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RESEARCH ARTICLE

Energy transfer to an anharmonic diatomic system

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We model an anharmonic diatomic molecule using deformed creation and annihilation operators such that the energy spectrum generated by a Hamiltonian of the harmonic oscillator's form written in terms of deformed operators is similar to that of a Morse potential. We construct an approximate time evolution operator and evaluate transition probabilities which are compared with those obtained by an expansion in a basis of Morse eigenfunctions. The algebraic results compare favorably with the numerical results.

Keywords: *ab initio*; electronic structure; quantum chemistry; computational chemistry

1. Introduction

Collinear atom–diatom molecular collisions have played an important role in understanding dynamical processes as well as assessing different approximations. Exact quantum mechanical calculations of transition rates between states of a diatomic system have been studied since the early 1960s [1,2] for the case of a harmonic intramolecular potential. Later, Clark and Dickinson [3] calculated the exact quantum mechanical results for a collinear collision between an atom and a Morse oscillator using the reactance matrix K. In certain cases, it is sufficient to use semiclassical approximations in which the motion of the external driving system is treated classically and the internal degrees of freedom are treated quantum mechanically [4,5]. In Ref. [4], use was made of algebraic methods to evaluate the transition probabilities in a collinear collision between an atom and a diatom modeled through a harmonic oscillator. It was found that the inclusion of quadratic terms in the interaction potential was relevant, their relevance depending upon the softness of the intramolecular potential. In Ref. [6], a study of the importance of higher than quadratic terms in the interaction was made, keeping the harmonic model for the intramolecular potential. Most efforts considering a binding Morse potential are focused on adding anharmonic terms to the harmonic potential [7] or by means of the isomorphism between the two-dimensional harmonic oscillator and the one-dimensional Morse potential [8,9] with the disadvantage that the correspondence between the su(2) algebra and the configuration space was not clear. In a recent series of works, the realization of the coordinate and the momentum in terms of creation and annihilation operators of the Morse functions was established [10,11]. Recently, Alvarez *et al.* [12] made a study of the atom–diatom inelastic collision in the semiclassical approximation using the dynamical algebra for the Morse potential bound states. In this work we make use of a different approach consisting of the deformation of the usual harmonic oscillator creation–annihilation operators in such a way that a Hamiltonian of the harmonic oscillator form, when expressed in terms of the deformed operators, yields the energy spectrum of a Morse potential. The commutation relations fulfilled by the deformed operators are similar to those of the SU(2) generators given in Ref. [11], which allows us to write an expansion for the deformed coordinate and momenta in terms of deformed creation and annihilation operators.

2. Theory

Let us consider a diatomic molecule with an anharmonic non-negligible component in interaction with an external perturbation. Numerical and algebraic approaches have been developed for the computation of vibrational transitions when the oscillator is either harmonic or anharmonic. For the anharmonic case it has been common practice to model the molecule by a Morse potential [3,12–19] or an expansion in

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which one incorporates higher than quadratic terms in the displacement coordinate of the molecular potential [20–25].

The deformed annihilation and creation operators $\hat{A}$ and $\hat{A}^\dagger$ are defined as [26]

$$\hat{A} = \hat{a}f(\hat{n}) = f(\hat{n}+1)\hat{a}, \qquad A^\dagger = f(\hat{n})\hat{a}^\dagger = a^\dagger f(\hat{n}+1), \tag{1}$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the usual harmonic oscillator operators and $f(\hat{n})$ is a *deformation function* that depends on the number operator $\hat{n} = \hat{a}^\dagger\hat{a}$.

The commutation relations between the deformed operators are given by

$$\begin{gathered}[\hat{n}, \hat{A}] = -\hat{A}, \qquad [\hat{n}, \hat{A}^\dagger] = \hat{A}^\dagger, \\ [\hat{A}, \hat{A}^\dagger] = (\hat{n}+1)f^2(\hat{n}+1) - \hat{n}f^2(\hat{n}),\end{gathered} \tag{2}$$

and a Hamiltonian of the harmonic oscillator's form written in terms of the deformed operators yields

$$\hat{H}_\mathrm{D} = \frac{\hbar\Omega}{2}(\hat{A}^\dagger\hat{A} + \hat{A}\hat{A}^\dagger) = \frac{\hbar\Omega}{2}(\hat{n}f^2(\hat{n}) + (\hat{n}+1)f^2(\hat{n}+1)). \tag{3}$$

