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Atom-molecule inelastic scattering: an algebraic approach

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ABSTRACT. Using an SU(2)–based model of triatomic molecules for vibrations and a coherent-state method to extract a classical variable for one of the bonds, we derive a scattering Hamiltonian for one-dimensional atom-diatom collisions which generalizes previous descriptions. The problem of the energy transfer from the atom to a diatomic molecule described by a Morse oscillator is considered in detail. We briefly discuss the generalization of the model to three-dimensional systems.

RESUMEN. Con base en el modelo SU(2) para la descripción de vibraciones moleculares y empleando un método de estados coherentes para extraer una variable clásica de uno de los enlaces, se deduce un hamiltoniano de dispersión para colisiones unidimensionales átomo-diátomo, el cual generaliza las descripciones anteriores. Se considera en detalle el problema de la transferencia de energía del átomo a la molécula diatómica, la cual se describe mediante un oscilador de Morse. Se examina brevemente la generalización del modelo al caso tridimensional.

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1. INTRODUCTION

Algebraic models have recently been proposed for the study of rotation-vibration molecular spectra [1–3]. Both the SU(4) [1–3] and the SU(2) [4–6] algebraic models constitute promising alternatives to the usual integro-differential techniques for the analysis of vibrational spectroscopic data, the latter being specially suited for the incorporation of discrete symmetries in a simple fashion [6]. On the other hand, atom-molecule one-dimensional collision processes have been studied in detail with different degrees of approximation by solving the Schrödinger equation in configuration space [7, 8]. In particular, collisions between an atom and a diatomic molecule represented by a Morse oscillator have been analyzed using classical [9], semiclassical [10] and quantum mechanical treatments [11]. In the last years Lie algebraic methods have also been applied to scattering problems in molecular physics [12–15]. In the framework of these techniques one-dimensional collisions have been studied in conjunction with time evolution operator methods for a variety of molecular potentials, including harmonic, anharmonic and Morse oscillators, where the atom-diatom interaction is usually restricted to an exponential form [13]. For three dimensional systems, however, no algebraic scheme has been implemented and thus one

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needs to resort to a number of computational integro-differential methods to describe such interactions [16].

In two recent papers, we proposed a new algebraic framework, based on the vibron model, that leads to a three-dimensional description of atom-diatom collision processes [17, 18]. Our basic idea was to first consider the atom-diatom system as a triatomic molecule, described algebraically by means of the vibron model. This model incorporates monopole, dipole and quadrupole interactions between the bonds and has been successfully applied to the description of molecular rotation-vibration spectra [1–3]. In addition, an attractive feature of this scheme is that the Hamiltonian and other operators can be transformed to configuration space by means of a coherent state basis, where coordinates can be defined for each bond in the molecule [19, 20]. In particular, a direct connection can be established between the SO(4) limit of the vibron model for diatomic molecules and a Morse potential [21]. Given the parametrized triatomic vibron Hamiltonian described in a $\mathrm{U}_1(4) \times \mathrm{U}_2(4)$ basis, we then apply the coherent-state method to only one of the U(4) spaces, thus extracting a coordinate dependence for the interaction between one of the atoms and the remaining diatom, while the latter is still described algebraically. Although we start from a bound-state description, the formalism can then be analytically continued to positive energies as will be shown in detail in the one-dimensional example below. The result is a mixed coordinate space-algebraic Hamiltonian, which is formally analogous to the ones used in one-dimensional schemes [12–15].As a bonus, all interactions are well defined and we do not need to restrict them in *ad-hoc* fashion to an exponential form [17, 18]. In principle, this Hamiltonian can then be solved in the interaction picture, including the evaluation of matrix elements and classical trajectories [17, 18].

Although the model introduced in Refs. [17, 18] is fully three-dimensional and we are hopeful that it will prove useful for the analysis and interpretation of real inelastic scattering data; its application is still a difficult task. While the diatomic molecule can be described to a good approximation in the vibron model framework, the parametrization of the interaction requires considerable computational trials, as well as the analysis of the approximations involved in the interaction picture. For this reason we have constructed a one-dimensional version of our model based on the $\mathrm{U}_1(2) \times \mathrm{U}_2(2)$ dynamical algebra, which generalizes previous one-dimensional descriptions and is simpler to analyze than the three-dimensional model, but already incorporates most of the attractive features (and difficulties) of the full model. In this case the analytic continuation to positive energies corresponds exactly to a U(1, 1) description of the potential associated to the incoming atom, as we show in the next section. For this system we can compare our results with exact calculations for the interaction of an atom with a Morse potential [11] and can thus gauge the accuracy of our approximations with the objective of extending them to the $3D$ case.

In the next section we introduce the general $\mathrm{U}_1(2) \times \mathrm{U}_2(2)$ algebraic Hamiltonian and derive the corresponding mixed Hamiltonian using the method described before. In Sect. 3 we analyze this Hamiltonian in the interaction picture and the procedure to obtain the wave functions. We use the sudden approximation in Sect. 4 to obtain the time-dependent solutions and describe new closed results for the time-dependent classical trajectories. In Sect. 5 we rewrite the interaction potential in a way which will later allow us to remove the sudden approximation. We present the harmonic limit of the model in Sect. 6, using the interaction potential previously obtained and then analyze the solutions for the case when the dipole moment is null. An interesting variation of the harmonic result is sketched in Sect. 7, while in Sect. 8 we consider a new method of approximation which goes beyond the sudden approximation for Morse oscillators. In Sect. 9 we compare our results with exact calculations carried out by Clark and Dickinson, while in the last section we present our conclusions and discuss how the present analysis can be used as a guide for the study of the three-dimensional model and its applications to real atom-diatom collisions.

