A Gaussian wave-packet propagation study of non-adiabatic dynamics

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Abstract. The Gaussian wave-packet propagation (GWP) approach in the coherent state algebraic formalism has been applied to calculate the dynamics of a few model single-mode systems and a model two-mode system. To circumvent the problems arising in defining the initial conditions and the potential surface for such systems in this formalism, we have constructed a new Hamiltonian which is derived by mapping the original Hamiltonian on to a single electronic surface. Good agreement with exact results have been obtained.

Keywords. Gaussian wave-packet dynamics; quantum dynamics of non-adiabatic systems; coherent state algebraic formalism.

1. Introduction

Many exact and approximate methods exist in literature to calculate the dynamics of a system. The Gaussian wave packet (GWP) dynamics (Heller 1975) approach is an approximate method in which the wave function is parametrized as a travelling Gaussian. The equations of motion for the centroid of the wave packet derived from the time-dependent Schroedinger equation (TDSE) in the local harmonic approximation turn out to be classical equations of motion. The consequential computational simplicity and the pictorial interpretation it provides in terms of classical trajectories are the attractions of this approach.

The GWP has so far been applied to study various dynamical systems of chemical interest such as atom–diatom collisions. (Heller 1975; Drolshagen and Heller 1983; Skodje and Truhlar 1984; Jackson and Metiu 1985, 1986; Kluk *et al* 1986; Sawada and Metiu 1986a, b), photodissociation dynamics (Kulander and Heller 1978; Brown and Heller 1981), calculation of Franck–Condon spectra (Heller 1981; Coalson and Kinsey 1986; Coalson 1987; Coalson and Karplus 1990), overtone widths (Heller and Davis 1980) and others (Sawada *et al* 1985; Blanco and Heller 1983). It provides a fairly accurate description of quantum dynamics, especially for short time intervals. One class of applications for which such short time dynamics is sufficient is the calculation of spectra of systems undergoing non-adiabatic dynamics. Although various methods to calculate these dynamics have been reported (Schneider and Domcke 1988, 1989; Jiang *et al* 1989; Manthe and Koppel 1990, 1991; Stock and Domcke 1990; Durga Prasad 1992; Stock and Miller 1992), very few attempts have been made so far in this area applying GWP (Coalson 1987; Coalson and Kinsey 1986; Sawada and Metiu 1986). Even these approaches utilize the GWP primarily

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to calculate the dynamics on one surface while other methods such as perturbation theory are used to account for the non-adiabatic coupling. Our own goal, in contrast, is to use the GWP consistently to obtain the full non-adiabatic dynamics.

In this paper, we specifically study the non-adiabatic dynamics within the framework of the linear coupling model (Koppel *et al* 1984). We assume that only two electronic states, belonging to different irreducible representations of the molecular point group and n vibrational modes, are relevant to the dynamics. The resultant Hamiltonian can be written as (Koppel *et al* 1984)

$$H = \sum_i |e_i\rangle \varepsilon_i \langle e_i| + \sum_n \omega_n a_n^+ a_n + \sum_{i,j,n} |e_i\rangle [V_n^{(ij)}(a_n^+ + a_n)]\langle e_j|. \tag{1}$$

Here $|e_i\rangle$'s are the electronic states and a_n^+ and a_n are the usual Boson ladder operators of the nth vibrational mode. This Hamiltonian has been extensively studied in the past and is found to be adequate for a large number of systems. The wave function for such systems is given by

$$\psi = \sum_i |e_i\rangle \phi_i(R, t), \tag{2}$$

where ϕ_i are the vibrational wave functions associated with the ith electronic state. The essential drawback in using GWP to study the non-adiabatic dynamics lies in choosing the initial conditions. This can be seen as follows. In matrix representation the vibrational wave function ϕ can be written as

$$\phi = \begin{pmatrix} \phi_1(R) \\ \phi_2(R) \end{pmatrix}. \tag{3}$$

The $\phi_i(R)$ are vibrational wave packets moving on different surfaces. They have different momenta and centroids. To obtain the equations of motion by GWP the potential is expanded as a Taylor series at the centroid of the wave packet. As both the nuclear wave functions ϕ_1 and ϕ_2 corresponding to the two electronic states have different centroids in general, choosing the point around which the potential is to be expanded becomes a problem. Second, if any one of the ϕ_i is equal to zero, the exponent in the Gaussian ansatz for ϕ_i should be equal to $-\infty$. Representing this logarithmic singularity is difficult in practice. We have circumvented this problem by mapping the Hamiltonian, (1), on to a purely vibrational Hamiltonian confined to a single electronic surface. The details of the mapping are presented in §2. In §3, we present the numerical calculations for some one- and two-dimensional model systems. Section 4 contains a summary of our work and a few concluding remarks.

