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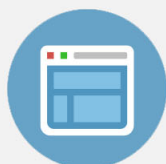
The generator coordinate method for a reaction coordinate coupled to a harmonic oscillator bath

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This paper investigates the usefulness of the generator coordinate method (GCM) for treating the dynamics of a reaction coordinate coupled to a bath of harmonic degrees of freedom. Models for the unimolecular dissociation and isomerization process (proton transfer) are analyzed. The GCM results, presented in analytical form, provide a very good description and are compared to other methods like the basis set method and multiconfiguration time dependent self-consistent field. © *1998 American Institute of Physics.* [S0021-9606(98)50934-8]

I. INTRODUCTION

Tunneling on a multidimensional energy surface is a challenging problem in several areas of physics. In molecular physics, several studies[1–12] demonstrated that purely one-dimensional calculations are not able to describe the isomerization and dissociation processes, as far as the effects of vibrational modes are not negligible. In nuclear physics, the observed fusion cross section of heavy ions collisions at energies below the Coulomb barrier is much larger than the prediction of one-dimensional potential models, and can only be explained by introducing the coupling to other degrees of freedom (for a recent review see Ref. 16).

In the literature, several papers[1–3,12–20] have been devoted to the development of reliable methods to treat the tunneling coupled to other modes.

In this work we investigate the applicability of the generator coordinate method (GCM) (Ref. 21) to treat a tunneling degree of freedom coupled to N harmonic oscillators. This investigation was largely stimulated by an old paper of Makri and Miller,[1] where the authors have analyzed the isomerization of the Malonaldehyde molecule using a basis set methodology. We tackle the same problem using an analytical version of the generator coordinate method.[22–24] We shall prove that it is possible to find an effective Hamiltonian which takes into account the role of the other degrees of freedom. We will apply the method to systems which are modeled by quartic and cubic potentials coupled to harmonic oscillators, although it can be applied to general Hamiltonians.

Section II gives a brief account of the generator coordinate method and how to obtain the effective Hamiltonian. In Sec. III we apply the method for two simple Hamiltonians describing the proton transfer and dissociation processes.

The formal developments of this section were then applied to the isomerization process of the malonaldehyde molecule, Sec. IV, and the unimolecular dissociation, Sec. V. In Secs. IV and V the results are compared to the basis set method,[1] semiclassical tunneling method[3] and multi-configuration time dependent self-consistent field.[2] In Sec. VI we present some final remarks.

II. THE GENERATOR COORDINATE METHOD

Let us consider a general Hamiltonian of the form

$$H(\boldsymbol{\pi},\mathbf{x},p,q) = H_1(q,p) + H_2(\mathbf{x},\boldsymbol{\pi}) + V(\mathbf{x},q), \tag{1}$$

where

$$H_1(q,p) = \frac{p^2}{2m} + U(q) \tag{2}$$

is related to the tunneling degree of freedom and

$$H_2(\mathbf{x},\boldsymbol{\pi}) = \sum_{i=1}^{N} h(x_i, \pi_i) \tag{3}$$

is the Hamiltonian describing the intrinsic degrees of freedom. They are assumed as an ensemble of harmonic oscillators. The coupling term is of the form:

$$V(\mathbf{x},q) = \sum_{i=1}^{N} v_i(q)x_i. \tag{4}$$

The main problem in the treatment of multidimensional tunneling is how to reduce the system dynamics to the relevant degree of freedom and, at the same time, take into account the effects of the other degrees of freedom. The generator coordinate method, originally derived to face the nuclear many-body problem, can be useful to define this reduced effective dynamics.

The crucial point in this method is how to define an appropriate variational subspace where the relevant dynam-

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ics can be realized. This is done by the introduction of the following ansatz for the system wave function (the Griffin-Hill-Wheeler ansatz),

$$\Psi(q,\mathbf{x}) = \int f(\alpha,\beta_1,\beta_2,\ldots,\beta_N)|\varphi(q,\alpha)\rangle$$
$$\otimes \Pi_{i=1}^{N}|\phi(x_i,\beta_i)\rangle d\alpha \, d\beta_1,\ldots,d\beta_N, \qquad (5)$$

where $|\varphi(q,\alpha)\rangle$ is a generator state associated to the tunneling degree of freedom, $|\phi(x_i,\beta_i)\rangle$ are generator states associated to the harmonic oscillators and $f(\alpha,\beta_1,\beta_2\ldots\beta_N)$ is the so-called weight function.

The ansatz above [Eq. (5)] defines a variational wave function. The generator states constitute a nonorthogonal basis. In some cases the variational subspace generated by the ansatz corresponds to the exact Hilbert space of the original problem. In this case the solution of the variational equation

$$\frac{\delta\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = 0 \qquad (6)$$

leads to the exact solution, and the anzatz above can be seen as just another representation of the initial problem. However, this method is quite powerful when it is necessary to reduce the problem to some relevant degree of freedom. In our specific case this should be done on physical grounds, that is, on an educated guess.