2. ATOM-MOLECULE INTERACTION HAMILTONIAN

We start by analyzing the stretching vibrations of triatomic molecules. A straightforward way to deal with this problem consists in considering harmonic interactions between the atoms. This assumption, although physically reasonable for small number of quanta, does not provide an adequate description of the system when the number of phonons increases. One of the simplest potentials displaying anharmonic effects is the Morse potential, which can give rise to dissociation, as expected for molecular systems. We shall consider Morse-like interactions between the atoms of the triatomic molecule in the framework of an algebraic approach, starting by establishing the algebraic representation of the Morse potential in the one dimensional case.

The Hamiltonian of a particle of reduced mass μ under a Morse potential is given by

$$\hat{\mathcal{H}}_{\mathrm{M}} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + D(e^{-\frac{2x}{d}} - 2e^{-\frac{x}{d}}), \tag{1}$$

whose eigenstates we denote by $\mathcal{E}$. These states can be associated with U(2) $\supset$ SO(2) states [22]. In order to see how this isomorphism comes about, consider the radial equation

$$\frac{1}{2}\left(-\frac{1}{r}\frac{d}{dr}r\frac{d}{dr} + \frac{\sigma^2}{r^2} + r^2\right)\phi(r) = (N+1)\phi(r), \tag{2}$$

which corresponds to a two-dimensional harmonic oscillator (in units where $\hbar = \mu = e = 1$) associated to a U(2) symmetry algebra [23]. By carrying out the transformation

$$r^2 = (N+1)e^{-\rho},$$

Eq. (2) transforms into

$$\left[-\frac{d^2}{d\rho^2} + \left(\frac{N+1}{2}\right)^2 (e^{-2\rho} - 2e^{-\rho})\right]\phi(\rho) = -\left(\frac{\sigma}{2}\right)^2\phi(\rho), \tag{3}$$

which can be identified with (1) after defining $x = \rho d$ and multiplying by $\hbar^2/2\mu d^2$, provided that

$$D = \frac{\hbar^2}{8\mu d^2}(N+1)^2, \tag{4}$$

$$\mathcal{E} = -\frac{\hbar^2}{2\mu d^2}m^2, \tag{5}$$

where we have defined $m = \sigma/2$. In the framework of the U(2) algebra, the operator $\hat{N}$ (whose eigenvalues are denoted by N) corresponds to the total number of bosons and is fixed by the potential shape according to (4), while m is the eigenvalue of the SO(2) generator J_z. In order to obtain the possible values of m in terms of N, we recall that a simple realization of the U(2) generators can be given in terms of the number operator $\hat{N}$ and the operators $\hat{J}_\mu$:

$$\{\hat{N}, \hat{J}_x, \hat{J}_y, \hat{J}_z\},$$

with

$$\hat{N} = s^\dagger s + t^\dagger t, \tag{6}$$

$$\hat{J}_z = \tfrac{1}{2}(t^\dagger s + s^\dagger t), \quad \hat{J}_x = \tfrac{i}{2}(t^\dagger s - s^\dagger t), \quad \hat{J}_y = \tfrac{1}{2}(s^\dagger s - t^\dagger t), \tag{7}$$

where $s^\dagger$ (s) and $t^\dagger$ (t) are bosonic operators satisfying the usual commutation relations

$$[s, s^\dagger] = [t, t^\dagger] = 1. \tag{8}$$

All other commutators vanish. The operators (6), (7) satisfy the usual angular momentum commutation relations, which in terms of the raising and lowering operators

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y, \tag{9}$$

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y, \tag{10}$$

are given by

$$[\hat{J}_z, \hat{J}_\pm] = \pm\hat{J}_\pm, \tag{11}$$

$$[\hat{J}_+, \hat{J}_-] = 2\hat{J}_z. \tag{12}$$

Computing $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$, we find

$$\hat{J}^2 = \frac{\hat{N}}{2}\left(\frac{\hat{N}}{2} + 1\right), \tag{13}$$

from which the identification

$$j = \frac{N}{2}, \tag{14}$$

between the eigenvalues j and N associated to $\hat{J}$ and $\hat{N}$, respectively, is readily made. One can show directly from (6)–(7) that $[\hat{J}^2, \hat{N}] = 0$. The set (7) thus defines the SU(2) subalgebra of U(2). In our applications $\hat{N} = N$ is fixed by the interatomic potential.

