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MOLECULAR VIBRATIONAL STATES DURING A COLLISION

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Abstract

Alternative algebraic techniques to approximate a given Hamiltonian by a harmonic oscillator are described both for time-independent and time-dependent systems. We apply them to the description of a one dimensional atom-diatom collision. From the resulting evolution operator, we evaluate vibrational transition probabilities as well as other time-dependent properties. As expected, the ground vibrational state becomes a squeezed state during the collision.

1 INTRODUCTION

Let us consider the problem of translation-vibration energy transfer in a colinear collision between an atom A and a diatomic molecule BC. The system is described by a Hamiltonian \mathcal{H}

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}_S(x, t),$$

with the molecule modeled by a Morse Hamiltonian

$$\mathcal{H}_0 = \frac{p^2}{2m} + D(e^{-Ax} - 1)^2$$

and we use a semiclassical approach [1] to construct an effective time-dependent interaction \mathcal{V}_S between the particle and the molecule.

A harmonic Hamiltonian is usually related to \mathcal{H}_0 just by making a Taylor series expansion of the potential around $x = 0$ and keeping up to second order terms. However, as we shall show here, this is not necessarily the best harmonic approximation to the Morse Hamiltonian.

In this work, we analyze the time evolution of several physical observables during the collision. To that end, we obtain an approximate time evolution operator by algebraic means. The resulting vibrational transition probabilities are compared with results obtained by other authors [2]. We also evaluate the occupancy of the ground state and the dispersion of the relative position and momentum of the atoms in the diatomic molecule during the collision.

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2 ALGEBRAIC TECHNIQUES

As usual in this type of problem, we shall work in the interaction picture where the behavior of the free molecule is separated from that of the total system. The observables \mathcal{O} evolve in time according to

$$\mathcal{O}_I(t) = \mathcal{U}_0^\dagger \mathcal{O} \mathcal{U}_0, \quad (1)$$

where \mathcal{U}_0 is the time evolution operator corresponding to the Hamiltonian \mathcal{H}_0 , while the time evolution of states is determined by the operator \mathcal{U}_I associated with the interaction picture Hamiltonian

$$\mathcal{H}_I(t) = e^{i\mathcal{H}_0(t-t_0)/\hbar} \mathcal{V}_S(x, t) e^{-i\mathcal{H}_0(t-t_0)/\hbar}. \quad (2)$$

For both time evolution operators we shall make a harmonic approximation described in the following paragraphs.

a) On the harmonic approximation to the Morse Hamiltonian.

The harmonic approximation to the Morse Hamiltonian is usually carried out by just considering the second order Taylor series expansion to the Morse potential

$$D(e^{-Ax} - 1)^2 \approx DA^2x^2. \quad (3)$$

Let us consider the introduction of creation and annihilation operators with arbitrary scale parameter α and a translation parameter d :

$$a = \frac{1}{\sqrt{2}} \left(\alpha x + \frac{i}{\alpha} p \right) - d \quad (4)$$

and

$$a^\dagger = \frac{1}{\sqrt{2}} \left(\alpha x - \frac{i}{\alpha} p \right) - d. \quad (5)$$

The usual commutation relation still holds and the position and momentum operators are given by

$$x = \frac{1}{\sqrt{2}\alpha} (a + a^\dagger + 2d) \quad p = \frac{\alpha}{\sqrt{2}i} (a - a^\dagger). \quad (6)$$

In terms of a and a^\dagger the Morse Hamiltonian can be written as

$$\mathcal{H}_0 = \sum_{i,j=0}^{\infty} G_{ij} a^\dagger{}^i a^j \quad (7)$$

as can be easily shown using the fact

$$e^{\alpha(a+a^\dagger)} = e^{\alpha a^\dagger} e^{\alpha a} e^{-\frac{1}{2}\alpha^2}. \quad (8)$$

The coefficient G_{00} can be interpreted as an estimate of the ground state energy on the harmonic basis determined by the scale parameter α and the translation parameter d . Invoking the variational principle we choose them such that

$$\left. \frac{\partial G_{00}}{\partial d} \right|_{d=d_0} = 0 \quad (9)$$

and

$$\frac{\partial G_{00}}{\partial \alpha} \Big|_{\alpha=\alpha_0} = 0. \quad (10)$$

