

Basis set methods for describing the quantum mechanics of a "system" interacting with a harmonic bath

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The case of a system (e.g., a one-dimensional reaction coordinate) coupled to a "bath" of many harmonic oscillators is treated by quantum mechanical basis set methods. By choosing the basis set for the bath to incorporate the coupling explicitly, it is shown how the bath can then be eliminated to obtain an effective Hamiltonian matrix for only the system. Numerical calculations are carried out which show that, even in the zeroth version of the approach, the effect on the system (e.g., the tunneling splitting in a double-well potential) of coupling to the bath is described well, even when the effect is extremely large.

I. INTRODUCTION

The model of a system, consisting of a few interesting degrees of freedom, coupled to a bath of many (less interesting) degrees of freedom, is ubiquitous in chemistry and physics. It is obviously a common situation in statistical mechanics, where the bath may consist of 10^{23} degrees of freedom, but it is also a very relevant and useful point of view in the field of reaction dynamics where the bath may consist of relatively few (e.g., 2–10) degrees of freedom, though still too many to be able to treat the complete system plus bath without approximation.

The specific system–bath model that has concerned this group in recent years arises from the reaction path (or reaction surface) Hamiltonian¹ description of a reactive process in a polyatomic molecular system. The reaction coordinate (or coordinates) constitute the system, and the remaining degrees of freedom, which are locally harmonic vibrations perpendicular to the reaction path (or reaction surface), are the bath. In this paper, though, we consider the simpler generic system–bath model that has been considered by many workers, which is characterized by the Hamiltonian

$$H(p_s, s, \mathbf{P}, \mathbf{Q}) = \frac{p_s^2}{2m} + V_0(s) + \sum_k \left\{ \frac{P_k^2}{2m} + \frac{1}{2} m \omega_k^2 Q_k^2 \right\} - \sum_k Q_k f_k(s). \quad (1.1)$$

The system here is the reaction coordinate s . The potential $V_0(s)$ has the topology of the chemical process being described; an intramolecular H-atom transfer process, for example, would be characterized by a double-well potential function. The bath consists of harmonic oscillators, which are linearly coupled to the system.

The universal strategy for dealing with a system–bath situation is to find some way, exact or approximate, to eliminate the bath and then to deal accurately with the system. Feynman path integral² methodology is one very attractive way for doing this that our group,³ and many others,⁴ have used. The most powerful feature of this approach is that the path integral over the bath degrees of freedom can be performed analytically, so that one is left with a path integral for only one degree of freedom which must be performed nu-

merically. For the case of real time dynamics (i.e., the propagator $e^{-iHt/\hbar}$), however, numerical (i.e., Monte Carlo) path integration is poorly behaved, even for only one degree of freedom. Although some progress has been made in this regard,^{3,5–7} the prognosis is not very encouraging. (For evaluating the Boltzmann operator $e^{-\beta H}$, on the other hand, Monte Carlo path integration^{5–8} is quite feasible and very attractive.)

If one were dealing only with the quantum mechanics of a one (or two) degree of freedom system, then much simpler than evaluating a path integral would be to diagonalize a matrix representation of the Hamiltonian in a basis set. This has been seen,⁹ for example, in evaluating quantum mechanical reactive flux correlation functions. This is because, as a rule of thumb, basis sets for molecular problems typically require 10–20 basis functions per degree of freedom; it is thus relatively trivial to deal with one or two degrees of freedom by straightforward matrix diagonalization, but not so for more than three degrees of freedom.

The best of all possible strategies, therefore, would be to use the path integral methodology to eliminate bath degrees of freedom, and then to solve the quantum mechanics of the low-dimensional system by basis set methods. Unfortunately, this seems not to be possible; once the bath modes have been dealt with by path integration, the quantum mechanics for the system does not correspond to a local Schrödinger equation, so that one is forced to deal with it also by path integral methods.

The purpose of this paper is to describe progress we have made using basis set methods to deal with system–bath problems. As with the path integral approach, we first take account of the bath degrees of freedom and eliminate them from the problem, and then deal accurately with the system. Unlike the path integral approach, though, these basis set methods are unable to incorporate the effects of the bath *exactly*. How well they are able to do so must thus be tested, and we consider some analytic and numerical examples in the paper. The results are very encouraging that relatively simple basis sets can account for the effect of the bath on the system quite accurately. Once the bath degrees of freedom have been eliminated, the quantum mechanics for the system is dealt with simply by diagonalizing a Hamiltonian matrix

whose dimension is only that of the basis set for the system degrees of freedom (i.e., a small matrix).

In concluding this Introduction, we note somewhat ironically that at the practical level quantum mechanics often seem to degenerate to the question of what is a good basis set. This seems to have long been the case in quantum chemistry (i.e., electronic structure) and will perhaps be the situation also in quantum descriptions of chemical dynamics. In this regard we note the recent interesting work by Hamilton and Light¹⁰ on basis sets for molecular vibrational problems.

