^{1/2} \} + \frac{1}{\sqrt{2}}(\gamma + s)(n + \Delta - E) [c_{n+1}(n+1)^{1/2} + c_{n-1}(n)^{1/2}].
\end{aligned}$$

APPENDIX B: BORN-OPPENHEIMER SEPARABILITY OF VIBRONIC STATES

Suppose we have a wave function

$$\Psi = \chi_a |a\rangle + \chi_b |b\rangle. \tag{B1}$$

We want to know the basis states $|\alpha\rangle$ and $|\beta\rangle$ for which the operator

$$\hat{H}_{\alpha\beta} = A_\alpha^* A_\alpha - A_\beta^* A_\beta \tag{B2}$$

will have the maximum expectation value when averaged over Ψ . We also want to express this value in terms of χ_a and χ_b . We write

$$\begin{aligned}
|\alpha\rangle &= \cos\theta |a\rangle + \sin\theta |b\rangle, \\
|\beta\rangle &= \cos\theta |b\rangle - \sin\theta |a\rangle.
\end{aligned} \tag{B3}$$

Then

$$\begin{aligned}
H_{\alpha\beta} &= \langle \Psi | \hat{H}_{\alpha\beta} | \Psi \rangle \\
&= (\cos^2\theta - \sin^2\theta) U_{ab} + 2 \cos\theta \sin\theta V_{ab},
\end{aligned} \tag{B4}$$

where

$$\begin{aligned}
U_{ab} &= \langle \Psi | A_\alpha^* A_\alpha - A_\beta^* A_\beta | \Psi \rangle = \langle \chi_a | \chi_a \rangle - \langle \chi_b | \chi_b \rangle, \\
V_{ab} &= \langle \Psi | A_\alpha^* A_\beta + A_\beta^* A_\alpha | \Psi \rangle = 2 \langle \chi_a | \chi_b \rangle.
\end{aligned} \tag{B5}$$

To find the maximum value of $H_{\alpha\beta}$, which we will call B , we set

$$\partial H_{\alpha\beta} / \partial \theta = 0 \tag{B6}$$

and solve for θ .

This yields

$$\begin{aligned}
\theta &= \frac{1}{2} \arctan(V_{ab}/U_{ab}), \\
B &= \max(H_{\alpha\beta}) = (U_{ab}^2 + V_{ab}^2)^{1/2}.
\end{aligned} \tag{B7}$$

APPENDIX C: OVERLAP INTEGRALS OF CONFIGURATION INTERACTION WAVE FUNCTIONS IN SCHEME 2

In order to calculate the localization and Born-Oppenheimer separability of $\Psi = |a\rangle\chi_a + |b\rangle\chi_b$ (the electronic states $|a\rangle$ and $|b\rangle$ are those in Sec. II A), we need the integrals

$$\begin{aligned}
U &= \langle \chi_a | \chi_a \rangle - \langle \chi_b | \chi_b \rangle, \\
V &= 2 \langle \chi_a | \chi_b \rangle.
\end{aligned} \tag{C1}$$

We shall assume that Ψ is composed primarily of two approximately degenerate states ψ_n^+ and ψ_m^- as described in Eq. (51); the energies are

$$\begin{aligned}
E_n^+ &= n + \left[\Delta^2 + \frac{g_n^2}{2}(2n+1) \right]^{1/2}, \\
E_m^- &= m - \left[\Delta^2 + \frac{g_m^2}{2}(2n+1) \right]^{1/2},
\end{aligned} \tag{C2}$$

and

$$E_n^+ \sim E_m^- \equiv E.$$

For large n , $s \rightarrow 0$, and we can set $g_n, g_m \approx g$, where

$$g = (\gamma^2 + v^2)^{1/2}. \tag{C3}$$

We set

$$\begin{aligned}
\Psi_{nm} &= \alpha_n \psi_n^+ + \alpha_m \psi_m^-, \\
\psi_n^+ &= |a\rangle\chi_a^n + |b\rangle\chi_b^n, \\
\psi_m^- &= |a\rangle\chi_a^m + |b\rangle\chi_b^m.
\end{aligned} \tag{C4}$$

For definiteness we shall consider the CI state which, in the limit as $CI \rightarrow 0$ becomes ψ_n^+ , i.e., α_{n-1} as $H_{nm}' \rightarrow 0$. Then we have

$$U_{nm} = \alpha_n^2 U_n + \alpha_m^2 U_m + v(\langle \chi_a^n | \chi_a^m \rangle - \langle \chi_b^n | \chi_b^m \rangle), \quad (C5)$$

$$V_{nm} = \alpha_n \alpha_m (\langle \chi_a^n | \chi_b^m \rangle + \langle \chi_a^m | \chi_b^n \rangle),$$

where in deriving the last line we have used the symmetry relation

$$\langle \chi_a^n | \chi_b^m \rangle = \langle \chi_a^m | \chi_b^n \rangle = 0 \quad (C6)$$

and

$$U_k = \langle \chi_a^k | \chi_a^k \rangle - \langle \chi_b^k | \chi_b^k \rangle. \quad (C7)$$