By direct evaluation of these derivatives it can be shown that the variational conditions are equivalent to the diagonalization of the approximate Hamiltonian

$$H_0 = \sum_{0 \leq i+j \leq 2} G_{ij} a^\dagger a^j \quad (11)$$

taking it to a form similar to the one of a harmonic oscillator

$$H_0 = G_{11} a^\dagger a + G_{00}, \quad (12)$$

but with a variationally optimized G_{00} .

b) Nonperturbative approximate solution for the time-dependent interaction Hamiltonian. In many scattering problems, a perturbative technique is applied to obtain the major effects of the collision on the state of the system. In the case of a collision between an atom and a diatom, even though transition probabilities may be small, perturbative results differ significantly from exact numerical results. Besides, as is well known, there are several successful nonperturbative methods to deal with the parametric harmonic oscillator model. Taking this into account, harmonic approximations to the time-dependent interaction between an atom and a diatom have been studied [3] [4]. In this section, we describe an iterative procedure which has proven to take advantage of this fact in an optimized way [6]. This method has been applied to the calculation of vibrational transition probabilities when the molecule is described by the usual harmonic oscillator derived from a Morse potential.

Once the time-independent Hamiltonian \mathcal{H}_0 has been approximated by the harmonic Hamiltonian H_0 the evolution operator is simply

$$\mathcal{U}_0 = e^{-i/\hbar G_{00} t} e^{-i/\hbar G_{11} t a^\dagger a} \quad (13)$$

thus, the interaction Hamiltonian $\mathcal{H}_I(t)$, can be easily written in terms of the creation and annihilation operators a and a^\dagger

$$\mathcal{H}_I(t) = \sum_{i,j} \Phi_{ij}^{(0)}(t) a^\dagger a^j \quad (14)$$

with the coefficients $\Phi_{ij}^{(0)}$ simple functions of time. Solving this problem corresponds to find an evolution operator $\mathcal{U}_I(t)$ solution of the equation

$$i\hbar \partial_t \mathcal{U}_I = \mathcal{H}_I \mathcal{U}_I, \quad (15)$$

with the initial condition $\mathcal{U}_I(t_0, t_0) = \mathcal{I}$.

In analogy with the time-independent problem we split \mathcal{H}_I as a sum of two terms [6]

$$\mathcal{H}_I = \mathcal{H}_{I_0}^{(I)} + \mathcal{H}_{I_0}^{(II)} \quad (16)$$

with

$$\mathcal{H}_{I_0}^{(I)} = \sum_{0 \leq i+j \leq 2} \Phi_{ij}^{(0)}(t) a^\dagger a^j \quad (17)$$

and

$$\mathcal{H}_{I_0}^{(II)} = \sum_{3 \leq i+j} \Phi_{ij}^{(0)}(t) a^\dagger{}^i a^j. \quad (18)$$

Accordingly, the time evolution operator will be a product,

$$\mathcal{U}_I = \mathcal{U}_{I_0}^{(I)} \mathcal{U}_{I_0}^{(II)} \quad (19)$$

with $\mathcal{U}_{I_0}^{(I)}$ such that

$$i\hbar \partial_t \mathcal{U}_{I_0}^{(I)} = \mathcal{H}_{I_0}^{(I)} \mathcal{U}_{I_0}^{(I)} \quad \mathcal{U}_{I_0}^{(I)}(t_0, t_0) = \mathcal{I}, \quad (20)$$

and $\mathcal{U}_{I_0}^{(II)}$ an analogous solution for the effective Hamiltonian

$$\mathcal{H}_{I_1} = \mathcal{U}_{I_0}^{(I)\dagger} \mathcal{H}_{I_0}^{(II)} \mathcal{U}_{I_0}^{(I)}. \quad (21)$$