II. LINEARLY SHIFTED OSCILLATOR BASIS

The Hamiltonian under consideration is that in Eq. (1.1). To motivate the choice of basis set below, consider first a self-consistent field (SCF) approximation to the wave function,

$$\psi(s, \mathbf{Q}) = \chi(s) \prod_k u_k(Q_k). \quad (2.1)$$

Taking the diagonal matrix element of the Hamiltonian with respect to $\chi(s)$ gives the following effective Hamiltonian for the Q degrees of freedom:

$$H_{\mathbf{Q}} \equiv \int ds \chi(s) H \chi(s) \\ = \text{const} + \sum_k \left\{ \frac{P_k^2}{2m} + \frac{1}{2} m \omega_k^2 Q_k^2 - \langle \chi | f_k | \chi \rangle Q_k \right\}. \quad (2.2)$$

Equation (2.2) is recognized to be the Hamiltonian for a set

of *uncoupled*, linearly displaced harmonic oscillators, the eigenfunctions of which are

$$\prod_k \phi_{n_k}(Q_k - \lambda_k)$$

with

$$\lambda_k = \langle \chi | f_k | \chi \rangle / m \omega_k^2, \quad (2.3)$$

where ϕ_{n_k} is the standard harmonic oscillator eigenfunction with frequency ω_k and vibrational quantum number n_k .

We are not interested at the moment in making an SCF approximation, but the above discussion suggests the following basis set for the complete system-bath Hamiltonian,

$$\psi_{in}(s, \mathbf{Q}) \equiv \langle s, \mathbf{Q} | i, \mathbf{n} \rangle \\ = \chi_i(s) \prod_k \phi_{n_k}(Q_k - \lambda_k^i), \quad (2.4a)$$

where

$$\lambda_k^i = \langle \chi_i | f_k | \chi_i \rangle / m \omega_k^2. \quad (2.4b)$$

Using the shifted oscillator basis functions in Eq. (2.4) takes some account of the coupling directly in the basis set. The amount of the shift for the k th oscillator, λ_k^i , is proportional to the expectation value of the force $f_k(s)$ with respect to basis function $\chi_i(s)$ and is thus different for different values of i . The basis $\{\chi_i(s)\}$ for the system is unspecified at present.

It is straightforward to construct the matrix representation of the Hamiltonian (1.1) in the basis (2.4), and one obtains

$$H_{i'n', in} = F_{i'n', in} \left\{ \langle \chi_{i'} | H_s | \chi_i \rangle + \sum_k \langle \chi_{i'} | \chi_i \rangle \left[\left(n_k + \frac{1}{2} \right) \hbar \omega_k + \frac{m \omega_k^2}{2} \lambda_k^{i'} \lambda_k^i \right] \right. \\ \left. - \sum_k \langle \chi_{i'} | f_k | \chi_i \rangle \frac{\lambda_k^{i'} + \lambda_k^i}{2} + \sum_k \frac{\hbar}{2m \omega_k} [\langle \chi_{i'} | \chi_i \rangle m \omega_k^2 \lambda_k^i - \langle \chi_{i'} | f_k | \chi_i \rangle] \right. \\ \left. \times \left[\sqrt{n_k} \frac{\langle \phi_{n_k-1}(Q_k - \lambda_k^{i'}) | \phi_{n_k}(Q_k - \lambda_k^i) \rangle}{\langle \phi_{n_k}(Q_k - \lambda_k^{i'}) | \phi_{n_k}(Q_k - \lambda_k^i) \rangle} + \sqrt{n_k} \frac{\langle \phi_{n_k}(Q_k - \lambda_k^{i'}) | \phi_{n_k-1}(Q_k - \lambda_k^i) \rangle}{\langle \phi_{n_k}(Q_k - \lambda_k^{i'}) | \phi_{n_k}(Q_k - \lambda_k^i) \rangle} \right] \right\}, \quad (2.5)$$

where

$$H_s = \frac{p_s^2}{2m} + V_0(s),$$

and F is the Franck-Condon factor between oscillator basis functions,

$$F_{i'n', in} = \prod_k \int dQ_k \phi_{n_k'}(Q_k - \lambda_k^{i'}) \phi_{n_k}(Q_k - \lambda_k^i). \quad (2.6)$$