2. The Hamiltonian

In this section, we discuss the mapping of the multisurface Hamiltonian, (1), of a system specifically consisting of two electronic surfaces belonging to different irreducible representations of the molecular point group, on to a single surface Hamiltonian. We first consider a situation where only one vibrational mode (the coupling mode) is relevant to the dynamics and describe the mapping. We then extend

it to the n vibrational mode problem. The Hamiltonian for the single mode case is given by

$$H = \sum_i |e_i\rangle \varepsilon_i \langle e_i| + \omega_c a_c^+ a_c + \sum_{i \neq j} |e_i\rangle [V_c^{ij}(a_c^+ + a_c)] \langle e_j|. \tag{4}$$

The subscript c indicates (here and in the following) that the normal coordinate is a coupling mode. Because the two states belong to different irreducible representations, the coupling coordinate is always non-totally symmetric and hence cannot have intrastate coupling. We take the zero of energy to be the midpoint of the two electronic states such that, $\varepsilon_1 = -\varepsilon$ and $\varepsilon_2 = \varepsilon$ where 2ε is the energy gap between the two states at the equilibrium geometry of the ground state.

Let us now analyse the structure of the Hilbert space $\mathbb{H}_s$ relevant to the dynamics of this system. This Hilbert space is formed by the direct product of the Hilbert spaces of the electronic and vibrational sub-systems.

$$\mathbb{H}_s = \mathbb{H}_e \oplus \mathbb{H}_v, \tag{5a}$$

$$\mathbb{H}_e = \{|e_1\rangle, |e_2\rangle\}, \tag{5b}$$

$$\mathbb{H}_v = \{\phi_n(q); 0 \leqslant n \leqslant \infty\}. \tag{5c}$$

Here ϕ_n are the harmonic oscillator eigenfunctions. Let $|e_1\rangle$ and $|e_2\rangle$ belong to the irreducible representations Γ_1 and Γ_2 respectively. Since the Hamiltonian must always transform as the totally symmetric representation, the coupling mode belongs to $\Gamma_r = \Gamma_1 \oplus \Gamma_2$. Consequently, all the elements in $\mathbb{H}_v$ belong to either the totally symmetric representation (when n is even) or to the Γ_r representation (when n is odd). Thus, the elements in $\mathbb{H}_s$ belong either to Γ_1 (when the electronic state is $|e_1\rangle$ and the vibrational quantum number is even or when the electronic state is $|e_2\rangle$ and the vibrational quantum number is odd since $\Gamma_2 \oplus \Gamma_r = \Gamma_1$) or to Γ_2 (in the opposite cases). Symbolically, this can be written as

$$\mathbb{H}_s = \mathbb{H}_1 \cup \mathbb{H}_2, \tag{6a}$$

$$\mathbb{H}_1 = \{|e_i\rangle \phi_n; \, i = 1 \text{ and } n \text{ even or } i = 2 \text{ and } n \text{ odd}\}, \tag{6b}$$

$$\mathbb{H}_2 = \{|e_i\rangle \phi_n; \, i = 1 \text{ and } n \text{ odd or } i = 2 \text{ and } n \text{ even}\}. \tag{6c}$$

Since the Hamiltonian cannot couple elements belonging to different symmetries, a wave packet initially started in one of the two subspaces ($\mathbb{H}_1$ or $\mathbb{H}_2$) would continue to evolve within that subspace. Thus, for such initial conditions it is sufficient to expand the wave packet in terms of the basis functions of either $\mathbb{H}_1$ or $\mathbb{H}_2$. We now note that the number of elements in $\mathbb{H}_1$ (or $\mathbb{H}_2$) and $\mathbb{H}_v$ is identical and hence it is possible to define a one-to-one correspondence between these two subspaces.