Due to the fact that the operators contained in $\mathcal{H}_{I_0}^{(I)}$ form a finite Lie algebra, the evolution operator $\mathcal{U}_{I_0}^{(I)}$ can be expressed as a product of exponentials [7]

$$\mathcal{U}_{I_0}^{(I)} = \prod_{0 \leq i+j \leq 2} e^{-\beta_{ij}^{(0)} a^\dagger{}^i a^j} \quad (22)$$

where the complex functions $\beta_{ij}^{(0)}(t)$ satisfy a set of coupled, first order differential equations which can be solved numerically. With this expression for $\mathcal{U}_{I_0}^{(I)}$ we can construct the Hamiltonian \mathcal{H}_{I_1} . It again comprises a part which forms a finite Lie algebra and a part which does not. The time evolution operator $\mathcal{U}_{I_0}^{(II)}$ is then again written as the product of two evolution operators and we can proceed in a completely analogous manner as before. The evolution operator obtained after k -iterations \mathcal{U}_{I_k} would correspond to the product

$$\mathcal{U}_{I_k} = \mathcal{U}_{I_0}^{(I)} \dots \mathcal{U}_{I_k}^{(I)}. \quad (23)$$

To approximate \mathcal{U}_I by \mathcal{U}_{I_k} corresponds to neglect the Hamiltonian $\mathcal{H}_{I_k}^{(II)}$ with respect to $\mathcal{H}_{I_k}^{(I)}$. We call this the time-dependent iterative Bogolubov transformation (TDITB) method in analogy with its quite efficient time-independent counterpart [8].

3 AN EXAMPLE

Let us consider, a colinear collision of an H_2 molecule with an H_e atom. For the H_2 molecule the parameters of the Morse potential are taken to be $A = 0.183385$ and $D = 2.33509$ so that comparison with the results of [2] can be done. To study how efficient is the TDITB method, consider first the H_2 molecule modeled by the *usual* harmonic oscillator. In Table I we show the transition probability from the ground to the first excited vibrational state for several values of the collision energy $E = N E_0$, $E_0 = \hbar\omega$ with ω as given by Secret and Johnson [5] and for different levels of approximation [6].

TABLE I. Transition probabilities using a harmonic oscillator representing the diatomic molecule and one (P_{01}) or two (P_{02}) iterations for the time-dependent interaction. Results are shown for comparison with the Basis Set (BS) and Exact Quantum Harmonic (UHA) of [5].

$E/\hbar\omega$	P_{01}	P_{02}	BS	UHA
4	9.20(-4)	9.73(-4)	9.84(-4)	7.20(-4)
6	3.50(-2)	3.76(-2)	3.89(-2)	2.95(-2)
8	1.38(-1)	1.47(-1)	1.55(-1)	1.33(-1)
10	2.61(-1)	2.73(-1)	2.87(-1)	2.92(-1)
12	3.45(-1)	3.49(-1)	3.59(-1)	4.28(-1)
16	3.44(-1)	3.29(-1)	2.96(-1)	4.07(-1)

The results obtained with a basis set expansion (BS) are *exact* numerical results within the semiclassical approximation. We also show in the table the exact quantum results of [5] (UHA). The transition probabilities using the TDITB method after one (P_{01}) or two transformations (P_{02}) are also reported. That is, P_{01} corresponds to approximating the time evolution operator in the interaction picture by

$$\mathcal{U}_I = \mathcal{U}_{I_0}$$

with \mathcal{U}_{I_0} the operator which evolves according to the Hamiltonian $\mathcal{H}_{I_0}^{(I)}$. Meanwhile P_{02} corresponds to

$$\mathcal{U}_I = \mathcal{U}_{I_0}^{(I)} \mathcal{U}_{I_1}^{(I)}. \quad (24)$$

In the procedure for finding $\mathcal{U}_{I_0}^{(I)}$ and $\mathcal{U}_{I_1}^{(I)}$, up to quartic, $0 \leq i + j \leq 4$, terms were kept.

Notice that for all the energies considered the transitions obtained after two transformations are closer to the (BS) results than those obtained after one transformation. We also see that if we compare our approximations with the exact quantum results (UHA) then for some energies the first iteration gives closer results than the second one. However this fact may be misleading since in our case the exact results are those obtained in the semiclassical approximation. Because the difference between the results obtained after two transformations and the exact ones is very small we did not pursue these transformations further. We believe that this example shows clearly that our method deals quite efficiently with the time-dependent anharmonicities.