Were it necessary to diagonalize this entire matrix, then nothing has been accomplished. As a zeroth order approximation, therefore, we choose the part of the Hamiltonian matrix that is diagonal in the bath quantum numbers \mathbf{n} ; i.e.,

$$H_{i'n', in}^{(0)} = \delta_{i'n', in} H_{i', i}^n, \quad (2.7a)$$

where $H_{i', i}^n \equiv H_{i'n', in}$. From Eq. (2.5) one sees that this zeroth order *effective system Hamiltonian* (ESH) is

$$H_{i', i}^n = F_{i', i}^n \left\{ \langle \chi_{i'} | H_s | \chi_i \rangle + \sum_k \left[\langle \chi_{i'} | \chi_i \rangle \hbar \omega_k \left(n_k + \frac{1}{2} \right) \right. \right. \\ \left. \left. + \langle \chi_{i'} | \chi_i \rangle \frac{m \omega_k^2}{2} \lambda_k^{i'} \lambda_k^i - \frac{1}{2} (\lambda_k^{i'} + \lambda_k^i) \right. \right. \\ \left. \left. \times \langle \chi_{i'} | f_k | \chi_i \rangle \right] \right\}, \quad (2.7b)$$

where

$$F_{i', i}^n \equiv F_{i'n', in}.$$

We will discuss later how the off-diagonal matrix elements in the bath can be included perturbatively to obtain an ESH to higher order, but the present discussion will deal with the zeroth approximation, Eq. (2.7).

By neglecting off-diagonal matrix elements in the bath quantum numbers, the only remaining step is to diagonalize

the ESH, Eq. (2.7), whose dimension is the number of $\{\chi_i\}$ basis functions. It should be emphasized, though, that the effect of the coupling between system and bath has *not* been neglected by this approximation because the coupling functions $\{f_k(s)\}$ enter via the quantities $\lambda_k^i \propto \langle \chi_i | f_k | \chi_i \rangle$; these parameters enter the ESH most importantly via the Franck-Condon factors in Eq. (2.7). For the ground state of the bath, $\mathbf{n} = \mathbf{0}$, for example, the Franck-Condon factor is

$$F_{i,i}^0 = \exp \left[- \sum_k \frac{m\omega_k}{4\hbar} (\lambda_k^i - \lambda_k^i)^2 \right] \quad (2.8)$$

which shows that the coupling functions $f_k(s)$ enter the ESH nonlinearly.

Another obvious, but important feature of the ESH of Eq. (2.7) is that a linear transformation of the basis $\{\chi_i\}$,

$$\chi_i \rightarrow \sum_j \chi_j U_{j,i}, \quad (2.9a)$$

does *not* lead to a unitary transformation of the Hamiltonian matrix; i.e., with Eq. (2.9a) one does *not* have

$$H_{i,i}^0 \rightarrow \sum_{j,j'} U_{i,j}^\dagger H_{j,j'}^0 U_{j',i}. \quad (2.9b)$$

This is because the ESH involves the basis functions $\{\chi_i\}$, via the parameters λ_k^i [Eq. (2.4b)], in a nonlinear fashion. The eigenvalues of the ESH are thus not invariant to a linear transformation of the $\{\chi_i\}$ basis, and this raises the question of which kind of basis $\{\chi_i\}$ gives the best approximation to the true eigenvalues of the complete system-bath Hamiltonian.

It is our intuitive feeling that the shifted oscillator basis of Eq. (2.4) will do the best job of describing the effect of the bath on the zeroth order effective system Hamiltonian, Eq. (2.8), if the $\{\chi_i\}$ basis is chosen to be one that is *localized* in coordinate space. The floating Gaussian basis,

$$\chi_i(s) = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp \left[- \frac{\alpha}{2} (s - s_i)^2 \right] \quad (2.10)$$

over some grid of $\{s_i\}$ values, as used recently by Hamilton and Light¹⁰ is an example of what we mean by a localized basis. In contrast, the eigenfunctions of the potential $V_0(s)$, which one might have guessed to be the best $\{\chi_i(s)\}$ basis, will typically be delocalized, and in our view the shifted oscillator basis then does not do as good a job of describing the effect of the bath in the zeroth order ESH.

To illustrate the validity of this point of view we consider the two-state approximation for a symmetric double well potential $V_0(s)$; cf. Fig. 1. With the specific choice

$$f_k(s) = c_k s, \quad (2.11)$$

this becomes the model considered by Harris and Silbey,¹¹ and a number of others.⁴ The phenomenon to be described is the effect of the coupling, Eq. (2.11), on the tunneling splitting of the two lowest vibration levels. In the two-state approximation, and with the zeroth order ESH of Eq. (2.8) (with $\mathbf{n} = \mathbf{0}$), this splitting is given by the usual expression

$$\Delta E = [(H_{22}^0 - H_{11}^0)^2 + 4(H_{12}^0)^2]^{1/2}. \quad (2.12)$$

With the localized basis, Eq. (2.10) with $\chi_1(s)$ located at $s_1 = -a$ and $\chi_2(s)$ at $s_2 = +a$, it is quite straightforward to show that Eq. (2.12) gives