$$\mathbb{H}_v \leftrightarrow \mathbb{H}_1, \tag{7a}$$

$$\phi_n \leftrightarrow \phi_n |e_i\rangle. \tag{7b}$$

The correspondence is completely defined when the electronic state index i is uniquely defined for a given n. In case of $\mathbb{H}_1$ the electronic state is $e_1(i = 1)$ whenever n is even and e_2 whenever n is odd. The opposite holds in case of $\mathbb{H}_2$. With this identification, the mapping between $\mathbb{H}_1$ and $\mathbb{H}_v$ is complete.

In the next step, we construct a model Hamiltonian $\bar{H}_1$ whose matrix elements in $\mathbb{H}_v$ are identical to the matrix of H in $\mathbb{H}_1$. For the first term in $H(\omega_c a_c^+ a_c)$, the matrix elements in $\mathbb{H}_1$ are $\langle e_i \phi_m | \omega_c a_c^+ a_c e_j \phi_n \rangle = m\omega_c \delta_{mn} \delta_{ij}$. The corresponding term in $\bar{H}_1$ is then simply $\omega_c a_c^+ a_c$. For the second term $(\Sigma_i \varepsilon_i | e_i \rangle \langle e_i |)$ the matrix elements are

$$\langle e_i \phi_n | \Sigma \varepsilon_R | e_R \rangle \langle e_R | | e_j \phi_n \rangle = \varepsilon_i \delta_{ij} \delta_{mn}. \tag{8a}$$

Recalling that ε_i are $\mp \varepsilon$ depending upon whether m is even or odd we find that the term in $\bar{H}_1$ is $-\varepsilon \cos(\pi a_c^+ a_c)$ since

$$\langle \phi_m | \cos(\pi a_c^+ a_c) | \phi_n \rangle = \langle \phi_m | \cos(n\pi) | \phi_n \rangle$$
$$= (-1)^m \delta_{mn}. \tag{8b}$$

Finally, the last term in the Hamiltonian $(\Sigma | e_i \rangle V_c(a_c^+ + a_c) \langle e_j |)$ maps on to $V_c(a_c^+ + a_c)$. With this, the model Hamiltonian $\bar{H}_1$ can be written as

$$\bar{H}_1 = \omega_c a_c^+ a_c - \varepsilon \cos(\pi a_c^+ a_c) + V_c(a_c^+ + a_c). \tag{9a}$$

Similarly, for $\mathbb{H}_2$ one can show that

$$\bar{H}_2 = \omega_c a_c^+ a_c + \varepsilon \cos(\pi a_c^+ a_c) + V_c(a_c^+ + a_c), \tag{9b}$$

simulates the dynamics in $\mathbb{H}_v$.

We now turn to the multimode problem. The most general Hamiltonian in this case is

$$H = \sum_i |e_i \rangle \varepsilon_i \langle e_i | + \omega_c a_c^+ a_c + \sum_{i \neq j} |e_i \rangle [V_c^{ij}(a_c^+ + a_c)] \langle e_j |$$

$$+ \sum_t \omega_t a_t^+ a_t + \sum_{t,i} |e_i \rangle (V_t^{(i)}[a_t^+ + a_t]) \langle e_i |. \tag{10}$$

Note that, the coupling modes cannot tune the electronic state energy and the tuning modes cannot cause coupling between the states due to symmetry constraints (Koppel *et al* 1984). Defining the auxiliary parameters

$$V_t = 0.5(V_t^{(1)} + V_t^{(2)}), \tag{11a}$$

$$U_t = 0.5(V_t^{(1)} - V_t^{(2)}), \tag{11b}$$

it can be shown that the model Hamiltonian

$$\bar{H}_1 = \sum_{n=t,c} \omega_n a_n^+ a_n + \sum_t V_t(a_t^+ + a_t) - \varepsilon \cos\left(\pi \sum_c a_c^+ a_c\right)$$

$$- \sum_t U_t(a_t^+ + a_t) \cos\left(\pi \sum_c a_c^+ a_c\right), \tag{12}$$

simulates the dynamics of H in $\mathbb{H}_1$ and $\mathbb{H}_v$. Change of sign in front of ε generates $\bar{H}_2$ which simulates the dynamics in $\mathbb{H}_2$.