From the identification (14) we obtain for m, the eigenvalue of J_z, the following values:

$$m = \pm\frac{N}{2}, \pm\frac{(N-2)}{2}, \dots \frac{1}{2} \quad \text{or} \quad 0.$$

According to (5) the Morse energy is given in terms of m^2, which means that the Morse spectrum is reproduced twice. Consequently, when calculating particular spectral properties the m-values must be restricted to be positive. We note that the fact that only part of the U(2) states in the representation $[N]$ correspond to physical states is a peculiarity due to the unphysical nature of the one-dimensional model. In the three-dimensional version of the model the physical states span the full $[N]$ representation of U(4) [17, 18]. For practical purposes we can work with the full representation of U(2) and only impose the $m \geq 0$ restriction when computing transition probabilities, as shown in the subsequent sections. In terms of the U(2) algebra, it is clear from (5) that the Morse Hamiltonian has the algebraic realization

$$\hat{H} = -\frac{\hbar^2}{2\mu d^2}\hat{J}_z^2 = -A\hat{J}_z^2. \tag{15}$$

The eigenfunctions of this Hamiltonian are then specified by the quantum numbers N and m, which are the eigenvalues of the invariant operators of the groups U(2) and SO(2), respectively. For this reason they are denoted in the following form:

$$\begin{array}{ccc} \mathrm{U}(2) & \supset & \mathrm{SO}(2) \\ \downarrow & & \downarrow \\ |[N], & & m\rangle, \end{array} \tag{16}$$

where in this case we take

$$m = \frac{N}{2}, \quad \frac{N-2}{2}, \dots, \frac{1}{2} \quad \text{or} \quad 0. \tag{17}$$

The Morse Hamiltonian (15) can be rewritten in the more convenient form

$$\hat{H} = A\hat{H}^{\mathrm{M}} = \frac{A}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ - \hat{N}), \tag{18}$$

where we have used the relation

$$\hat{J}_z^2 = \hat{J}^2 - \tfrac{1}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+)$$

and added the constant term $\frac{A\hat{N}^2}{4}$ in order to place the ground state at zero energy. The parameters N and A appearing in (18) are related with the usual harmonic and leading-anharmonic constants ω_e and $x_e\omega_e$ used in spectroscopy. To obtain this relation it is convenient to introduce the quantum number

$$v = j - m = \frac{N}{2} - m, \tag{19}$$

which corresponds to the number of quanta in the Morse oscillator as indicated by its eigenvalues

$$v = 0,\, 1,\, 2, \ldots \frac{N-1}{2} \quad \text{or} \quad \frac{N}{2}, \tag{20}$$

for N odd or even, respectively. In terms of v, the Morse eigenfunctions are given by

$$\begin{array}{ccc} \mathrm{U}(2) & \supset & \mathrm{SO}(2) \\ \downarrow & & \downarrow \\ |[N], & & v\rangle, \end{array} \tag{21}$$

where

$$|[N], v\rangle = \sqrt{\frac{(N-v)!}{N!\, v!}}\, (\hat{J}_-)^v |[N], 0\rangle, \tag{22}$$

and $|[N], 0\rangle$ is the Morse vacuum state. In terms of v, the eigenvalues of the Hamiltonian (18) are given by

$$E_{\mathrm{M}} = -\frac{A}{2}(N + 1/2) + A(N+1)(v + 1/2) - A(v + 1/2)^2, \tag{23}$$

from which we make the identification

$$\omega_e = A(N+1), \tag{24}$$

$$x_e\omega_e = A. \tag{25}$$

Thus, in a diatomic molecule the parameters A and N can be determined by the spectroscopic constants ω_e and $x_e\omega_e$.

Before considering the model for the case of a triatomic molecule, we discuss the harmonic limit of the U(2) model. The purpose of this analysis is two-fold. On the one hand it clarifies the physical meaning of the algebraic model. On the other, it paves the way for the subsequent analysis of the harmonic limit in the case of the atom-diatom system. We start by establishing the action of the $\hat{J}_\pm$ operators on the Morse states (21)

$$\hat{J}_+|[N], v\rangle = \sqrt{v(N - v + 1)}\, |[N], v-1\rangle, \tag{26}$$

$$\hat{J}_-|[N], v\rangle = \sqrt{(N - v)(v + 1)}\, |[N], v+1\rangle. \tag{27}$$

Defining the change of scale transformation

$$\bar{b} \equiv \frac{\hat{J}_+}{\sqrt{N}}, \qquad \bar{b}^\dagger \equiv \frac{\hat{J}_-}{\sqrt{N}}, \tag{28}$$

it is clear that

$$\lim_{N\to\infty} \bar{b}\,|[N],v\rangle = \sqrt{v}\,|[N],v-1\rangle, \tag{29}$$

$$\lim_{N\to\infty} \bar{b}^\dagger|[N],v\rangle = \sqrt{v+1}\,|[N],v+1\rangle. \tag{30}$$

which correspond to the harmonic limit of the model, as expected from the role of N in Eq. (4), *i.e.*, for infinite potential depth the Morse potential cannot be distinguished from an harmonic potential. Using the definitions (19) and (28) we can rewrite the commutation relations (12) in the alternative form

$$[\bar{b},\bar{b}^\dagger] = 1 - \frac{2\hat{v}}{N}, \tag{31}$$

where

$$\hat{v} = \frac{\hat{N}}{2} - \hat{J}_0, \tag{32}$$

is the Morse phonon operator corresponding to the definition (19). The limit $N \to \infty$ leads to the contraction of the SU(2) algebra to the Weyl algebra generated by b, $b^\dagger$ and 1, with the usual boson commutation relation $[b,b^\dagger] = 1$. Expression (11) can also be rewritten as

$$[\bar{b},\bar{b}^\dagger] = \frac{2\hat{J}_0}{N}, \tag{33}$$

which means that in the harmonic limit

$$\lim_{N\to\infty} \frac{2J_0}{N} = 1. \tag{34}$$

Relations (28)–(34) indicate the procedure to arrive at the harmonic limit of the model, *i.e.*, the $\hat{J}_+$, $\hat{J}_-$ should be renormalized by dividing by $\sqrt{N}$ and then take the limit $N \to \infty$.