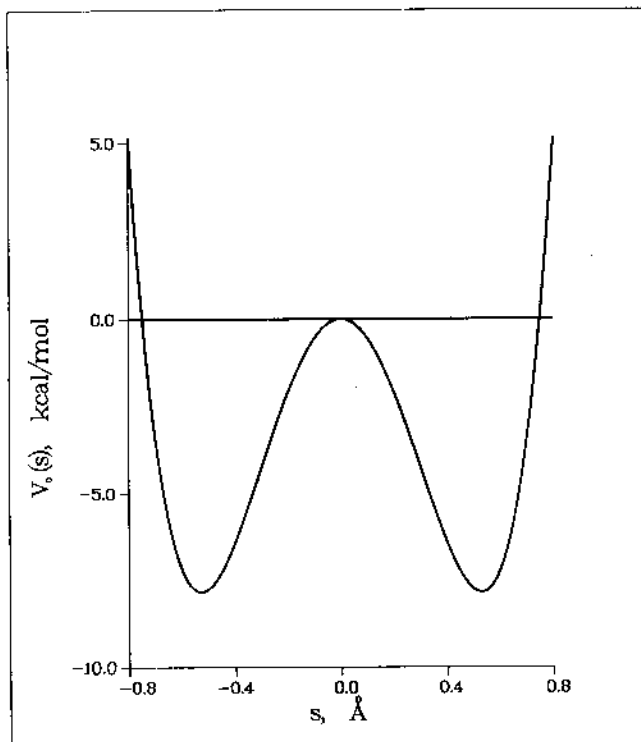


FIG. 1. The double well potential $V_0(s)$.

$$\Delta E = \Delta E_0 F_{1,2}^0, \quad (2.13)$$

where $\Delta E_0 = 2\langle \chi_1 | H_s | \chi_2 \rangle$ is the splitting that would result if there were no coupling to the bath ($c_k = 0$), the Franck-Condon factor is

$$F_{1,2}^0 = \exp \left[- a^2 \sum_k \frac{c_k^2}{\hbar m \omega_k^3} \right], \quad (2.14)$$

and nonorthogonality has been neglected. This is essentially the correct result, as obtained by other workers^{4,11}; the Franck-Condon factor "renormalizes" the tunneling integral.

If, on the other hand, one chooses the two-state basis to be the delocalized functions $\chi_g(s)$ and $\chi_u(s)$ [which are better approximations to the eigenfunctions of the potential $V_0(s)$],

$$\chi_g(s) = \frac{\chi_1(s) + \chi_2(s)}{\sqrt{2}}, \quad (2.15a)$$

$$\chi_u(s) = \frac{\chi_1(s) - \chi_2(s)}{\sqrt{2}}, \quad (2.15b)$$

then one can easily show that Eq. (2.14) gives

$$\Delta E = \Delta E_0; \quad (2.16)$$

i.e., in this case the zeroth order ESH shows no effect of the coupling on the tunneling splitting, which is incorrect.

This example illustrates very dramatically that the eigenvalues of the zeroth order effective system Hamiltonian, Eq. (2.8), are not invariant to a linear transformation of the $\{\chi_i\}$ basis, and furthermore that the effect of coupling to the bath is best described by the zeroth order ESH if the

$\{\chi_i\}$ basis is chosen to be localized. Thus, one should *not* choose the basis $\{\chi_i\}$ to try to diagonalize the potential $V_0(s)$, for the zeroth order ESH then does not do a good job of incorporating the effect of coupling to the bath. By choosing a localized basis the effective system Hamiltonian matrix H_{ii}^n is very nondiagonal, but the effect of coupling to the bath is described well. One then diagonalizes H_{ii}^n .

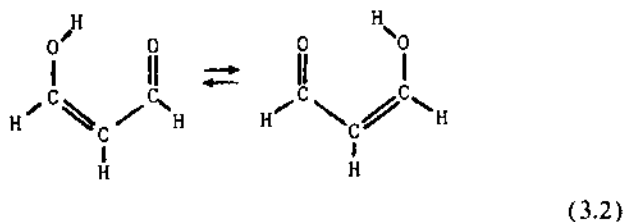
The situation is somewhat reminiscent of the path integral methodology.²⁻⁴ Here one makes progress by doing the path integral over the harmonic bath first, and then afterwards solving the quantum mechanics (i.e., doing the path integral) for the system degree of freedom. The analogy with the present basis set methodology is that one does not choose the basis $\{\chi_i\}$ to try to diagonalize the s degree of freedom first, but rather chooses it so that when $n \neq n'$ matrix elements are neglected the effect of coupling to the bath is described well by the zeroth order ESH. With this choice of the $\{\chi_i\}$ basis, the effective system Hamiltonian matrix H_{ii}^n is then diagonalized.