We now choose the deformation function [27]

$$f^2(\hat{n}) = \frac{1-\chi\hat{n}}{1-\chi}, \tag{4}$$

where $\chi = 1/(2N+1)$ with N an integer. Then, the deformed Hamiltonian becomes

$$\hat{H}_\mathrm{D} = \hbar\Omega'\left(\hat{n} + 1/2 - \chi\left(\hat{n} + \frac{1}{2}\right)^2 - \frac{\chi}{4}\right), \tag{5}$$

with $\Omega' = \Omega/(1-\chi)$. Equation (5) is the Hamiltonian of a displaced harmonic oscillator plus a nonlinear contribution quadratic in the number operator. Thus, its eigenfunctions $|n\rangle$ are also eigenfunctions of the harmonic oscillator, but it supports only a finite number of bound states $N_\mathrm{max} = N+1$; n can take values $0, 1, \ldots, N$. Apart from a constant term, the resulting spectrum is similar to that of the Morse and the Pöschl–Teller Hamiltonians [28],

$$E_\mathrm{M} = \hbar\omega_\mathrm{e}\left(n + \frac{1}{2}\right) - \hbar\chi_\mathrm{e}\omega_\mathrm{e}\left(n + \frac{1}{2}\right)^2, \tag{6}$$

corresponding to the integers $0 \le n \le N$. Direct comparison of Equations (5) and (6) allows the identification

$$\omega_\mathrm{e} = \Omega', \qquad \chi_\mathrm{e} = \chi. \tag{7}$$

With this choice for the deformation function and keeping up to linear terms in the anharmonicity parameter χ, the commutation relations for the deformed operators are

$$\begin{gathered}[\hat{A}, \hat{A}^\dagger] = 1 - \frac{\chi}{1-\chi}\hat{n}, \qquad [\hat{A}, \hat{n}] = \hat{A}, \\ [\hat{A}^\dagger, \hat{n}] = -\hat{A}^\dagger,\end{gathered} \tag{8}$$

which coincide with those obtained by Carvajal *et al.* [11] in their study of the SU(2) model for vibrational excitations. In the same work, they gave the displacement and momentum operators as a series expansion involving all powers of the renormalized SU(2) operators. From those expressions we obtained the corresponding expressions in terms of deformed creation and annihilation operators,

$$\hat{x}_\mathrm{D} = \sqrt{\frac{\hbar}{2m\Omega'}}(f_{00} + f_{10}\hat{A}^\dagger + \hat{A}f_{01} + f_{20}\hat{A}^{\dagger^2} + \hat{A}^2 f_{02} + \cdots), \tag{9}$$

$$\hat{p}_\mathrm{D} = i\sqrt{\frac{\hbar m\Omega'}{2}}(g_{10}\hat{A}^\dagger + \hat{A}g_{01} + g_{20}\hat{A}^{\dagger^2} + \hat{A}^2 g_{02} + \cdots), \tag{10}$$

where the expansion coefficients f_{ij} and g_{ij} are functions of the number operator, the explicit form of which was obtained in Ref. [29].

Let us now consider a one-dimensional Hamiltonian with a Morse potential characterized by its depth D and inverse length scale parameter a,

$$H_\mathrm{M} = -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + D[e^{-2ax} - 2e^{-ax}], \tag{11}$$

with μ the reduced mass of the system. The number of bound states supported by the potential is [8]

$$N = \left[K - \frac{1}{2}\right], \tag{12}$$

where the square bracket indicates the integer part and the dimensionless variable K is defined by

$$K^2 = \frac{2\mu D}{\hbar^2 a^2}. \tag{13}$$

Then, once we specify the particle's mass, the inverse scale parameter and the potential's depth, the number of bound states is fixed as well as the angular frequency of the oscillator associated with the Morse potential

$$\omega = \sqrt{\frac{2D}{\mu}}a.$$

Since the expressions we have for the deformed coordinate are independent of the mass, we will set $\hbar = \mu = 1$ in the following and fix the scale parameter

$a = 1/4$ and $D = 8$ so that $K = 16$, $\omega = 1$ and $N = 15$, corresponding to a H_2 molecule in its ground state [9]. In order to test the accuracy obtained when we make an expansion of the deformed coordinate x_D keeping up to first-order terms, we evaluated its matrix elements $\langle i|x_D|j\rangle$ and those of the Morse coordinate $\langle \Psi_i|x|\Psi_j\rangle$ between eigenfunctions of the Morse Hamiltonian Ψ_n characterized by the above parameters [8]. Some of the numerical results are given in Tables 1–3 for three different regions of matrix elements.