Following the above procedure we obtain for the harmonic limit of the Morse Hamiltonian (18)

$$\begin{aligned}
\lim_{N\to\infty} \frac{1}{N}\hat{H}^{\mathrm{M}} &= \lim_{N\to\infty} \frac{1}{N}\left[\frac{1}{2}\left(\hat{J}_-\hat{J}_+ + \hat{J}_+\hat{J}_-\right) - \frac{\hat{N}}{2}\right] \\
&= \frac{1}{2}(b^\dagger b + bb^\dagger) - \frac{1}{2} \\
&= b^\dagger b,
\end{aligned}$$

which is the usual harmonic oscillator Hamiltonian. Here we have denoted with $b_i^\dagger$ (b_i) the corresponding harmonic creation (annihilation) operators defined by $b_i^\dagger = \lim_{N\to\infty} \bar{b}_i^\dagger$, $b_i = \lim_{N\to\infty} \bar{b}_i$.

We remark that Eq. (28) can be applied in the opposite sense, *i.e.*, as a way to construct the anharmonic representation of harmonic operators. Any given function of b, $b^\dagger$ can be mapped into the same function of $\hat{J}_+$, $\hat{J}_-$ through the correspondence

$$b \to \frac{\hat{J}_+}{\sqrt{N}}, \qquad b^\dagger \to \frac{\hat{J}_-}{\sqrt{N}}. \tag{35}$$

For example, the one-dimensional harmonic oscillator (with atomic units)

$$\hat{H} = \frac{1}{2}(b^\dagger b + bb^\dagger)$$

with eigenvalues $E = v + 1/2$, can be transformed to its anharmonic representation by means of (35) and using Eqs. (13) and (32)

$$\begin{aligned}\hat{H} &\to \frac{1}{2N}(\hat{J}_-\hat{J}_+ + \hat{J}_+\hat{J}_-)\\ &= \frac{1}{N}(\hat{J}^2 - \hat{J}_z^2) = (\hat{v} + 1/2) - \frac{\hat{v}^2}{N},\end{aligned} \tag{36}$$

which corresponds to the algebraic realization of the Morse oscillator. This prescription can be applied to every oscillator in the system and to the interaction terms among them [24]

We now turn our attention to a triatomic molecular system. In this case we assign a $U^i(2)$ algebra to each interatomic interaction, which means that we describe each relative interaction with a Morse potential. In addition, we may include bond-bond interactions using the group generators, as explained below. All relevant operators in the model are then expressed in terms of the generators of the group

$$U^1(2) \otimes U^2(2) \tag{37}$$

which corresponds to the dynamical group of the system. In particular, the Hamiltonian of the system can be expanded in terms of the dynamical group generators, taking into account its hermiticity and its invariance with respect to the symmetry group of the system. There is no point symmetry for $A-A-B$ and $A-B-C$ molecules, while for $A-B-A$ and $A-A-A$ molecules (in one-dimension) it is isomorphic to the permutation group S_2. Since we shall focus on the system H_2–He, we do not worry about the point symmetry of the triatom. The simplest molecular Hamiltonian describing the stretching vibrational excitations can be written as [23]

$$\hat{\mathcal{H}} = A\hat{J}_{z,1}^2 + B\hat{J}_{z,2}^2 + C\hat{J}_{z,1}\hat{J}_{z,2} + D\hat{J}_1 \cdot \hat{J}_2, \tag{38}$$

where $\hat{J}_{\xi,i}$, $\xi = x, y, z$, are the generators of the $SU^i(2)$ groups. A possible basis to diagonalize the Hamiltonian (38) is the one associated to the local mode chain

$$\begin{array}{ccccccccc} U^1(2) & \times & U^2(2) & \supset & SO^1(2) & \times & SO^2(2) & \supset & SO(2) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ |[N_1], & & [N_2]; & & v_1, & & v_2; & & V\rangle, \end{array} \tag{39}$$

where below each group we have indicated the eigenvalues characterizing the invariant operators associated to each group. Explicitly the basis (39) is given by

$$|[N_1],[N_2];v_1,v_2;V\rangle = |[N_1],v_1\rangle\,|[N_2],v_2\rangle, \tag{40}$$

where $|[N_i],v_i\rangle$ are given by (22), and V is the total number of quanta defined as

$$V = v_1 + v_2. \tag{41}$$

The first two terms in (38) correspond to two independent Morse oscillators, as (15) indicates. The third term represents a weak coupling between the oscillators, whose form can be seen by its action on the basis (40)

$$\hat{J}_{z,1}\hat{J}_{z,2}|[N_1][N_2];v_1,v_2;V\rangle = \left(\frac{N_1N_2}{4} - \tfrac{1}{2}(N_1v_2 + N_2v_1) + v_1v_2\right)|[N_1][N_2];v_1,v_2;V\rangle, \tag{42}$$

where (19) was used. Note that in the harmonic limit both N_1 and $N_2 \to \infty$, so that

$$\lim_{N\to\infty}\left(\frac{\hat{J}_{z1}\hat{J}_{z2}}{N} - \frac{N^2}{4}\right) = -\frac{1}{2}(v_1+v_2). \tag{43}$$