In nuclear and molecular physics the usual picture of the tunneling energy surface is that the reaction coordinate or the fission (fusion) degree of freedom, corresponds to two valleys connected through a saddle point on a barrier. The orthogonal degrees of freedom, usually depicted as parabolas with pronounced curvatures, are naturally taken as harmonic oscillators. Within that framework we can suppose that the harmonic oscillators are kept along the path close to their minimum energy states. Thus we can impose a minimum condition, along the path, for the orthogonal degrees of freedom:

$$\delta_{\beta_i}\langle\varphi(q,\alpha)|\otimes\langle\Pi_{i=1}^{N}\phi(x_i,\beta_i)|H|\varphi(q,\alpha)\rangle$$
$$\otimes|\Pi_{i=1}^{N}\phi(x_i,\beta_i)\rangle = 0. \qquad (7)$$

The condition above defines a functional relation between the β_i and α and we can rewrite the anzatz in Eq. (5) as:

$$|\Psi(q,\mathbf{x})\rangle = \int f(\alpha)|\alpha\rangle d\alpha, \qquad (8)$$

where

$$|\alpha\rangle = |\varphi(q,\alpha)\rangle\otimes|\Pi_{i=1}^{N}\phi(x_i,\beta_i(\alpha))\rangle. \qquad (9)$$

The introduction of Eq. (8) in the variational equation (6) leads to the well known Griffin-Hill Wheeler equation,

$$\int_{-\infty}^{\infty}\{\langle\alpha|H|\alpha'\rangle - E\langle\alpha|\alpha'\rangle\}f(\alpha')d\alpha' = 0. \qquad (10)$$

As long as it is possible to define this variational space as a complete and closed subspace,[23] the Griffin-Hill-Wheeler problem is equivalent to the solution of the Schrö-

dinger equation for the projected Hamiltonian onto the variational space. Further on we call this subspace as the effective space.

The projection operator can be obtained by diagonalizing the overlap kernel of the generator states, $\langle\alpha|\alpha'\rangle$,

$$\int_{-\infty}^{\infty}\langle\alpha|\alpha'\rangle u_k(\alpha')d\alpha' = 2\pi\lambda_k u_k(\alpha), \qquad (11)$$

where $u_k(\alpha)$ is the eigenfunction and λ_k the eigenvalue. This allows us to define the momentum representation of the effective space with basis vectors as

$$|k) = \frac{1}{\sqrt{\pi}}\int d\alpha \frac{u_k(\alpha)|\alpha\rangle}{\sqrt{\lambda_k}}, \qquad (12)$$

where we use round bras and kets for states in the effective space. (For details see Refs. 23 and 24).

The effective Hamiltonian in the momentum representation is

$$H_{\text{eff}} = \hat{S}H\hat{S}^{\dagger}, \qquad (13)$$

where the projection operator $\hat{S}$ is

$$\hat{S} = \int dk|k)(k|. \qquad (14)$$

H_{eff} can also be written as a function of the effective momentum and position operators (see details in Ref. 23):

$$H_{\text{eff}} = \hat{S}\left(\sum_{m=0}^{\infty}\frac{1}{2^m}:\tilde{P}^m\tilde{H}^{(m)}(\tilde{Q}):\right)\hat{S}^{\dagger}, \qquad (15)$$

where the ordering : .... : is

$$:\tilde{P}^m\tilde{H}^{(m)}(\tilde{Q}): = \underbrace{\{\tilde{P},\{\tilde{P},\ldots\{\tilde{P},\tilde{H}^{(m)}(\tilde{Q})\}\ldots\}\}}_{m \text{ anticommutators}} \qquad (16)$$

and

$$\tilde{H}^{(m)}(x) = \int d\xi \frac{(-i\xi)^m}{m!}\left(x+\frac{\xi}{2}|\hat{H}|x-\frac{\xi}{2}\right)$$
$$= \int d\xi \frac{(-i)^m}{m!}$$
$$\times\left(x+\frac{\xi}{2}|\underbrace{[\tilde{Q},[\tilde{Q},\ldots[\hat{H},\tilde{Q}]\ldots]]}_{n \text{ commutators}}|x-\frac{\xi}{2}\right), \qquad (17)$$

where $\{\tilde{P},\tilde{Q}\}$ are the canonical operators in the effective subspace such that

$$\tilde{P}|k) = k|k), \qquad (18)$$

$$\tilde{Q}|k) = -i\partial/\partial k|k), \qquad (19)$$

$$\tilde{Q}|x) = x|x). \qquad (20)$$

We should stress that for analytical results it's important to solve exactly the overlap eigenvalue problem in order to obtain a complete and closed representation of the effective subspace. As it was noted elsewhere[24] this is possible for any overlap of the Hilbert-Schmidt-type. Nevertheless it could be

hard to find the solution in some practical cases. Such drawbacks can however be circumvented by a numerical approach or a generalized Griffin-Hill-Wheeler anzatz.[25]