We now use the Gaussian wave packet propagation technique in the coherent state operator algebra formalism to calculate the dynamics of this system (Gazdy and

Micha 1985; Benjamin 1986; Yuan and Gilmore 1987). In this method, we parameterize the evolution operator as a product of exponentials generated by the elements of the n-dimensional harmonic oscillator algebra,

$$L_n = \{1, a_i^+, a_i, a_i^+ a_j^+, a_i a_j, a_i^+ a_j\}. \tag{13}$$

Since we are particularly interested in the dynamics of the vacuum state, it is convenient to parametrize the evolution operator as

$$U = \exp\left[\sum_i S_1^i a_i^+ + \sum_{i \leqslant j} S_2^{ij} a_i^+ a_j^+\right] \exp\left[\sum_i T_1^i a_i + \sum_{i \leqslant j} T_2^{ij} a_i a_j\right] \times \exp[S_0]. \tag{14}$$

For computational simplicity, we have included only diagonal terms in S_2 and T_2. This corresponds to the thawed Gaussian approximation (Heller 1975). We have dropped the diagonal operators from the ansatz (14) since the phases they contribute do not effect the evolution of the vibrational vacuum state. Substituting the above ansatz in the TDSE, we obtain the following equations of motion for the case of one coupling and one tuning mode. The equations of motion for the case of only the coupling mode are obtained by putting $V_t = U_t = \omega_t = 0$.

$$iS_2^c = 2\omega_c S_2^c - 2c(\varepsilon - u)S_1^{c2}, \tag{15a}$$

$$iS_1^c = 4c(\varepsilon - u)S_1^{c2} T_1^c + \omega_c S_1^c + V_c + 2V_c S_2^c + 2(\varepsilon - u)cS_1^c, \tag{15b}$$

$$iT_2^c = -2\omega_c T_2^c + 2c(\varepsilon - u)(S_1^{c2} - 4S_1^c T_2^c T_1^c), \tag{15c}$$

$$iT_1^c = -\omega_c T_1^c - V_c - 2cT_1^c(-\varepsilon + u) - 8c(-\varepsilon + u)S_1^c T_2^c, \tag{15d}$$

$$iS_2^t = 2\omega_t S_2^t, \tag{15e}$$

$$iS_1^t = \omega_t S_1^t + V_t + 2V_t S_2^t + cU_t(1 + 2S_2^t), \tag{15f}$$

$$iT_2^t = -2\omega_t T_2^t, \tag{15g}$$

$$iT_1^t = -\omega_t T_1^t - V_t - cU_t, \tag{15h}$$

$$iS_0 = V_c S_1^c + V_t S_1^t + (-\varepsilon + u)c[2S_1^{c2} T_1^{c2} - 4S_1^{c2} T_2^c + 2S_1^c T_1^c],$$
$$+ c[-\varepsilon + U_t S_1^t], \tag{15i}$$

where,

$$c = \exp[4T_2^c S_1^{c2}]\exp[-2T_1^c S_1^c], \tag{16a}$$

and

$$u = \sum_t U_t(S_1^t + T_1^t + 2S_2^t T_1^t). \tag{16b}$$

Here the subscripts c and t refer to the coupling and the tuning modes respectively.