The last term $\hat{J}_1 \cdot \hat{J}_2$ gives rise to a strong interaction of the two Morse oscillators. This interaction is not diagonal in the basis (40) and in the harmonic limit it reduced to

$$\begin{aligned}\lim_{N\to\infty}\frac{\hat{J}_1\cdot\hat{J}_2}{N} &= \lim_{N\to\infty}\frac{\hat{J}_{01}\hat{J}_{02}}{N} + \frac{1}{2}\lim_{N\to\infty}\left(\frac{\hat{J}_{+1}\hat{J}_{-2} + \hat{J}_{-1}\hat{J}_{+2}}{N}\right)\\ &= -\tfrac{1}{2}(v_1+v_2) + \tfrac{1}{2}(b_1b_2^\dagger + b_2^\dagger b_1).\end{aligned} \tag{44}$$

The Hamiltonian (38) thus corresponds to the anharmonic form of the simple Hamiltonian

$$H^{\text{h.o.}} = \alpha b_1^\dagger b_1 + \beta b_2^\dagger b_2 + \gamma(b_1^\dagger b_1 + b_2^\dagger b_2) + \delta(b_1^\dagger b_2 + b_2^\dagger b_1). \tag{45}$$

While the Hamiltonian (38) incorporates the dominant interactions in triatomic molecules as shown in several papers on this subject [4–6], it is not the most general one. We propose a simple generalization of (38) consisting of the following molecular Hamiltonian

$$\hat{\mathcal{H}}_{\text{Mol}} = A\hat{J}^2_{z,1} + B\hat{J}^2_{z,2} + C\hat{J}_{z1}\hat{J}_{z2} + D\hat{J}_1\cdot\hat{J}_2 + F\hat{N}_2\hat{J}_{y,1}. \tag{46}$$

We stress that (46) is chosen for simplicity and that in order to include long range polarization or Van der Waals interactions additional terms must be included. Note that the last term in (46) does not conserve the v quantum number and that it is asymmetric in the two bonds. This fact reflects the different roles played by these interactions for the scattering atom-molecule system.

Before we can apply this formalism to atom-molecule scattering, we shall show that Eq. (3) can be analytically continued to positive energies and that this procedure corresponds to a description of the system in terms of the U(1,1) algebra [25] To achieve this goal, we first note that Eq. (3) suggests that the continuous part of the spectrum can be obtained by analytically continuing $m \rightarrow ik$, where k is then proportional to the momentum and in the range $0 \leq k < \infty$. Since (2) and (3) are associated to a U(2) algebra and it is well known that this algebra can be transformed into U(1,1) by analytic continuation [25], we now study the chain of algebras

$$\mathrm{U}(1,1) \supset \mathrm{O}(1,1) \tag{47}$$

arising from (21) by this continuation. The SU(1,1) subalgebra of U(1,1) is generated by the set of operators $\hat{K}_+$, $\hat{K}_-$, $\hat{K}_z$ satisfying the commutation relations [26]

$$[\hat{K}_+, \hat{K}_-] = -2\hat{K}_z, \tag{48}$$

$$[\hat{K}_z, \hat{K}_\pm] = \pm\hat{K}_\pm, \tag{49}$$

where $\hat{K}_\pm = \hat{K}_x \pm i\hat{K}_y$, whose only difference with the SU(2) commutators is the minus sign in (48). The quadratic SU(1,1) invariant is given by

$$\hat{C} = \hat{K}_z^2 - \hat{K}_x^2 - \hat{K}_y^2, \tag{50}$$

which can be related to the linear U(1,1) invariant by the relation [25]

$$\hat{C} = \frac{1}{4}(\hat{M}+1)(\hat{M}-1). \tag{51}$$

This linear invariant takes integer values and for positive energies plays the role of the total boson number N in Eq. (2). A coordinate realization for the $\hat{K}_i$ and $\hat{M}$ operators can be written as [25]

$$\hat{K}_x = \frac{1}{4}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + x^2 + y^2\right), \tag{52}$$

$$\hat{K}_y = \frac{1}{2}\left(\frac{\partial^2}{\partial x \partial y} + xy\right), \tag{53}$$

$$\hat{K}_z = \frac{i}{2}\left(x\frac{\partial}{\partial y} + y\frac{\partial}{\partial x}\right), \tag{54}$$

and

$$\hat{M} = \frac{1}{2}\left(x^2 - y^2 - \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}\right)\right). \tag{55}$$