III. THE MODEL

Now we use our method to study a system-bath model which is well known in the literature. For the *proton transfer* case it consists of a quartic double well potential linearly coupled to an harmonic oscillator and for the *dissociation* case it is a cubic potential barrier coupled to the oscillator. That is:

$$H(x,q) = H_{re}(q) + H_{osc}(x) + cxq \qquad (21)$$

with

$$H_{re}(q) = \begin{cases} \dfrac{P^2}{2m} + \dfrac{1}{2}a_o q^2 - \dfrac{1}{3}b_o q^3 & \text{dissociation} \\[2mm] \dfrac{P^2}{2m} - \dfrac{1}{2}a_o q^2 + \dfrac{1}{4}d_o q^4 & \text{proton-transfer} \end{cases} \qquad (22)$$

and

$$H_{osc}(x) = \frac{\pi^2}{2m} + \frac{1}{2}m\omega^2 x^2. \qquad (23)$$

For the sake of simplicity we shall restrict ourselves to the case of coupling to a single oscillator. As discussed in Ref. 1, a term

$$\Phi(q) = \frac{c^2 q^2}{2m\omega^2}, \qquad (24)$$

is sometimes introduced to guarantee that the height of the barrier in the original energy surface remains roughly constant with increasing value of the coupling constant. As far as we are interested in the comparison of our method to others presented in the literature, we will mention whether this term is introduced or not.

To construct our generator states, we start from a direct product of two coherent states,[26] $|\alpha\rangle \otimes |\beta\rangle \equiv |\alpha,\beta\rangle$, related respectively to the $\{q,x\}$ degrees of freedom. That is:

$$|\beta\rangle = \exp[\beta a^\dagger - \beta^* a]|\phi_0\rangle,$$

where $|\phi_0\rangle$ is the harmonic oscillator ground state with characteristic width $\sqrt{(\hbar/2m\omega)}$, and

$$\beta a^\dagger - \beta^* a = \sqrt{\frac{m\omega}{\hbar}}\left(\frac{\beta - \beta^*}{\sqrt{2}}\right)x - \frac{i}{\sqrt{m\hbar\omega}}\left(\frac{\beta + \beta^*}{\sqrt{2}}\right)\pi. \qquad (25)$$

For the reaction degree of freedom, we have

$$|\alpha\rangle = \exp[\alpha A^\dagger - \alpha^* A]|\varphi_0\rangle,$$

where

$$\alpha A^\dagger - \alpha^* A = \sqrt{\frac{m\Omega}{\hbar}}\left(\frac{\alpha - \alpha^*}{\sqrt{2}}\right)q - \frac{i}{\sqrt{m\hbar\Omega}}\left(\frac{\alpha + \alpha^*}{\sqrt{2}}\right)P$$

and $|\varphi_0\rangle$ is the harmonic oscillator ground state related to the pair $\{A,A^\dagger\}$. The width of the α coherent state is

$\sqrt{(\hbar/2m\Omega)}$, where Ω, called *generator frequency,* is a free parameter. The results will depend strongly on this parameter and its choice will be discussed later.

The reasons to employ coherent states for the harmonic oscillator is natural, because they do form an overcomplete basis and the variational space generated by them is exact. For the reaction coordinate the reasons are the following: first, a real parameter coherent state is a localized function (a Gaussian), and as it was already noticed by the basis set approach[1] it can provide a good description for barrier penetration problems; second, coherent states have a series of useful analytical properties and they especially have a diagonalizable *Gaussian overlap.*[23]

In order to obtain a one parameter generator state, we shall enforce the condition (7):

$$\partial_\beta \langle \alpha,\beta|H|\alpha,\beta\rangle = 0,$$

which gives us

$$\beta = -\chi\alpha, \qquad (26)$$

where

$$\chi = \frac{c}{\hbar\omega}\sqrt{\frac{\hbar}{m\omega}}\sqrt{\frac{\hbar}{m\Omega}}.$$