III. APPLICATION OF THE SHIFTED OSCILLATOR BASIS: A NUMERICAL EXAMPLE

To test the above ideas more fully, we have carried out numerical calculations for the model discussed in Sec. II, i.e., tunneling splitting in a symmetric double well potential. The specific form of the potential is

$$V_0(s) = -\frac{1}{2}a_0 s^2 + \frac{1}{4}c_0 s^4, \quad (3.1)$$

with the constants chosen so that the barrier height is 7.8 kcal/mol and the minima are located at $s = \pm 0.53 \text{ \AA}$; the mass is chosen to be that of a hydrogen atom. These values correspond roughly to the double-well potential for H-atom transfer in malonaldehyde:



that we have treated earlier by other means.¹²

We considered two types of coupling: (i) Linear coupling, i.e., $f_k(s) = c_k s$, which breaks the even symmetry of the double-well potential (one may think of such a coupling as applying in the case of malonaldehyde for a C–O stretch), and (ii) quadratic coupling, i.e., $f_k(s) = c_k s^2$, which preserves the symmetry. (The O–O wag in malonaldehyde is an example of this type of mode.)

As the coupling is turned on, the two wells move away from one another and their depth increases, i.e., the height of the barrier increases. As a consequence, the tunneling splitting drops off very rapidly as a function of the coupling strength. Furthermore, the potential shows a singularity (i.e., an infinitely deep well) above some value of the coupling constant in the case of the quadratic coupling, and therefore becomes unphysical. For these reasons, we have incorporated the term

$$\sum_k \frac{[f_k(s)]^2}{2m\omega_k^2} \quad (3.3)$$

in the potential.¹³ The addition of this term guarantees that the height of the barrier remains constant with increasing coupling constant. The only effect of the coupling is then to change the shape of the double well, i.e., to shift the location of the minima. Contour plots of the double well potential surface are shown in Figs. 2(a), 2(b), and 2(c) for the cases of no coupling, linear coupling, and quadratic coupling, respectively.

Only one oscillator is used for these calculations, so in addition to diagonalizing the zeroth order effective system Hamiltonian, Eq. (2.8), it is possible to diagonalize the complete system–bath Hamiltonian, Eq. (2.5), to obtain the exact result. To illustrate the applicability of the method, we considered two extreme cases: a fast ($\omega \sim 3000 \text{ cm}^{-1}$) and a slow ($\omega \sim 300 \text{ cm}^{-1}$) bath.

The case of the fast harmonic bath is very easy to deal with, as one would expect: The potential along the Q coordinate is narrow and very steep and the one-dimensional eigenvalues lie far apart from one another. The ESH with $n = 0$ would then be very efficient in describing the lowest doublet of the double well, and indeed this is the case. The exact result is already obtained by including the $n = 1$ excited state of the Q oscillator. Figures 3(a) and 3(b) show the tunneling splitting, referenced to the value with no coupling, as a function of the coupling constant c . The linearity of the curves in Fig. 3(a) (linear coupling) is an illustration of the approximate result given by Eq. (2.14), and the decrease of the splitting is a consequence of the increase (with respect to the uncoupled case) in the distance between the two minima. The slight increase of the tunneling splitting in Fig. 3(b) is a result of the higher curvature of the wells, which shifts the eigenvalues higher up with respect to the barrier.

The case of the low frequency bath, however, is considerably more challenging because the Q eigenstates are now closely packed and interact strongly. As many as five excited states were required for the tunneling splittings to converge to two significant figures at large couplings. The damping of the splitting is much greater here, since a much larger Q amplitude is involved with significant probability within the broader harmonic potential. The results from the ESH with $n = 0$ are not as good as in the case of fast Q motion. They can be optimized by varying the width of the Gaussians, a nonlinear parameter. The optimum width is larger here than in the high frequency case, as expected intuitively.

The optimized zeroth order version of this calculation is correct to within a factor of 4, even when the coupling is so strong as to have altered the splitting by two orders of magnitude [cf. Fig. 4(a)]. This is quite encouraging, particularly so when one notes that if the zeroth order Hamiltonian, Eq. (2.7), were used without the oscillator basis being shifted, the splitting would be independent of the coupling. Thus, the shifted oscillator basis, even at the zeroth order level, does a reasonably good job of describing the effect of coupling of the bath on the system.

Furthermore, it is relatively simple to go beyond the zeroth level of the theory and include off-diagonal coupling in the ESH, without much more computational effort. The