Now, consider the H_2 molecule modeled by the alternative harmonic oscillator defined using the variationally optimized displacement and scale parameters. In this case $d_0 = 0.17$ while α_0 differs from the usual α in less than two percent. In Table II, we show the results obtained for the transition probabilities from the lowest three states for several values of the collision energy. This table also shows the transition probabilities obtained numerically for the exact Morse potential (MP)[2] and the usual harmonic approximation (UHA)[5]. These results do not comprise the semiclassical approximation for the atom-molecule interaction and use is made of the full exponential function.

TABLE II. Transition probabilities using the modified harmonic oscillator for different energies and transitions. The upper value corresponds to Exact Quantum Morse Results (MP), the next corresponds to our's and the last to (UHA).

$E/\hbar\omega$.P(0-1)	P(1-2)	P(0-2)	P(1-3)	P(2-3)	P(0-3)
6	7.31(-3)	1.25(-3)	2.30(-6)			
	2.00(-2)	2.75(-4)	1.44(-6)			
	2.95(-2)	1.42(-3)	1.07(-5)			
10	7.39(-2)	8.15(-2)	1.66(-3)	1.22(-3)	5.47(-2)	1.17(-5)
	2.07(-1)	1.62(-1)	1.22(-2)	2.16(-3)	4.25(-2)	7.04(-5)
	2.92(-1)	2.17(-1)	2.25(-2)	5.39(-3)	7.70(-2)	2.31(-4)
16	2.45(-1)	3.18(-1)	3.38(-2)	5.72(-2)	3.34(-1)	2.72(-3)
	3.13(-1)	1.92(-1)	1.57(-1)	1.72(-1)	2.07(-1)	3.30(-2)
	4.07(-1)	1.56(-1)	3.30(-1)	2.85(-1)	1.89(-1)	9.88(-2)

We observe that our results are in general in better agreement with the exact quantal (MP) results than the (UHA). If we compare P_{02} in Table I with the corresponding results in Table II we see a large difference between them and this is due entirely to the slight change in frequency that we have done defining the frequency of the transformed oscillator. Though the difference in frequencies is rather small the differences in the values of the transition probabilities are rather large, for example, for a collision energy $E/\hbar\omega = 4$ we go from $P_{02} = 9.73 \times 10^{-4}$ to 2.51×10^{-4} which is very close to the (MP) value of 2.46×10^{-4} . This is an indication of the quality of the approximation made for the Morse oscillator.

Once we have constructed the matrix elements of the time evolution operator, we can calculate the survival probability, that is, the probability for the molecule to remain in the initial state. We have done that from a time long before the collision takes place up to a time where the collision is over.

We see that the collision lasts the order of 1.5 time units ($t_{col} \approx 3 \times 10^{-14}$ sec); the permanency probability is one long before the collision begins and starts to decrease around $t_0 = -0.75$ time units reaching an asymptotic value at approximately $t_{as} = 1$ time units. The frequency of the H_2 oscillator is $\omega_{H_2} = 8.054 \times 10^{14}$ /sec and the corresponding period is of the order of $T_{H_2} \approx 3/2t_{col}$ so that the molecule is able to make a couple of oscillations before the collision is over. From this figure it becomes evident why a perturbative treatment of the problem may lead to wrong results. Although the asymptotic transition probability may be small, in a short interval around $t = 0$ the state of the molecule highly differs from the initial state.

In the interaction picture, the creation-annihilation operators can be written in the form

$$a(t) = d_1(t)a^\dagger + d_2(t)a + d_3(t)$$

where $d_i(t)$ are functions of the time, and we have used the fact that the set of operators appearing in the time evolution operators is closed under the operation of commutation. We can now consider the time evolution of the expectation value of the momentum $\langle \mathbf{p} \rangle$, the coordinate $\langle \mathbf{x} \rangle$ and the dispersions Δx and Δp using the expressions for the momentum and the coordinate operators in terms of the creation-annihilation operators.