This minimization leads to the constraint relation between the generator coordinate α and β, where we assumed, without loss of generality, that α is real. It was proved elsewhere[23] that the same effective space is generated by either complex or real parameter coherent states. It is important to notice that the generator states $|\alpha\rangle$ constitute a nonorthogonal basis. This nonorthogonality implies that the dynamics, given by the Griffin-Hill-Wheeler equation (GHW) (10), couples the intrinsic states corresponding to different points along the path (here defined by the generator coordinate α). Hence, if one remembers that the coherent states corresponds to displaced harmonic oscillators states, the nondiagonal terms of the GHW equation would lead to the coupling between several harmonic oscillators levels. This permits us to consider that, even with the implementation of the minimum condition in Eq. (7), the effective dynamics described by Eq. (10) take into account much more than the average effect of the intrinsic harmonic oscillators along the path. Therefore it allows a better description of the coupling dynamics and makes the difference between our method and others like the self-consistent field and even the basis set method.[1,2]

With the constraint relation (26) the $|\alpha,\beta\rangle$ state can be described by a single parameter, α, yielding $|\alpha,\beta\rangle \equiv |\alpha,\beta(\alpha)\rangle \equiv |\alpha\rangle$ and the overlap function is

$$(\alpha|\alpha') = \exp[-\tfrac{1}{2}(1+\chi^2)(\alpha-\alpha')^2]. \qquad (27)$$

This overlap can be easily diagonalized [Eq. (11)] by a Fourier transform giving the following eigenfunctions and eigenvalues:

$$u_k(\alpha) = \exp[ik\alpha], \qquad (28)$$

$$2\pi\lambda_k = \sqrt{\frac{2\pi}{1+\chi^2}}\exp\left[-\frac{1}{2}\frac{k^2}{(1+\chi^2)}\right]. \qquad (29)$$

Now, using Eqs. (12), (14) and (15) we obtain the effective Hamiltonians,

$$H_{\text{eff}} = \frac{P^2}{2m_{\text{eff}}} + V_{\text{eff}}(q), \tag{30}$$

where

$$m_{\text{eff}} = m \varepsilon_m(c, \Omega),$$

$$V_{\text{eff}}(q)$$

$$= \begin{cases} \left(\frac{1}{2} a_o - \frac{1}{2} \frac{c^2}{m\omega^2} \right) q^2 - \frac{1}{3} b_o q^3 - c_d \, q & \text{dissociation} \\ -\left(\frac{1}{2} a_o + \frac{1}{2} \frac{c^2}{m\omega^2} - c_{pt} \right) q^2 + \frac{1}{3} d_o q^4 & \text{proton-transfer.} \end{cases} \tag{31}$$

The effect of the coupling to the oscillator is present in the enhancement factor, defined as the ratio between the effective mass and the mass itself,

$$\varepsilon_m(c, \Omega) = \frac{m_{\text{eff}}}{m} = \frac{[1 + (\omega/\Omega)(c/m\omega^2)^2]^2}{1 + (\omega/\Omega)^2(c/m\omega^2)^2}, \tag{32}$$

and by terms modifying the potential which are characterized by the coefficients

$$c_d = \frac{3}{4} \frac{\hbar b_o}{m\omega} (\omega/\Omega)^2 (c/m\omega^2)^2 / (1 + (\omega/\Omega)(c/m\omega^2)^2), \tag{33}$$

$$c_{pt} = \frac{3}{2} \frac{\hbar d_o}{m\omega} \frac{(\omega/\Omega)^2(c/m\omega^2)^2}{1 + (\omega/\Omega)(c/m\omega^2)^2}. \tag{34}$$

One can easily see that, independently of the generator frequency Ω, as the coupling strength c goes to zero, the effective Hamiltonians revert back to the reaction part of the original ones. This is a desired consistency property. One can also see that as a consequence of the linear coupling and the particular choice of generator states the effective mass is the same for the cubic (dissociation) and for the quartic potential (proton transfer). In the two cases, the factor $[\frac{1}{2}(c^2/m\omega^2)]$ in the quadratic coefficient can be eliminated if the original Hamiltonian has the renormalization term $\Phi(q)$.

The generator frequency Ω is a free parameter, however, rather than fit, we decided to choose the parameters based on an educated guess. This will be discussed with the presentation of the results for each case.

Since the effective mass is common for the two cases above, we can make some remarks valid for both cases. The mass is, as expected, renormalized by the presence of the other degree of freedom. Thus the effective mass has an enhancement factor which depends on the coupling constant, c, on the parameters of the oscillator and also on the ratio (ω/Ω) between the generator frequency and the oscillator frequency. It does *not* depend on the position, nevertheless the enhancement factor can be quite large in some cases.

Now we shall deal in detail with each case to present and discuss our results.

IV. PROTON TRANSFER CASE: SYMMETRIC DOUBLE WELL POTENTIAL

We applied the method to the proton or H-transfer process in the malonaldehyde molecule which is fairly well modeled by the double well potential coupled linearly to one harmonic oscillator. We use two different sets of parameters.