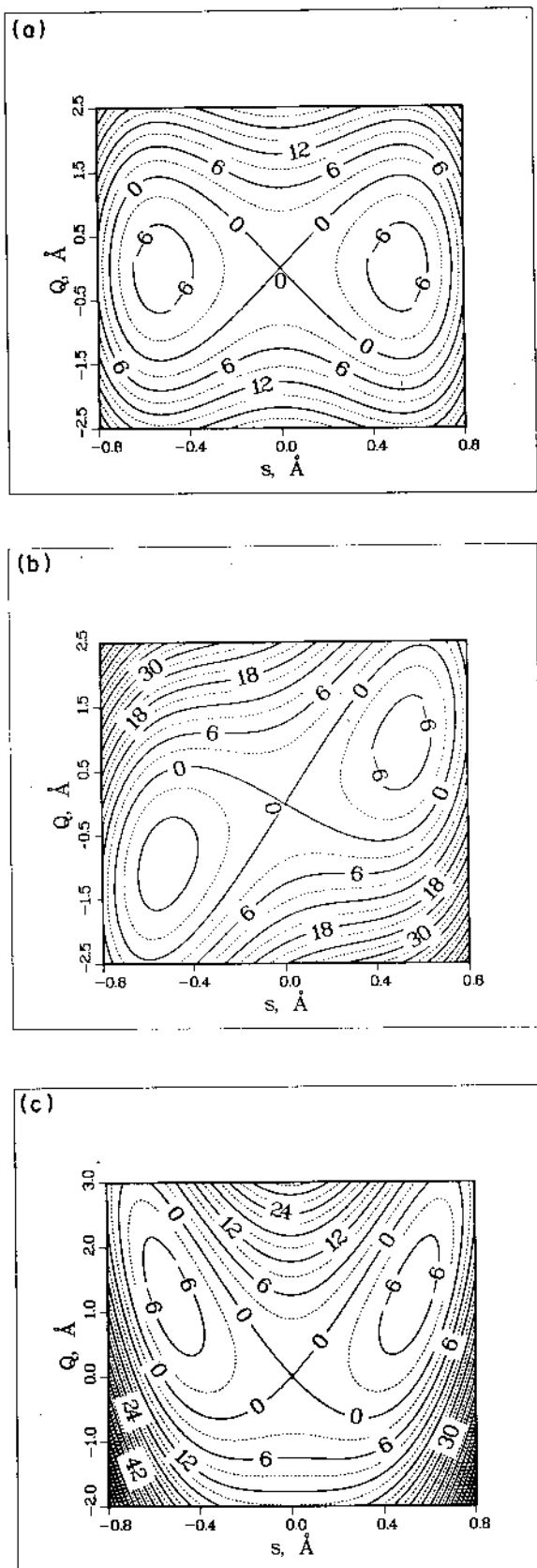


FIG. 2. Contour plots of the potential surface $V_0(s) + \frac{1}{2}m\omega^2\{Q - f(s)/m\omega^2\}^2$ for $\omega = 298 \text{ cm}^{-1}$. (a) No coupling, i.e., $f(s) = 0$. (b) Linear coupling, i.e., $f(s) = cs$, with $c = 0.093 \text{ m dyn/\AA}$. (c) Quadratic coupling, i.e., $f(s) = cs^2$, with $c = 0.24 \text{ m dyn/\AA}^2$. The numbers labeling the curves indicate the height of the potential surface in kcal/mol. It can be seen that the barrier height remains constant, while the minima are shifted from the zero-coupling location.