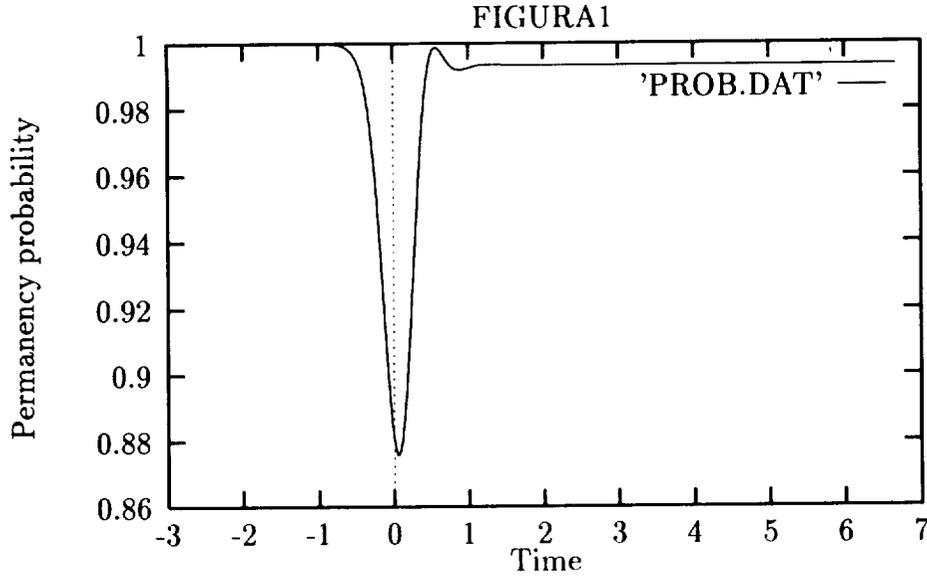


Figure 1: Time dependent survival probability for the ground state of an H_2 molecule colliding with a He atom for a collision energy $E = 4\hbar\omega$.

It can be seen in figure 2 that, when the atom is far apart from the molecule, the average value of the position operator in the ground state is zero as it should since we are dealing with an effective harmonic oscillator.

As the atom approaches the molecule, this one recedes, taking also negative values of the momentum, when $t \approx 0$ the momentum changes sign and the average value of the position initiates an increase towards the origin. Since the collision time is larger than the frequency of oscillation, the projectile is hit again and the oscillator's momentum changes sign, the position does not reach the origin and moves away from the origin. After that, the projectile leaves the range of the interaction and the molecule is left in an excited state as indicated by the oscillatory behavior of the position and momentum operators around the zero value.

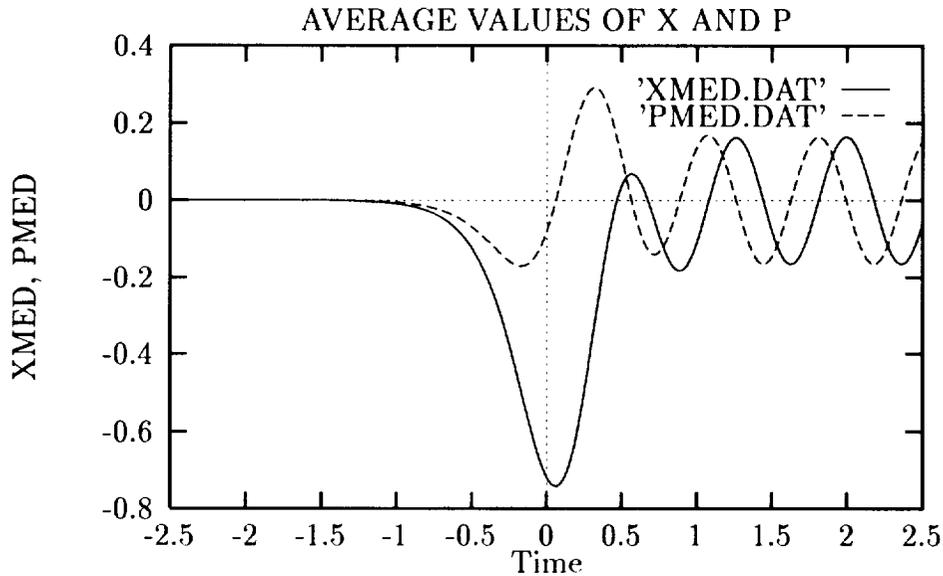


Figure 2: Time evolution of the average values of P (squares) and X (continuous line) as the collision takes place.