In the first case, a_0 and d_0 were chosen so that the barrier height is 7.8 kcal/mol, and the local minima are localized at ± 0.53 Å. We consider two bath frequencies: a slow $\omega = 298$ cm^{-1} and a fast one $\omega = 2982$ cm^{-1}. Those values were the same as used in Ref. 1 and this choice allows us to compare our results to the results obtained by the Basis set method. In this case the renormalization term $\Phi(q)$ is present.

In order to compare our results with a time dependent self-consistent field approximation, we also consider another set of values for a_0 and d_0 such that the frequency at the local minima is 1530 cm^{-1} and the barrier height is 6.3 kcal/mol.[2]

Our first task is to choose the generator frequency Ω. In the double well case we have three ''natural'' frequencies: the oscillator frequency, the bottom of the well frequency and the barrier frequency (associated to the curvature at the barrier). Our intention was to choose among those natural frequencies a value for Ω. As far as we are interested in the tunneling process in the presence of the oscillator, we pay special attention to the oscillator frequency ω and the barrier frequency ω_{barrier}. It can be seen in the expressions for the effective potential and mass that (ω/Ω) acts as a multiplicative factor for the coupling. Thus the choice of Ω is crucial. We tried then to find a domain of Ωs, within which, changes of the value of Ω would not lead to a meaningful modification of the dependence of the effective potential and mass on the coupling constant. This would give a region which would be the most independent of the choice of Ω and which depends almost exclusively on the coupling constant. In order to do so, we analyzed the curvature of the potential, the height of the barrier and the mass as a function of the generator frequency and the coupling constant c, and we chose Ω as one of the already mentioned natural frequencies, ω or ω_{barrier}, depending on which one was in this most Ω stable region.

This analysis lead us to the following choices:

(a) for the fast bath case ($\omega > \omega_{\text{barrier}}$) the best choice is $\Omega = \omega$;
(b) for the slow bath case ($\omega < \omega_{\text{barrier}}$) is $\Omega = \omega_{\text{barrier}}$.

In Figs. 1 and 2 we have the mass enhancement factor for the fast and slow bath cases as a function of the coupling constant. We notice that for the slow bath case the enhancement can be quite large. A typical dependence of the effective potential on the coupling is also depicted in Fig. 3.

We now compare the GCM results with numerically generated exact results and with the basis set method.[1,27]

First, for the slow bath case, the GCM results are compared to the ones obtained with the effective system Hamiltonian (ESH) of the basis set method of Makri and Miller (see Fig. 4). We can see that the GCM results are better even
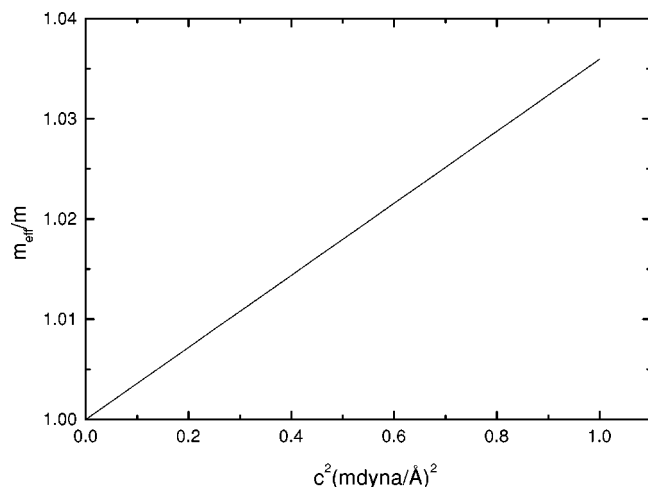
FIG. 1. Mass enhancement factor ε_m as a function of the square of the coupling constant c^2, for an oscillator frequency $\omega = 2980$ cm^{-1} and a generator frequency $\Omega = \omega$.

when compared to the second order corrections.

In the fast bath case the GCM and the second order corrections for the basis set method cannot be distinguished from the exact result (see Fig. 5).

It is worth mentioning that if we had considered only the diagonal part of the GCM kernel we would have a treatment equivalent to the self-consistent field method. For the sake of completeness we also compare our results to the ones obtained by the multiconfiguration time dependent self-consistent field presented by the same authors[2] (Fig. 6). In this case we use the second set of parameters for the potential. The comparison favors again the GCM calculations.