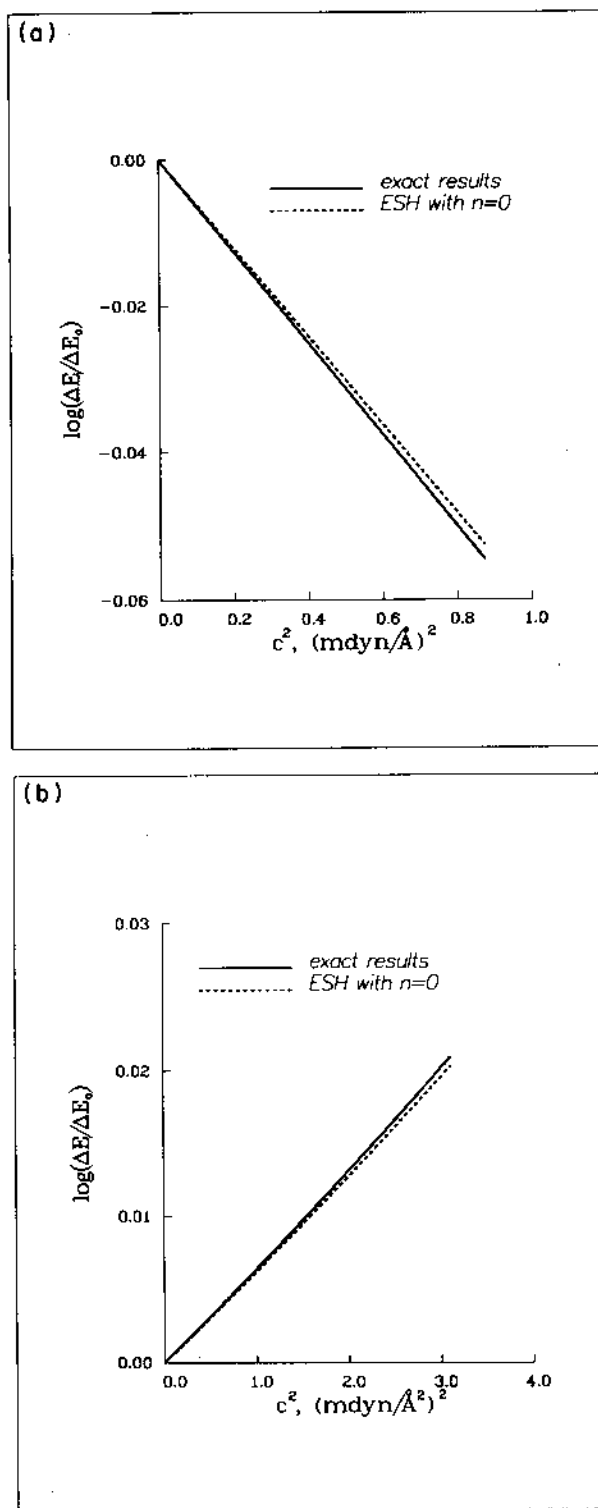


FIG. 3. Tunneling splitting for the lowest doublet in the case of fast Q motion ($\omega = 2980 \text{ cm}^{-1}$) vs the square of the coupling constant c . (a) Linear coupling. (b) Quadratic coupling. The results with the ESH, $n = 0$ have been optimized variationally. ΔE_0 is the tunneling splitting at $c = 0$.

methodology for this is known variably as Van Vleck perturbation theory,¹⁴ Löwdin partitioning theory,¹⁵ or the Feshbach optical potential¹⁶ (in scattering theory). For the present situation, this gives the effective system Hamiltonian matrix, through second order in the off-diagonal bath coupling, as

$$H_{i,i}^{\text{eff}} = H_{i,i}^n + \sum_{n'} \sum_{i',i''} H_{i,n',i''} \times (E(\chi_{i'} | \chi_{i''}) - H_{i',i''}^n)^{-1} H_{i',i''}^n. \quad (3.4)$$

The first term of Eq. (3.3) is the zeroth order ESH matrix considered so far, and the second term the approximate (second order perturbation theory) contribution from non-diagonal coupling ($n' \neq n$) in the bath. [The notation $(M_{i',i''})^{-1}$ is shorthand for the (i', i'') element of the inverse of the matrix $(M_{i',i''})$.]

The results of the application of this method are very satisfactory. In the high frequency case, the splittings obtained this way are essentially indistinguishable from the exact ones. The second order low frequency results, although still different from the exact ones, nevertheless represent an appreciable improvement over the zeroth order ESH results. It is worth emphasizing that this approximation is particularly good, especially for low couplings, and is easily manageable, because it does not increase the size of the matrix to be diagonalized. However, since no variational principle holds here, there is no criterion for the quality of the results and optimization is not possible.

IV. VIBRATIONAL ADIABATIC BASIS AND SCF CALCULATION

As mentioned above, the idea underlying the construction of the shifted oscillator basis is that the matrix element of the coupling function $f_k(s)$ with respect to the s -basis function χ_i represents the average force felt at $s = s_i$. If the Gaussians are peaked around s_i , as is the case in the high frequency limit, then

$$\langle \chi_i | f_k | \chi_i \rangle \approx f_k(s_i),$$

which represents the instantaneous force at s_i . Since the basis functions $\chi_i(s)$ are localized to the regions $s \approx s_i$, the replacement of $f_k(s_i)$ by $f_k(s)$ would not make a significant difference. This suggests the vibrationally adiabatic basis for the coupled oscillators,

$$\psi_m(s, \mathbf{Q}) = \chi_i(s) \prod_k \phi_{n_k} \left(Q_k - \frac{f_k(s)}{m\omega_k^2} \right). \quad (4.1)$$

The matrix elements of the Hamiltonian with respect to this basis do not involve any Franck-Condon factors and the eigenvalues are thus invariant to any linear transformation of the basis functions. The vibrationally adiabatic basis has been tested and found to be very similar to the basis discussed above in the limit of high frequencies.

On the other hand, the more demanding case is the low frequency well, as shown above. One may suggest adopting an SCF scheme, as motivated in Sec. II, i.e., average over the fast s motion and solve iteratively. We tested this idea vs the ones mentioned above, and the results are shown in Fig. 4(a).

In order to apply the analytic SCF scheme, we expand the s eigenfunctions in terms of Gaussian basis functions:

$$\chi_i(s) = \sum_j c_{ij} \chi_j(s),$$

where the coefficients c_{ij} are to be determined. The matrix elements of the effective SCF Hamiltonian are