From these relations it is simple to verify the commutators (48) and (49) and that

$$[\hat{K}_i,\, \hat{M}] = 0, \tag{56}$$

which proves the invariance of $\hat{M}$. Using Eq. (51) and denoting the eigenvalues of $\hat{C}$ by

$$\langle \hat{C} \rangle = j(j+1), \tag{57}$$

we find that

$$M = -(2j+1). \tag{58}$$

The generator $\hat{K}_z$ of (54) has been chosen to be a non-compact generator (associated to O(1,1) in (47)) and thus it will have a continuous spectrum [27]. We are concerned with the simultaneous eigenfunctions of $\hat{M}$ and $\hat{K}_z$, which we denote by $|M,k\rangle$,

$$\hat{M}|M,k\rangle = M|M,k\rangle, \tag{59}$$

$$\hat{K}_z|M,k\rangle = k|M,k\rangle. \tag{60}$$

Returning to the realization (54) and (50) we introduce hyperbolic coordinates

$$x = r\cos h\theta, \tag{61}$$

$$y = r\sin h\theta. \tag{62}$$

In these variables, the operators $\hat{M}$ and $\hat{K}_z$ are given by

$$\hat{M} = \frac{1}{2}\left(r^2 - \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right), \tag{63}$$

$$\hat{K}_z = \frac{i}{2}\frac{\partial}{\partial \theta}. \tag{64}$$

The solutions of Eqs. (59), (60) can be written as

$$\psi_{M,kz}(r,\theta) = \Phi_{M,kz}(r)\, e^{2ik\theta}, \tag{65}$$

where Φ satisfies

$$\frac{1}{2}\left(-\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} - \frac{4k^2}{r^2} + r^2\right)\Phi_{M,k}(r) = M\,\Phi_{M,k}(r), \tag{66}$$

which is the analog of Eq. (2). Finally, carrying out the transformation

$$r^2 = Me^{-\rho}, \tag{67}$$

we find

$$\left[-\frac{d^2}{d\rho^2}+\left(\frac{M}{2}\right)^2\left(e^{-2\rho}-e^{-\rho}\right)\right]\Phi_{M,k}(r)=k^2\Phi_{M,k}(r). \tag{68}$$

This is again the one-dimensional Morse-oscillator equation, but associated to the scattering solutions, $k^2 > 0$. Comparing (68) with (3) we see that $M = N + 1$, in order that both equations arise from the same potential. Also note that k is a continuous variable, since θ in (61) is an hyperbolic angle and hence is not periodic. We have carried out this derivation of the scattering Morse equation in terms of $\mathrm{U}(1,1)$ in order to show that the analytic continuation $m \rightarrow ik$ of Eqs. (2) and (3) has a precise mathematical meaning. We stress the fact that both (3) and (68) correspond to *the same* potential, as long as we take $M = N + 1$. Having done so we return to the $\mathrm{U}_1(2) \times \mathrm{U}_2(2)$ Hamiltonian (46) and derive below a classical coordinate for $\mathrm{U}_2(2)$. Strictly speaking, the scattering Hamiltonian corresponds to $\mathrm{U}_1(2) \times \mathrm{U}_2(1,1)$, but we shall derive an energy surface for the simpler $\mathrm{U}_1(2) \times \mathrm{U}_2(2)$ system and then proceed to carry out the analytic continuation to the positive energies corresponding to a scattering regime.

We now introduce a classical distance between one of the atoms and the center of mass of the other two, by taking the expectation value of (16) with respect to a coherent state basis associated to one of the bonds (*e.g.*, bond number 2) [19–21]

$$|[N];r\rangle=\frac{1}{\sqrt{N!(1+r^2)^N}}\left(s^\dagger+rt^\dagger\right)^N|0\rangle, \tag{69}$$

where $s^\dagger$ and $t^\dagger$ are the two scalar boson creation operators (6), (7) and (8), with even and odd parity, respectively, through which the $\mathrm{U}^2(2)$ algebra is realized [23].The variable r in (69) is a radial parameter, which is related to the distance x between the atom and diatom center of mass by [21]

$$r=\sqrt{\frac{e^{-b(x-x_e)/a_0}}{2-e^{-b(x-x_e)/a_0}}}, \tag{70}$$

where x_e is the value of x for which the Morse potential acquires its minimum value, *i.e.*, if only $B\hat{J}^2_{z,2}$ was present in the Hamiltonian (16), x_e would correspond to the equilibrium bond distance, while b is a potential parameter whose value depends on the molecule to be considered and a_0 is a scale parameter which we take as the Bohr radius. The justification for this change of variable will become clear below. Taking into account the explicit realization (7) of the generators of the $\mathrm{U}^2(2)$ group, we can compute the expectation value of (46) with respect to (69). We arrive at a Hamiltonian which depends on the first bond through the operators $\{\hat{J}_{\alpha,1}\ \alpha = x, y, z\}$, and is a function of the second bond coordinate x:

$$\hat{H}=\hat{H}_0+\hat{V}_1(x)+\hat{V}_2(x)+\hat{V}_3(x), \tag{71}$$

with

$$\hat{H}_0 = h_0(N_1) + A\hat{J}_{z,1}^2, \tag{72}$$

$$\hat{V}_1(x) = -\alpha'\hat{J}_{z,1}\, e^{-\frac{b(x-x_e)}{2a_0}} \left(2 - e^{-\frac{b(x-x_e)}{a_0}}\right)^{\frac{1}{2}}, \tag{73}$$