V. DISSOCIATION PROBLEM

The effective potential displays a very familiar quadratic correction $-(c^2/k_o)x^2$ which would disappear if $\Phi(q)$ were present. There is also a more complicated linear correction,
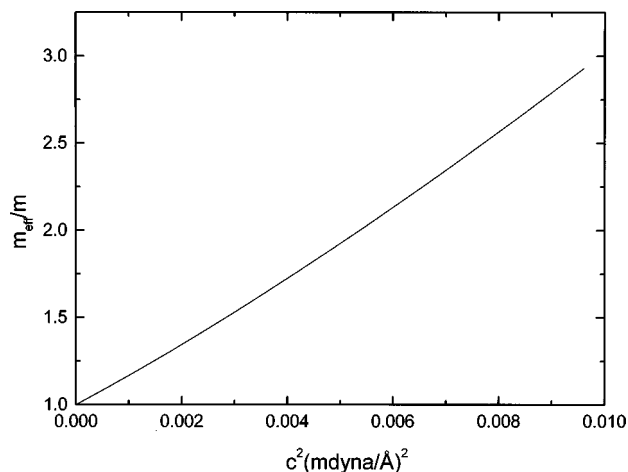

FIG. 2. Mass enhancement factor ε_m as a function of the square of the coupling constant c^2, for an oscillator frequency $\omega = 298$ cm^{-1} and a generator frequency $\Omega = \omega_{\text{barrier}}$.
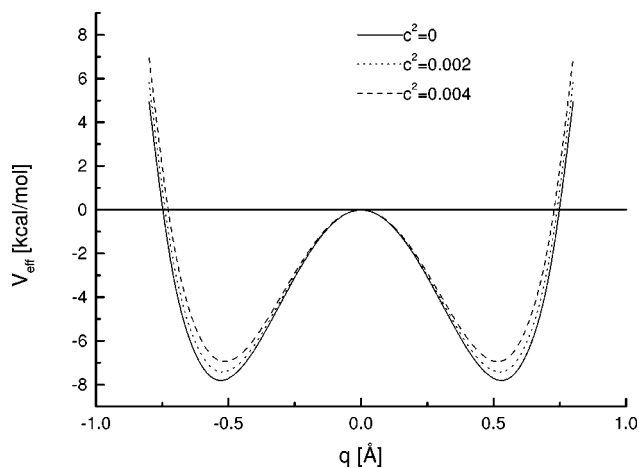

FIG. 3. Typical behavior of the effective potential for some values of the coupling constant.

which depends explicitly on the generator frequency Ω, and is quite similar to one of the quadratic corrections in the proton transfer case.

The behavior of the effective potential with respect to the coupling can be seen in Fig. 7, where it becomes clear that the effective potential can be extremely sensitive to the coupling constant, which makes the choice of the generator frequency much more delicate.[28] Following the same basic arguments of the previous section we again examined the behavior of the barrier height, curvature of the potential and mass as a function of the coupling constant and the generator frequency. In this case the strong sensitivity of the potential led us to chose as a first hint $\Omega = \omega$, which seems to be a good zero order choice. In Fig. 8 we have results obtained with this choice. The results are compared to the one obtained by the Makri and Miller semiclassical tunneling model[3] and the exact one. The results are good for small values of the coupling constant, but we can see that they start
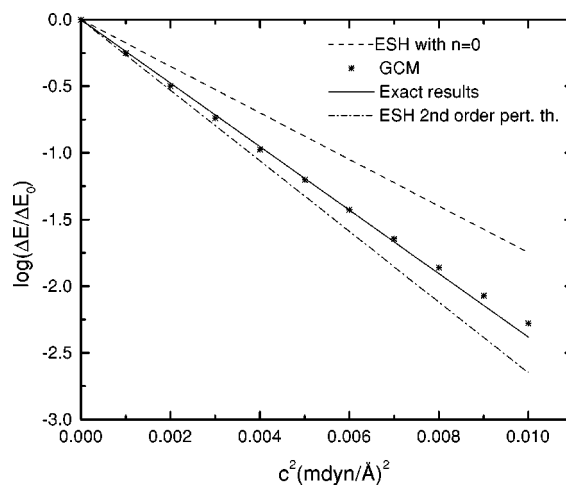