We see that even for a system supporting a relatively small number of bound states, such as that under consideration here, the expansion of the deformed coordinate keeping only up to first-order terms already yields matrix elements in reasonable agreement with the exact Morse matrix elements, not only for the lowest part of the spectrum but also for states in the middle and in the high part of the spectrum. In a forthcoming work, we will consider higher than linear terms in the expansion in order to evaluate their contribution.

3. Transition probabilities

Consider now an external interaction $V(x, t)$ that may be present in a collinear collision between an atom and a diatom in the semiclassical approximation [4,12] or due to an interaction with an external electric field [30], among other possibilities. The Hamiltonian for the system is

$$\hat{H} = \hat{H}_0 + V(x, t), \tag{14}$$

where $\hat{H}_0$ is the free Hamiltonian for the diatom. In order to evaluate the transition probabilities we make an expansion in terms of eigenfunctions of the unperturbed Hamiltonian

$$\hat{H}_0|\psi_n\rangle = E_n^{(0)}|\psi_n\rangle, \qquad |\Psi\rangle = \sum_n a_n(t)e^{-iE_n^{(0)}t/\hbar}|\Psi_n\rangle. \tag{15}$$

Substitution into Schrödinger's equation yields the following set of equations for the expansion coefficients:

$$\dot{a}_m = \frac{1}{i\hbar}\sum_n a_n e^{-(i/\hbar)(E_n^{(0)} - E_m^{(0)})t} V_{mn}, \tag{16}$$

with

$$V_{mn} = \langle \Psi_m|V|\Psi_n\rangle, \tag{17}$$

the matrix element of the interaction. For simplicity, we now make a Taylor series expansion of the interaction and write it as

$$V(x, t) = \phi_0(t) + \phi_1(t)x, \tag{18}$$

where x is the displacement from the equilibrium position. We will consider as the unperturbed Hamiltonian a Morse Hamiltonian. Then, solving the set of differential equations given by (16) we obtain the transition probability from state i to state m as

$$P_{i,m}(t) = |a_m(t)|^2, \tag{19}$$

with the initial condition $a_m(t_0) = \delta_{m,i}$.

Instead of a numerical calculation, we could also proceed with an algebraic treatment. To that end we first go into the interaction picture where the evolution due to the unperturbed Hamiltonian has been taken into account [31]

$$i\hbar\frac{\partial U_I}{\partial t} = [U_0^\dagger V(x, t)U_0]U_I \equiv H_I(t)U_I(t), \quad U_I(t_0) = 1, \tag{20}$$

and where we have set the initial time $t_0 \to -\infty$ as that when the interaction is null; U_0 is the time evolution operator corresponding to the unperturbed system, in this case a deformed oscillator whose parameters are fixed by the depth and scale parameters of the Morse system we want to approximate.

Table 1. Matrix elements of the deformed displacement x_D and the Morse coordinate between states 0–0, 0–1, 0–2, 1–1, 1–2 and 1–3.

	0–0	0–1	0–2	1–1	1–2	1–3
$\langle x\rangle$	0.1919	0.7180	−0.092	0.5965	1.0321	−0.1656
$\langle x_D\rangle$	0.1951	0.7071	0.0	0.3332	1.0171	0.0

Table 2. Matrix elements of the deformed displacement x_D and the Morse coordinate between states 5–5, 5–6, 5–7, 6–6, 6–7 and 6–8.

	5–5	5–6	5–7	6–6	6–7	6–8
$\langle x\rangle$	2.6171	1.9191	−0.5055	3.2642	2.1133	−0.606
$\langle x_D\rangle$	2.3444	1.8974	0.0	2.9925	2.0917	0.0

Table 3. Matrix elements of the deformed displacement x_D and the Morse coordinate between states 11–11, 11–12, 11–13, 12–12, 12–13 and 12–14.

	11–11	11–12	11–13	12–12	12–13	12–14
$\langle x\rangle$	6.9579	2.8805	−1.0932	8.3754	3.0741	−1.2280
$\langle x_D\rangle$	8.2072	3.0779	0.0	10.116	3.2914	0.0

The unperturbed time evolution operator is

$$U_0 = \exp\left[-i\Omega t\left(\hat{n}+\frac{1}{2}-\chi\left(\hat{n}+\frac{1}{2}\right)^2-\frac{\chi}{4}\right)\right], \tag{21}$$

and the deformed coordinate x_D is approximated by Equation (9) keeping only up to first-order terms. The deformed coordinate in the interaction picture is then

$$x_\mathrm{D}(t) = \sqrt{\frac{\hbar}{2m\Omega}}\left(f_{00} + \hat{A}e^{-i\Omega t(1-2\chi\hat{n})}f_{01} + f_{10}e^{i\Omega t(1-2\chi\hat{n})}\hat{A}^\dagger\right). \tag{22}$$