U_k is evaluated by the identity

$$U_k = \partial E_k / \partial \Delta = \pm \left[\Delta + \frac{g^2}{2} (2k+1) \right]^{1/2}. \quad (C8)$$

The last term of U_{nm} would be zero if $s_n = s_m$; it is of the form

$$\sum_k \sum_l \bar{c}_{2k}^n \bar{c}_{2l+1}^m \langle \phi_{2k}^{s_n} | \phi_{2l+1}^{s_m} \rangle. \quad (C9)$$

We expect this sum to be small in amplitude because of the limiting effects of the overlap integrals (numerical calculations show this to be the case); it will also fluctuate as a function of n and m . We group its effect in this analysis with other small, fluctuating effects (mixing in of states other than ψ_n^+ and ψ_m^- , for example) in a function η_{nm} :

$$U_{nm} = \alpha_n^2 \left[\Delta^2 + \frac{g^2}{2} (2n+1) \right]^{1/2} - \alpha_m^2 \left[\Delta^2 + \frac{g^2}{2} (2m+1) \right]^{1/2} + \eta. \quad (C10)$$

Thus, $\lim_{n \rightarrow \infty} U_{nm} = \eta$. When $\Delta \gg (g^2/2)(2n+1)$, there is little CI (see Sec. II C) and we have

$$U_{nm} \sim \left[\Delta^2 + \frac{g^2}{2} (2n+1) \right]^{1/2}. \quad (C11)$$

We now approximate V_{nm} in an analogous manner. First, we show that

$$\langle \chi_a^n | \chi_b^m \rangle \approx \langle \chi_a^m | \chi_b^n \rangle. \quad (C12)$$

The functions χ_a^n and χ_b^n satisfy the equations

$$(h + s_n Q - E_n + \Delta) \chi_a^n = -g(Q + s_n) \chi_b^n, \quad (C13a)$$

while χ_a^m and χ_b^m satisfy

$$(h + s_m Q - E_m + \Delta) \chi_a^m = -g(Q + s_m) \chi_b^m. \quad (C13b)$$

We multiply Eq. (C13a) by χ_b^m , Eq. (C13b) by χ_a^n , and integrate:

$$\begin{aligned} (\Delta - E_n) \langle \chi_a^n | \chi_b^m \rangle + \langle \chi_b^m | h + s_n Q | \chi_a^n \rangle \\ = -g \langle \chi_b^m | Q | \chi_a^n \rangle - g s_n \langle \chi_b^m | \chi_b^n \rangle, \\ (\Delta - E_m) \langle \chi_a^m | \chi_b^n \rangle + \langle \chi_a^n | h + s_m Q | \chi_b^m \rangle \\ = -g \langle \chi_a^n | Q | \chi_b^m \rangle - g s_m \langle \chi_a^n | \chi_b^n \rangle; \end{aligned} \quad (C14)$$

as $s \rightarrow 0$ for large n , we can neglect s_n and s_m in each equation; we also set $E_n \sim E_m = E$. Then, equating the two lhs yields

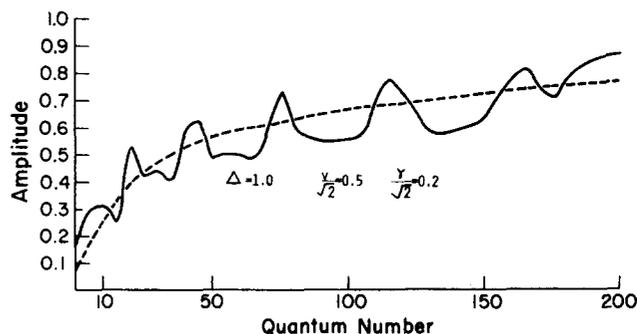


FIG. 2. Plot of V_{nm} versus eigenstate energy. The abscissa is defined as in Fig. 1.

$$(\Delta - E) (\langle \chi_a^n | \chi_b^m \rangle - \langle \chi_a^m | \chi_b^n \rangle) = \langle \chi_a^n | h | \chi_b^m \rangle - \langle \chi_a^m | h | \chi_b^n \rangle. \quad (C15)$$

We estimate the terms in the rhs by

$$\begin{aligned} \langle \chi_a^n | h | \chi_b^m \rangle &\approx \langle \chi_a^n | \chi_b^m \rangle \frac{1}{2} \left(\frac{\langle \chi_a^n | h | \chi_a^n \rangle}{\langle \chi_a^n | \chi_a^n \rangle} + \frac{\langle \chi_b^m | h | \chi_b^m \rangle}{\langle \chi_b^m | \chi_b^m \rangle} \right), \\ \langle \chi_a^m | h | \chi_b^n \rangle &\approx \langle \chi_a^m | \chi_b^n \rangle \frac{1}{2} \left(\frac{\langle \chi_a^m | h | \chi_a^m \rangle}{\langle \chi_a^m | \chi_a^m \rangle} + \frac{\langle \chi_b^n | h | \chi_b^n \rangle}{\langle \chi_b^n | \chi_b^n \rangle} \right). \end{aligned} \quad (C16)$$