FIG. 4. The tunneling splitting as function of the square coupling for $\omega = 298$ cm^{-1}, $\Omega = \omega_{\text{barrier}}$. The barrier height is 7.8 kcal/mol and the minima position are ± 0.53 Å. The GCM results ($*$) are compared to the exact results (solid line), the zero order results (dashed line) and the second order perturbation theory (dot-dashed line) obtained from the effective system Hamiltonian (ESH) of the basis set method in Ref. 1.
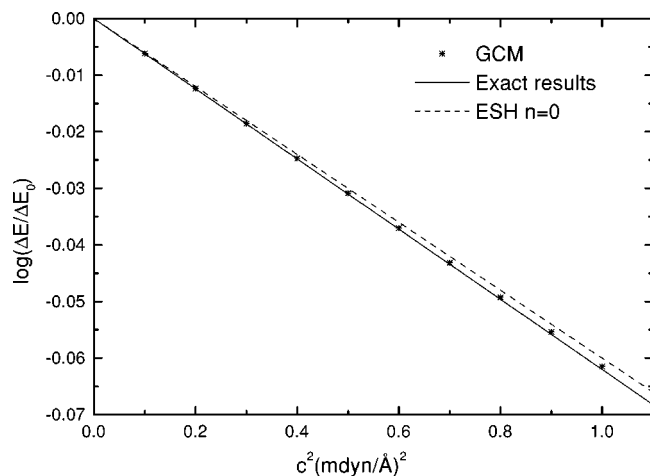
FIG. 5. The tunneling splitting as function of the square coupling for $\omega = 2980$ cm^{-1}, $\Omega = \omega$. The barrier height is 7.8 kcal/mol and the minima position are ± 0.53 Å. The GCM results (*) are compared to the exact results (solid line), the zero order results (dashed line) obtained from the effective system Hamiltonian (ESH) of the basis set method in Ref. 1. The second order perturbation theory of the basis set method gives results that cannot be distinguished from the GCM and exact ones.

to drift apart for values of c^2 around 0.0005 (mdyn/)Å^2. This feature seems to come from the strong dependence of the effective potential with the coupling constant. An analysis of the main features of the effective potential showed that for high coupling, the effective Hamiltonian no longer displays a region stable against variations of Ω. We try then to introduce a generator frequency depending itself on the coupling constant. Keeping in mind that in the small coupling region the initial choice $\Omega = \omega$ shows good results, we tried to identify Ω as a renormalized ω. Observing the presence of the correction on the quadratic term of the effective potential and also the mass enhancement factor, we propose the following correction:
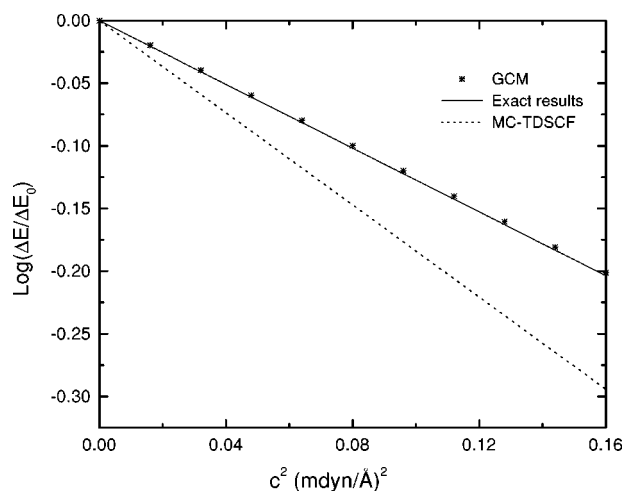

FIG. 6. The GCM tunneling splitting is compared to the results obtained with the multiconfiguration time dependent self-consistent field (Ref. 2) and the exact results. In this case, the barrier height is 6.3 kcal/mol and the frequency at the local minima is 1530 cm^{-1}. The frequency of the bath mode is 2980 cm^{-1}.
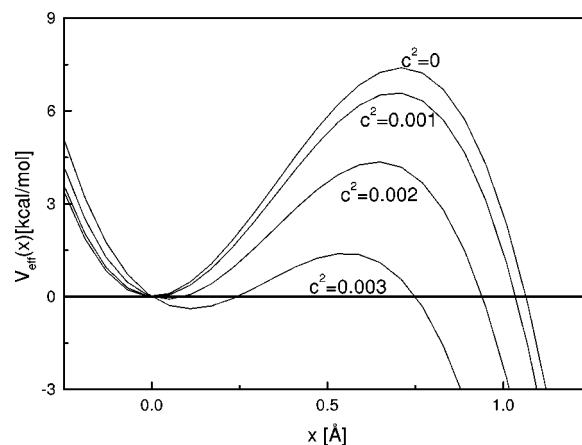

FIG. 7. Typical behavior of the cubic effective potential as a function of the square of the coupling constant for the dissociation case.

$$\Omega = \sqrt{\frac{k_0 - (c^2/a_0)}{m_{\text{eff}}}} = \omega \sqrt{\frac{1 - (c^2/a_0 m \omega^2)}{\varepsilon_m(c,\omega)}}. \qquad (35)$$

There is a good improvement with this prescription as it can be seen in Fig. 9. We stress the excellent results obtained in the small and intermediary regions. We also point out that this "intermediary regions" present a tunneling rate around 10 000 times larger than the ones in the small coupling region. So, the word "intermediary" is, as a matter of physical effects, a bit misleading, and the agreement achieved by the method is remarkable.