Finally, in figure 3 we see that, since we begin with a minimum uncertainty state the dispersion in each coordinate is $\sqrt{1/2}$ and it remains being a minimum uncertainty state during the collision because we are dealing with an harmonic oscillator.

However, due to the time dependence of the parameters defining the oscillator, we can see that there is squeezing in the dispersions which become more pronounced as the energy increases. Notice that as the projectile approaches the molecule, the dispersion in the momentum decreases while that of the coordinate increases in such a way as to keep their product constant. The squeezing of the dispersion reaches its peak value at the time of the collision ($t=0$). The presence of squeezing is to be expected since the time dependence of the creation-annihilation operators which define our harmonic oscillator has the form of a generalized Bogoliubov transformation. Not long ago it was shown that states of light with nonclassical properties can be generated if the frequency of the harmonic oscillator is swept as a function of time [12]. In that work, the authors dealt with a simple time dependence for the frequency of the oscillator in order to obtain exact analytical results. As we have shown here, the presence of these nonclassical properties is due to the time dependence of the frequency irrespective of the functional form used to describe it.

4 CONCLUSIONS

In this work we have shown that a suitable harmonic approximation for the description of an anharmonic potential like, for instance, the Morse potential, can yield very good results when one is looking for properties like the transition probabilities between the vibrational states of the oscillator. We found that a slight change in the parameters defining the oscillator with respect to

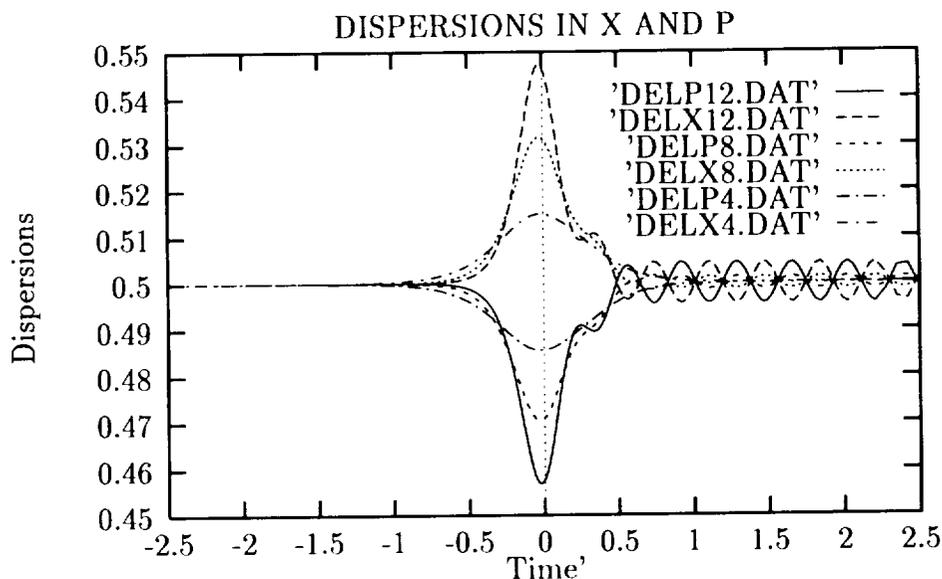


Figure 3: Time evolution of the dispersion of the coordinate and momentum values for the ground state of the molecule during the collision for $E=4\hbar\omega$ (thin lines) and $E=12\hbar\omega$ (thick lines).

their original values, when no optimization is made, can have a great importance for the evaluation of transition probabilities. However, when we evaluate the dispersions and the average values of the position and momentum operators we get essentially the same results for the oscillator before and after the optimization, this leads us to believe that the non classical behavior that we have found, like the squeezing, is a property of the system and not of the particular model we are using for its description.

The method we have used can be taken as a starting point for more accurate calculations when anharmonic potentials are studied. Here, we are searching for the *best* harmonic potential to mimic the anharmonic one and at least part of the information coming from the anharmonic part of the potential is accounted for with the use of the generalized Bogoliubov transformations.

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