Note that due to the nonlinearity of the Hamiltonian the number operator appears in the exponents so that we have a system whose frequency $\Omega(\hat{n}) = \Omega(1-2\chi\hat{n})$ depends upon the number operator. In order to circumvent this difficulty we will replace the number operator by the initial number eigenvalue, thus attaining a frequency that is a function of the degree of excitation of the initial state, and fix the coefficients f_{ij} of the expansion of the coordinate. In this approximation, the interaction picture Hamiltonian can be written as

$$H_\mathrm{I}(t) = \psi_0(t) + \psi_1\hat{a} + \psi_1^*\hat{a}^\dagger, \tag{23}$$

where the time-dependent functions $\psi_n(t)$ are given by

$$\psi_0(t) = \phi_0(t) + \phi_1(t)\sqrt{\frac{\hbar}{2m\Omega}}f_{00}, \tag{24}$$

$$\psi_1(t) = \phi_1(t)\sqrt{\frac{\hbar}{2m\Omega}}f_{10}e^{i\Omega t(1-2\chi n_i)}, \tag{25}$$

and we have used the fact that $f_{01} = f_{10}$. Since the Hamiltonian in the interaction picture has been written as a linear combination of operators that form a finite Lie algebra, we can write the corresponding time evolution operator as a product of exponentials [4,32]

$$U_\mathrm{I} = \prod_{n=0}^{2} e^{\alpha_n X_n}, \tag{26}$$

with the operators X_n arranged in normal order, $X_0 = 1$, $X_1 = \hat{a}^\dagger$, $X_2 = \hat{a}$. Substitution into Schrödinger's equation yields a set of three coupled, first-order, nonlinear ordinary differential equations for the complex functions α_n

$$\dot{\alpha}_0 = -\frac{i}{\hbar}(\psi_0 + \alpha_1\psi_1), \tag{27}$$

$$\dot{\alpha}_1 = -\frac{i}{\hbar}\psi_1^*, \tag{28}$$

$$\dot{\alpha}_2 = -\frac{i}{\hbar}\psi_1. \tag{29}$$

Numerically solving the set of equations given above we can evaluate the temporal evolution of any observable, for instance the transition probabilities are given by

$$P_{i,m}(t) = |\langle m|U_\mathrm{I}(t,t_0)|i\rangle|^2. \tag{30}$$

In the following, we evaluate the transition probabilities as a function of time for several transitions and compare the results from the numerical and algebraic approaches. For the numerical evaluation of the transition probabilities we choose a time-dependent interaction of the form

$$V(x,t) = A_0 sech^2(\beta t)\left(1 + \frac{1}{4}x\right), \tag{31}$$

with $A_0 = E/4$ and $\beta = 1/4\sqrt{E/2}$, reminiscent of the collision between an atom and a diatom (E being the collision energy) in the semiclassical approximation (see Refs. [2,3,12]), and we set the parameters for the Morse potential $N = 15$, $a = 1/4$, $D = 8$ and $\omega = 1$ as before.

In Figure 1, we show the permanency probability (0–0) as a function of the parameter $E/\hbar\omega$ for the cases when the probabilities are evaluated by an expansion in eigenfunctions of the Morse potential (dotted line) and when we apply the algebraic method with deformed operators (full line). The probabilities were evaluated at times where the interaction is less than $10^{-9}A_0$. It can be seen that, for values of the parameter $E/\hbar\omega$ smaller than 10, both methods yield almost the same results. However, for larger values of the parameter, differences begin to appear. For the system under consideration here supporting 15 bound states, an interaction energy of the order of $10\hbar\omega$ is capable of exciting states in the upper part of the spectrum where anharmonic effects are non-negligible. It is important to recall that, in the algebraic method, we have approximated the displacement coordinate by

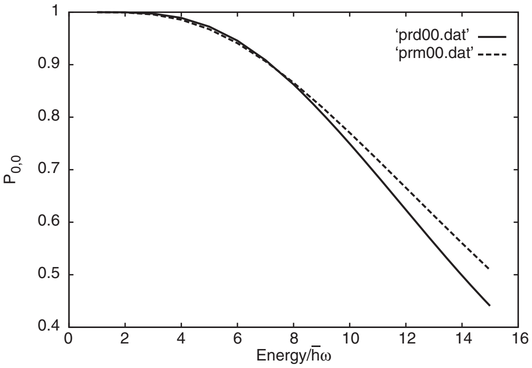

Figure 1. Permanency probability P_{0-0} for a Morse oscillator (dotted line) and a deformed oscillator (full line) as a function of the parameter $E/\hbar\omega$.

a first-order polynomial in terms of deformed operators and neglected quadratic and higher-order terms.