One of the interesting features of the effective Hamiltonian is the resemblance with the one obtained by Brink et al.,[29] with a completely different approach. In fact, both are identical in the small coupling region and in the limit $\omega \gg \omega_{\text{barrier}}$. In this very region, Brink et al. analyze the spontaneous fission of ^{239}U, and obtain very reasonable results. Due to the completely different approaches it is difficult to compare the higher order corrections from the formal point of view, however, it seems to have a similar behavior. The relationship between the two methods might be better discussed in a subsequent paper.
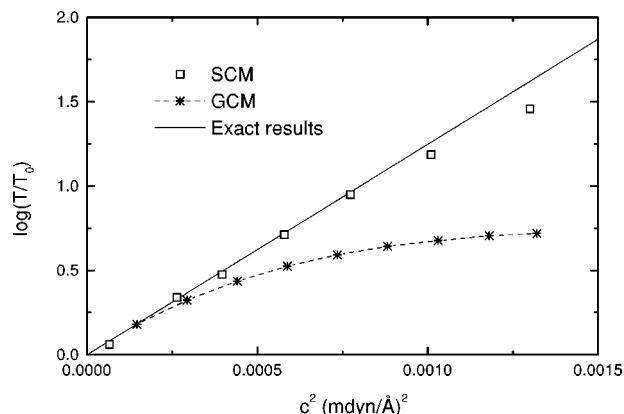

FIG. 8. The GCM results, with $\Omega = \omega$, for the log of decay rate T normalized by the decoupled ($c=0$) decay rate T_0 is compared to the exact and semiclassical method (SCM) results (Ref. 3). The barrier height is 7.4 kcal/mol and the local maximum occurs at 0.71 Å.
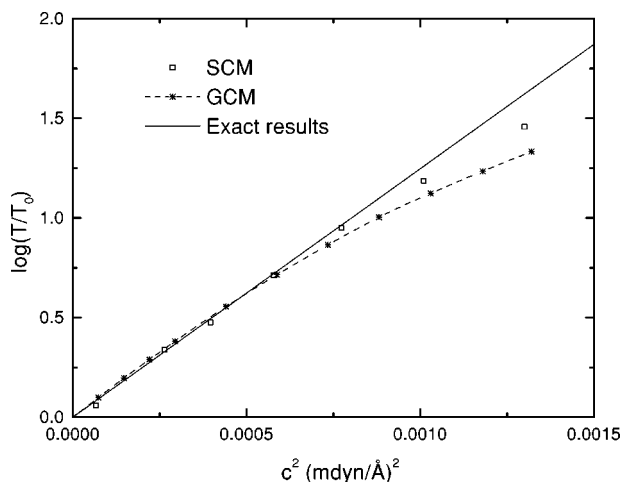
FIG. 9. The same as the previous figure using the normalized generator frequency [see Eq. (35)].

VI. CONCLUDING REMARKS

As seen in all results shown, the GCM provided a good description for the system-bath model. In the proton-transfer process the results are virtually exact, and no further corrections on the generator frequencies were needed. In the dissociation like case the effective Hamiltonian is consistent with the one obtained with a semiclassical approximation by Brink et al.[29] for a nuclear case, and the molecular dissociation rates predicted are quite as good as the ones provided by the semiclassical tunneling model.

In this work, the main results were obtained analytically which allowed us to analyze in a more transparent way and with no numerical cost the role of the coupling to other degrees of freedom. As an example, we should mention the role of the mass enhancement factor. The presence of this factor which comes naturally from the method turns out to be, in some cases, more important than the modifications of the one-dimensional effective potential. This suggests that sometimes the intrinsic degrees of freedom can affect the system more on its inertia than on its potential. The role of the mass renormalization is also stressed in some papers.[20] Furthermore the analytical form of the effective Hamiltonian gave us means to choose the generator frequency on physical grounds rather than fitting.

The GCM is a variational method and the accuracy of the results depends on a good choice of the generator states. The fact that our effective subspace (variational space) is virtually the correct one for the isomerization problem shows that coherent states do provide a good ansatz for this type of problem. In the dissociation problem we have a good agreement for the small coupling region, however, a renormalization of the frequency was required for large values of the coupling constant. In this case, a new choice of generator states could improve the predictions, but, it is quite sure that we will not have the simplicity of the analytical results we have with coherent states. Nevertheless we can use the generalized generator coordinate method as proposed in Ref. 25. In this case, to solve the quantum mechanical problem using the nonorthogonal basis, we will need only low dimension matrices. So we do not expect a large computational cost. Such improvements are being presently investigated.

So, the GCM, although based on a very heavy mathematical foundation (one of the reasons of its accuracy), is fairly simple to apply and it generates an analytical effective Hamiltonian which allows a rich problem analysis giving extremely good results.

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