Terms like $\langle \chi_a^n | h | \chi_a^n \rangle$ are found by multiplying Eq. (C13a) by χ_a^n and integrating:

$$\frac{\langle \chi_a^n | h | \chi_a^n \rangle}{\langle \chi_a^n | \chi_a^n \rangle} = (E - \Delta) - \frac{g(\partial E / \partial g)}{\langle \chi_a^n | \chi_a^n \rangle}. \quad (C17)$$

This permits evaluation of Eq. (C16). In the large n limit [$(g^2/2)(2n+1) \gg \Delta$] we set $E_n \approx n + g\sqrt{n}$, $E_m \approx m - g\sqrt{m}$, and

$$\langle \chi_a^n | \chi_a^n \rangle \approx \frac{1}{2} (1 + \Delta / g\sqrt{n}),$$

resulting in

$$\langle \chi_a^n | h | \chi_b^m \rangle \approx (n + g\sqrt{n}) \langle \chi_a^n | \chi_b^m \rangle, \quad (C18)$$

$$\langle \chi_a^m | h | \chi_b^n \rangle \approx (m + g\sqrt{m}) \langle \chi_a^m | \chi_b^n \rangle.$$

Then

$$\langle \chi_a^n | \chi_b^m \rangle - \langle \chi_a^m | \chi_b^n \rangle \approx \frac{g\sqrt{n} - g\sqrt{m}}{\Delta}. \quad (C19)$$

Using the relation $n - m \sim 2g\sqrt{n}$ yields

$$\langle \chi_a^n | \chi_b^m \rangle - \langle \chi_a^m | \chi_b^n \rangle \approx \frac{g}{\Delta\sqrt{n}}, \quad (C20)$$

which is very small in this limit. We now have

$$V_{nm} = 8\alpha_n \alpha_m \langle \chi_b^n | \chi_a^m \rangle. \quad (C21)$$

Now, we define normalized $\hat{\chi}_b^n$ and $\hat{\chi}_a^m$, so that

$$\begin{aligned} V_{nm} &= 8\alpha_n \alpha_m \langle \hat{\chi}_b^n | \hat{\chi}_a^m \rangle \langle \chi_b^n | \chi_a^m \rangle \langle \chi_a^m | \chi_a^m \rangle \\ &= 2\alpha_n \alpha_m \langle \hat{\chi}_b^n | \hat{\chi}_a^m \rangle \left\{ 1 - \frac{\Delta^2}{\left[\Delta^2 + \frac{g^2}{2} (2n+1) \right]^{1/2}} \right\} \\ &\quad \times \left\{ 1 - \frac{\Delta^2}{\left[\Delta^2 + \frac{g^2}{2} (2m+1) \right]^{1/2}} \right\}. \end{aligned} \quad (C22)$$

For large n we expect $\alpha_n \alpha_m \approx \frac{1}{2}$, so we write V_{nm} as

$$V_{nm} = k \left\{ 1 - \frac{\Delta^2}{[\Delta^2 + g^2(2n+1)]^{1/2}} \right\} \\ \times \left\{ 1 - \frac{\Delta^2}{[\Delta^2 + g^2(2m+1)]^{1/2}} \right\} + \delta, \quad (\text{C23})$$

where k is the average value of $\langle \hat{\chi}_b^n | \hat{\chi}_a^m \rangle$ in the large n limit and δ is a small, fluctuating function of n and m which incorporates variation in $\langle \hat{\chi}_b^n | \hat{\chi}_a^m \rangle$, $\alpha_n \alpha_m$, and mixing in of other basis states.

In Fig. 2, we plot $|V_{nm}|$ versus eigenstate energy for a typical parameter point in scheme 2. The approximate curve is calculated as $V_{nm} - \delta$ from Eq. (C23) with $k=1$; agreement is excellent for the average value, although fluctuations are not insignificant. For larger γ , fluctuations become more important because mixing of other basis states increases; this corresponds to the breakdown of scheme 2. The success in setting $k=1$ indicates that $\hat{\chi}_b^n \sim \hat{\chi}_a^m$ for large n ; this is not surprising

when one considers the identical dimer equations for nearly degenerate states.

¹R. Friesner and R. Silbey, *J. Chem. Phys.* **74**, 1166 (1981).

²Similar models have been treated by A. Witkowski and W. Moffitt, *J. Chem. Phys.* **33**, 872 (1960); R. L. Fulton and M. Gouterman, *J. Chem. Phys.* **33**, 872 (1961); R. Merrifield, *Radiat. Res.* **20**, 154 (1963); R. L. Fulton and M. Gouterman, *J. Chem. Phys.* **41**, 2280 (1964); A. Suna, *Phys. Status Solidi B* **45**, 591 (1971); S. Rackovsky and R. Silbey, *Mol. Phys.* **25**, 611 (1973); I. Abram and R. Silbey, *J. Chem. Phys.* **63**, 2317 (1975); J. W. Allen and R. Silbey, *Chem. Phys.* **43**, 341 (1979).

³This formula can be obtained by using the expression for the overlap of displaced harmonic oscillators in P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953); and subsequently using the approximations for the confluent hypergeometric function in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (National Bureau of Standards, Washington, D.C., 1964).