In Figure 2, we show the transition (0–1) as a function of the parameter $E/\hbar\omega$ for the same set of parameters as in the previous figure. It can be seen that the qualitative behavior is similar in both cases, although the quantitative values start to deviate for large values of $E/\hbar\omega$. As in the previous case we believe that this is due to the fact that the expansion of the deformed coordinate in terms of deformed operators was cut at first order, so that only direct transitions between neighboring states were taken into account.

Figure 3 shows the temporal evolution of the transition (1–2) for a fixed value of the strength parameter ($E/\hbar\omega = 5$) in the two approximations discussed above. It is clear that the qualitative behavior is similar along the whole interaction path. We can state that the approximations made in the interaction picture Hamiltonian in order to obtain a closed Lie algebra (see Equation (23)) are adequate since, for this interaction strength (recall that $A_0 = E/4$) and strength parameter, the average occupation number remains close to the initial value and the replacement of the number operator by a constant is reasonable.

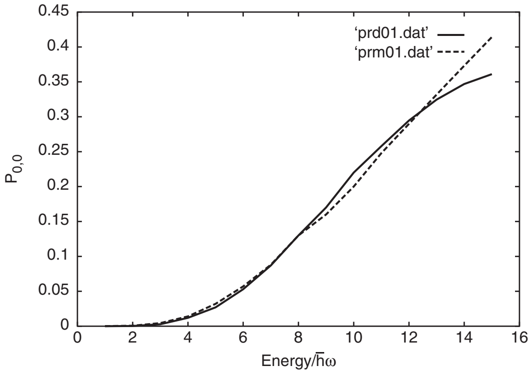

Figure 2. Transition probability P_{0-1} for a Morse oscillator (dotted line) and a deformed oscillator (full line) as a function of the parameter $E/\hbar\omega$.

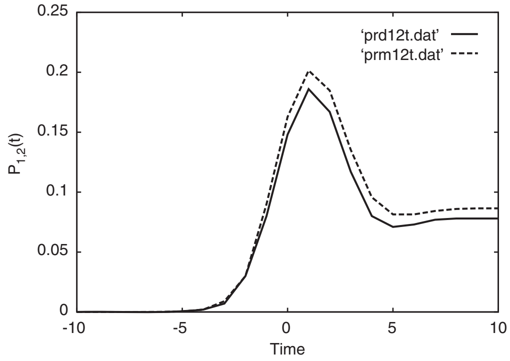

Figure 3. Transition probability (1–2) for a Morse and a deformed oscillator as a function of time.

4. Discussion

In this work we used a deformed algebra in order to describe anharmonic potentials. An adequate choice of the deformation function allowed us to reproduce the energy spectrum of a Morse potential when a potential of the harmonic oscillator form is written in terms of deformed operators. Using these deformed operators we can express the displacement coordinate as a polynomial in terms of the deformed operators. Keeping only up to linear terms in the expansion we calculated its matrix elements between bound states of the spectrum and compared them with those of the Morse coordinate. We found reasonable agreement. We constructed an approximate time evolution operator, from which we calculated permanency and transition probabilities and contrasted them with those obtained by the use of an expansion in terms of eigenfunctions of the Morse potential. The results agree for small and intermediate interaction strengths and differences appear when the strength of the interaction is such that the average value of the number operator $\langle n|U_{\mathrm{I}}^{\dagger}\hat{n}U_{\mathrm{I}}|n\rangle$ during the interaction differs significantly from the initial value n_i, and the assumption of a constant effective frequency $\Omega(n_i) \rightarrow \Omega(1 - 2\chi\hat{n})$ in the exponents of the deformed coordinate and momentum in the interaction picture breaks down (see Equation (22)). The more general case when higher than linear terms are incorporated in the interaction potential can be treated in an approximate form through an iterative method where the part of the interaction that forms a finite Lie algebra is taken into account in an exact form and the rest is treated as a perturbation [7,20]. The relevance of quadratic terms in the interaction and the inclusion of bilinear terms in the expansion of the deformed coordinate and momentum is under study and will be published elsewhere [33].

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