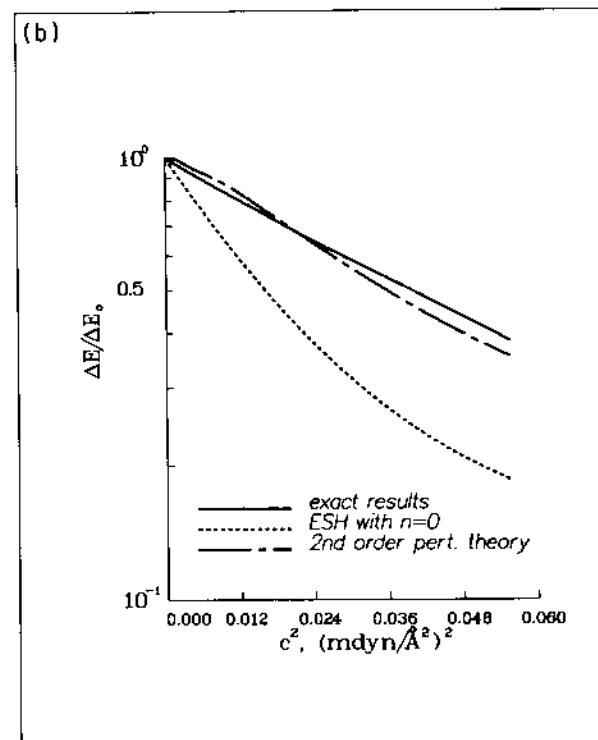
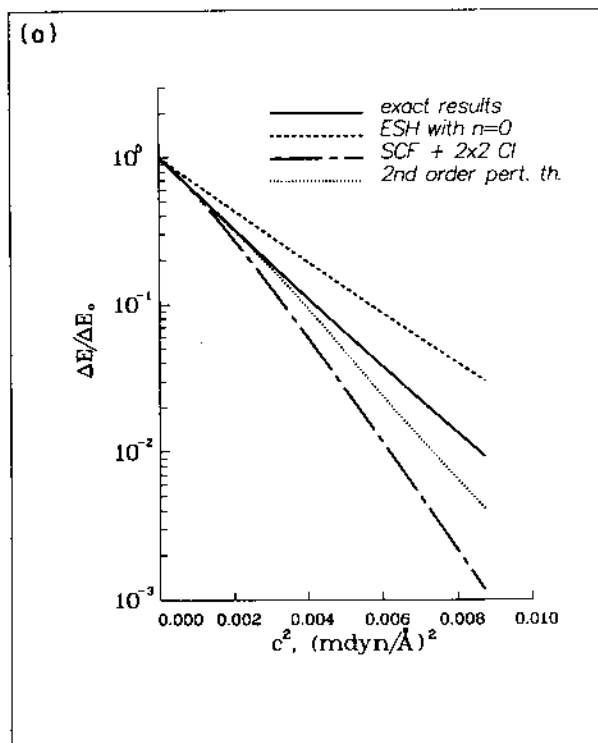


FIG. 4. Tunneling splittings for the lowest doublet in the case of slow Q motion ($\omega = 298 \text{ cm}^{-1}$) vs the square of the coupling constant c . (a) Linear coupling. (b) Quadratic coupling. Note the much faster damping of the tunneling splittings compared to the high frequency case of Fig. 3.

$$H_{r,i}^{\text{eff,SCF}} = \langle \chi_r | H_s | \chi_i \rangle - \sum_k \left\{ \frac{\langle \chi_r | f_k | \chi_i \rangle}{m\omega_k^2} \right. \\ \left. \times \sum_{r',j} C_{r'j} C_{ij} \langle \chi_{r'} | f_k | \chi_j \rangle + \frac{\langle \chi_r | f_k^2 | \chi_i \rangle}{2m\omega_k^2} \right\}.$$

For the SCF scheme to succeed in the case of linear coupling, the initial coefficients must not represent a symmetric function, otherwise the odd symmetry of the coupling force would give $\langle \chi_i | f_k | \chi_i \rangle = 0$. One iteration is enough to break the even symmetry of the uncoupled problem, so that the eigenfunctions after each iteration are asymmetric. Starting from a left (or right) localized function, we obtain a left (or right) localized solution. The method converges within 10–20 iterations, and the SCF limit is reached with ~ 25 Gaussians. The left and the right solution consist a pair of degenerate eigenfunctions at the SCF level, and one must perform a 2×2 configuration interaction (CI) calculation to obtain tunneling splittings. Since the calculation of the splittings for the lowest doublet involves only the ground state SCF solution, which is the one that was optimized, the results are expected to be good. Figure 4(a) shows that the SCF splittings are somewhat worse than the zeroth order ESH splittings at high couplings, but they are substantially better at low couplings. However, the results obtained by second order perturbation theory are by far the best ones obtained within this level of computational effort, so that the SCF scheme does not constitute any improvement.

On the other hand, the SCF results are less promising in the case of quadratic coupling, where their disagreement from the exact calculations is large. This is to be expected, since both of the g and u solutions are involved in the calculation of the tunneling splitting, while only the lowest (g) wave function has been optimized.

V. CONCLUDING REMARKS

We conclude that the shifted oscillator basis presented in Sec. II, even in its zeroth order version, does a very good job of describing the effect on a reaction coordinate of coupling to a harmonic bath, even when the effect of the coupling is quite large. (For this to be true, however, it is necessary that a localized basis set be used for the reaction coordinate.) The numerical examples treated in this paper utilized only one mode for the harmonic bath—so as to be able to compare with exact values—but it should be clear

that the methods of Secs. II and III are readily applicable with little additional effort to the case of many harmonic modes in the bath. Indeed, this was the motivation for their development.

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