3. Results and discussion

We have applied the formalism to evaluate the Franck–Condon spectra of some model one-dimensional systems containing only a coupling mode and a two-mode
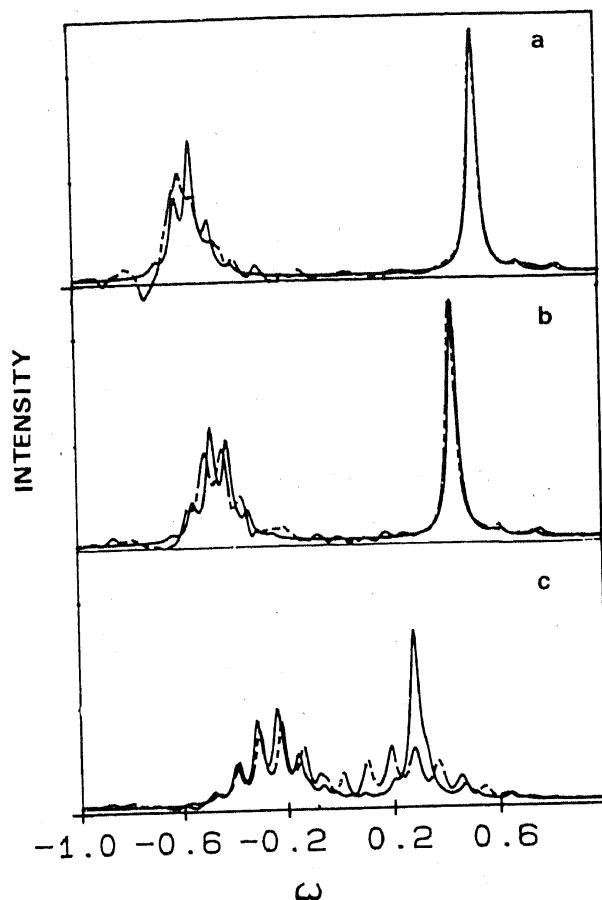
Figure 1. Franck–Condon spectra of model one-dimensional systems for different values of ε at $V_c = 0.318$ and $\omega_c = 0.091$: $\varepsilon = 0.5$ (a), 0.4 (b) and 0.2 eV (c). The solid line indicates the exact spectrum and the dashed line indicates the spectrum obtained by algebraic calculations.

system. The Franck–Condon spectrum is obtained by Fourier-transforming the autocorrelation function $C(t)$ which is given by

$$C(t) = \langle 0 | U | 0 \rangle$$

$$= \exp(S_0). \tag{17}$$

We first discuss the model single-mode systems. The spectra for $\varepsilon = 0.2, 0.4, 0.5$ eV and $V_c = 0.318$ eV are shown in figures 1a–c. For $\varepsilon = 0.2$, the spectrum corresponding to the lower surface has been reproduced fairly well compared to the exact one. In contrast, the upper surface is not well reproduced. Instead of a single peak as seen in the exact spectrum, the GWP produces a harmonic-like progression. As the energy gap ε is increased to 0.4 and 0.5 eV, the agreement between the GWP and the exact spectrum increases. This implies that as the energy gap increases, the validity of GWP improves. The reason for this behaviour can be explained as follows. Consider the case when ε is equal to zero. The adiabatic Hamiltonians associated with the Hamiltonian, (2), on both surfaces are essentially that of a displaced harmonic oscillator. This property is retained for small ε values and hence a harmonic progression for the upper surface for $\varepsilon = 0.2$ eV is seen (the lower surface anyway shows a harmonic-like progression). For large energy gaps i.e., $\varepsilon = 0.4$ and 0.5 eV this

progression is not seen since the deformations in the potential are small and the spectra by GWP are in good agreement with the exact spectra.