$$\hat{V}_2(x) = -\beta \left(2e^{-\frac{b(x-x_e)}{a_0}} - e^{-\frac{2b(x-x_e)}{a_0}}\right), \tag{74}$$

$$\hat{V}_3(x) = \gamma'\hat{J}_{y,1}\, e^{-\frac{b(x-x_e)}{a_0}}, \tag{75}$$

where

$$\alpha' = -\tfrac{1}{2}(C+D)N, \tag{76}$$

$$\beta = -\tfrac{1}{4}BN(N-1), \tag{77}$$

$$\gamma' = -\tfrac{1}{2}DN. \tag{78}$$

The potential $\hat{V}_2(x)$ arises from the $\hat{J}_{z,2}^2$ operator in (46) and we see from (74) that the application of (69) and (70) indeed leads to a Morse potential for this term, as expected. In (71) $\hat{H}_0$ corresponds to the Morse-like Hamiltonian of the diatomic molecule, with $h_0(N_1)$ chosen to place the ground state at null energy. In order to understand the meaning of the $\hat{V}_1(x)$ term in the Hamiltonian, it is convenient to recall the explicit realization (7) of the operators $\{\hat{J}_{\xi,1}\}$ in terms of boson operators $s^\dagger(s)$ and $t^\dagger(t)$ [23]. In analogy to the situation in the three-dimensional model [17] where the space is generated by $s^\dagger$ and $p_\mu^\dagger$ boson operators with positive and negative parity, respectively [1], in the one-dimensional case $t^\dagger$ is assigned negative parity while $s^\dagger$ remains with positive parity [23]. Thus $t^\dagger$ is the one-dimensional projection of the $p_\mu^\dagger$ boson and can in fact be identified with $p_0^\dagger$. Given that $t^\dagger$ is odd and $s^\dagger$ is even the operator $\hat{J}_{z,1}$, which appears in $\hat{V}_1(x)$, has odd parity and can be identified with the one-dimensional projection of the dipole interaction. The term $\hat{V}_2(x)$ does not involve the SU(2) operators and as mentioned above corresponds to a Morse-like interaction. Finally, the potential $\hat{V}_3(x)$ contains the even parity operator $\hat{J}_{y,1}$ and can be identified with the monopole interaction considered in previous analyses [7]. We note that the parameter F of (46) does not appear in (76)–(78) because its value was fixed to be $-D/2$ in order to exactly reproduce an exponential potential in (75) and thus be able to compare our results with other calculations [11–13]. In the 3-dimensional model this interaction appears without the need of fixing particular parameter values [17].

The hybrid Hamiltonian (71) depends on the molecular coordinates, through the operators $\hat{J}_{\xi,1}$, and on the relative coordinate x. This coupled system is quite complicated, however, and we need to resort to approximations in order to solve it. When the energy of the projectile is high compared with the molecular vibrational energy an adiabatic approximation can be applied. We can then "freeze" the molecular coordinates by substituting

$\hat{J}_{z,1}$ and $\hat{J}_{y,1}$ in (73) and (75) by appropriate expectation averages defined by

$$\hat{J}_{z,1} \rightarrow \mathcal{J}_{z,1}(v) = \langle j,v|\hat{J}_{z,1}|j,v\rangle = (N2 - v)\,, \tag{79}$$

$$\hat{J}_{y,1} \rightarrow \mathcal{J}_{y,1}(j,v) = \sqrt{\frac{|\langle j,v-1|\hat{J}_{y,1}|j,v\rangle|^2 + |\langle j,v+1|\hat{J}_{y,1}|j,v\rangle|^2}{2}}, \tag{80}$$

where $|j,v\rangle$ corresponds to the vibrational states of the molecule (21), characterized by the number of bosons $N_1 = 2j$ and the number of quanta $v = j - m$ [23]. The substitution of (79) and (80) into (73) and (75), respectively, leads to an v-dependent (or m-dependent) Hamiltonian which is only a function of the relative coordinate x. This approximation allows the computation of classical trajectories followed by the atom. This task is achieved by writing the classical Lagrangian for the system, which is given in general by

$$L = E_K - V(x), \tag{81}$$

where E_K and $V(x)$ correspond to the kinetic and potential energies, respectively. In our case we are interested in describing the classical trajectory of an atom subject to the interactions (71). According to (79), the contribution (72) is a constant during the motion of the atom and consequently we identify the potential energy felt by the atom with the energy surface (72)–(75):

$$V(x) = V_1(x) + V_2(x) + V_3(x). \tag{82}$$

We note that (82) generalizes the exponential interaction $V_3(x)$ assumed in previous one-dimensional analyses [12–14]. Once the form of the potential has been established, we can consider the classical equations of motion for the incoming particle. Since x corresponds to the relative coordinate from the atom to the diatom center of mass, we write the kinetic energy in the form

$$E_K = \frac{\mu}{2}\dot{x}^2, \tag{83}$$

where μ is the reduced mass given by

$$\mu = \frac{(m_A + m_B)m_C}{m_A + m_B + m_C}, \tag{84}$$

where m_A and m_B correspond to the diatomic molecule, and m_C is the mass of the incoming atom.