Increasing the coupling constant has an effect equivalent to decreasing the energy gap since the stabilization energy is proportional to the square of the coupling constant. As can be seen in figure 2, the quality of the spectra deteriorates when $V_c = 0.718\,\text{eV}$ even for $\varepsilon = 0.5\,\text{eV}$.
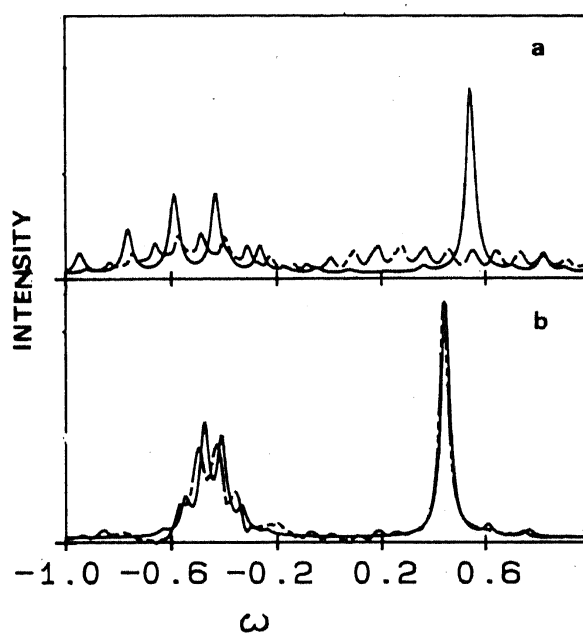
Figure 2. Franck–Condon spectra of mode one-dimensional systems for different values of V_c at $\varepsilon = 0.091$ and $\omega_c = 0.091$: $V_c = 0.718$ (a) and $0.318\,\text{eV}$ (b) (figure conventions as in figure 1).
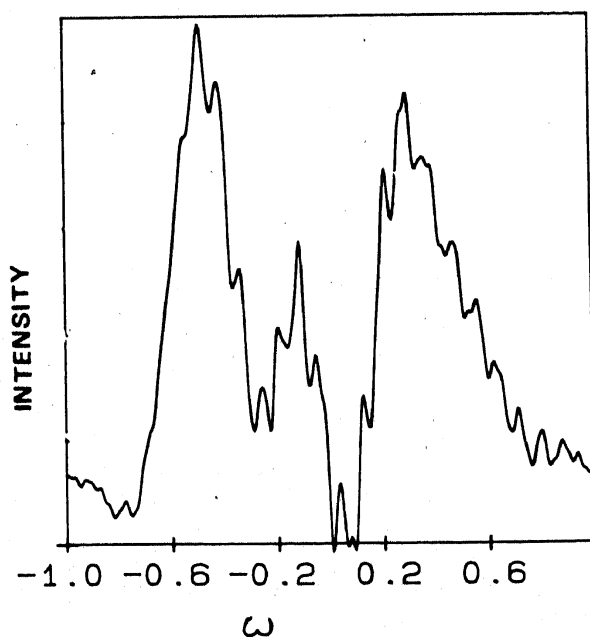
Figure 3. Photoelectron spectrum of energy gap-doubled butatriene by GWP. The band at $0.15\,\text{eV}$ is the mystery band.

As a last example we have calculated the photoelectron spectrum of a model system that is identical to the butatriene cation in all aspects except that the energy gap at the origin is taken as 0·8 eV (double the value of butatriene). This energy gap-doubled butatriene is an example of a two-mode system (Koppel, *et al* 1984). It consists of one coupling mode and one tuning mode. Calculations have been performed by rearranging the term $[U^{-1}\cos(\pi a_c^+ a_c)U]$ in $U^{-1}HU$ as $[e^{Xa^+}e^{Ya}\cos(\pi a^+ a)]$ where X and Y are constants. An interesting feature of this system and the original butatriene system is that the spectrum shows three distinct bands while there are only two electronic states. The middle band in the PES of butatriene was named the mystery band by Brogli and coworkers (Brogli *et al* 1974) for this reason. That this band appears due to vibronic coupling was shown by Cederbaum and co-workers (Koppel *et al* 1984). As can be seen, the spectrum obtained from GWP is in good agreement with the exact spectrum and even the mystery band is generated in it. Less than five vibrational periods were required to obtain the spectrum. We note in passing that the working equations of GWP are quite stiff and required careful handling. In most cases, we have not been able to integrate them beyond about five vibrational periods.

4. Conclusions

In this work we have applied GWP in the coherent state algebraic formalism to calculate the dynamics of non-adiabatic systems, specifically consisting of two electronic states belonging to different symmetries. In GWP the potential is expanded as a Taylor series around the centroid of the wave packet. The difficulty in chosing the centroid of the wave packet which comprises two nuclear wave functions corresponding to two electronic functions having two different centroids and momenta, has led us to construct a new Hamiltonian which is explicitly independent of the involved electronic states. This has been done by mapping the original Hamiltonian on to a Hamiltonian associated with a single electronic surface.

Using the new Hamiltonian we have calculated the spectra for a few model systems comprising two electronic states and one vibrational (coupling) mode. We have also performed calculations for a model system (butatriene) which comprises two vibrational modes. It has been found that for the single vibrational mode case the accuracy of GWP increases as the energy gap between the two surfaces increases. For a small ε, the spectrum associated with the lower surface is well reproduced, but the upper surface dynamics are quite inaccurate. Energy gap-doubled butatriene which is an example of a two-mode system gave a good overall spectrum in spite of minor shifts of the peaks in the spectrum. The central mystery band in butatriene is also well reproduced.