The Lagrangian is then given by

$$\begin{aligned} L = {} & \frac{\mu}{2}\dot{x}^2 + \alpha e^{-b(x-x_e)/2a_0}(2 - e^{-b(x-x_e)/a_0})^{\frac{1}{2}} \\ & - \beta(e^{-2b(x-x_e)/a_0} - 2e^{-b(x-x_e)/a_0}) - \gamma e^{-b(x-x_e)/a_0}, \end{aligned} \tag{85}$$

with

$$\alpha = \alpha' \mathcal{J}_{z,1}(m),$$

$$\gamma = \gamma' \mathcal{J}_{y,1}(m).$$

The differential equations to be solved are

$$\dot{x} = P_x/\mu, \tag{86}$$

$$\begin{aligned} \dot{P}_x = &-\frac{\alpha b}{2a_0} e^{-b(x-x_e)/2a_0} \left(2 - e^{-b(x-x_e)/a_0}\right)^{\frac{1}{2}} \\ &+ \frac{\alpha b}{2a_0} e^{-3b(x-x_e)/2a_0} \left(2 - e^{-b(x-x_e)/a_0}\right)^{-\frac{1}{2}} \\ &+ \frac{2\beta b}{a_0} \left(e^{-2b(x-x_e)/a_0} - e^{-b(x-x_e)/a_0}\right) \\ &+ \frac{\gamma b}{a_0} e^{-b(x-x_e)/a_0}, \end{aligned} \tag{87}$$

where $\dot{P}_x$ is the conjugate momentum of x. The solution of the set of Eqs. (86)–(87) gives rise to the classical trajectory $x(t)$, whose substitution in (72)–(75) leads a Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \tag{88}$$

with a time-dependent interaction given by

$$\hat{V}(t) = \hat{V}_1(t)\hat{J}_{z,1} + \hat{V}_2(t) + \hat{V}_3(t)\hat{J}_{y,1} + \hat{V}_4(t)\hat{J}_{x,1}, \tag{89}$$

where

$$\hat{V}_1(t) = \tfrac{1}{2}(C+D)N\mathcal{J}_{z,1} e^{-b(x(t)-x_e)/2a_0} \left(2 - e^{-b(x(t)-x_e)/a_0}\right)^{\frac{1}{2}}, \tag{90}$$

$$\hat{V}_2(t) = -\tfrac{1}{4}BN(N-1)\left(e^{-2b(x(t)-x_e)/a_0} - 2e^{-b(x(t)-x_e)/a_0}\right), \tag{91}$$

$$\hat{V}_3(t) = -\tfrac{1}{2}DN\mathcal{J}_{y,1} e^{-b(x(t)-x_e)/a_0}, \tag{92}$$

$$V_4(t) = 0. \tag{93}$$

We have included the potential $V_4(t)$ in order to show that $\hat{V}(t)$ can be expressed in terms of a set of operators which closes into a Lie algebra.

3. TIME-EVOLUTION OPERATOR

We now turn our attention to the eigenfunctions of the atom-molecule interaction Hamiltonian. A suitable procedure to obtain the wave functions of a Hamiltonian of the form (88) is provided by the interaction picture [28]. In the framework of this scheme the wave function $\psi(t)$ is given in terms of the time evolution operator

$$\psi(t) = U(t, t_0)\psi(t_0),$$

where the wave function $\psi(t_0)$ corresponds to an eigenfunction of $\hat{H}_0$, provided that $\hat{V}(t_0) = 0$. In our case

$$\psi(t_0) = |[N_1], m\rangle. \tag{94}$$

In turn, the evolution operator $U(t, t_0)$ can be written in the form [28].

$$U(t, t_0) = U^{(0)}(t, t_0)U_I(t, t_0), \tag{95}$$

where $U^{(0)}(t, t_0)$ is the time-evolution operator corresponding to H_0:

$$U^{(0)}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}_0(t-t_0)}, \tag{96}$$

while $U_I(t, t_0)$ satisfies the equation

$$i\hbar\frac{\partial U_I(t, t_0)}{\partial t} = \hat{V}_I(t)U_I(t, t_0) \tag{97}$$

with

$$\hat{V}_I(t) = e^{\frac{i}{\hbar}\hat{H}_0(t-t_0)}\hat{V}(t)e^{-\frac{i}{\hbar}\hat{H}_0(t-t_0)}. \tag{98}$$

Now the problem reduces to solving the differential equation (97) for $U_I(t, t_0)$. This in general is still a difficult task, and consequently approximations for $\hat{V}_I(t)$ must be sought.

Since we are working in an algebraic framework we look for approximations which are based on algebraic considerations, such as the one arising from the following theorem [29].

THEOREM: The solutions of equations of the form

$$\frac{d\hat{U}(t)}{dt} = \hat{A}(t)\hat{U}(t), \quad U(0) = 1, \tag{99}$$

where $\hat{A}(t)$ is an operator which can be written as a linear combination of generators $\hat{X}_i$ of a Lie algebra

$$\hat{A}(t) = \sum_{i=1}^{k} a_i(t)\hat{X}_i, \quad k \text{ finite}, \tag{100}$$

can be written in the form

$$\hat{U}(t) = \prod_{i=1}^{k} \exp(g_i(t)\hat{X}_i). \tag{101}$$

The coefficients $a_i(t)$ are scalar functions of t and the operators $\hat{X}_i$ time-independent. It is further required that the Lie algebra generated by the $\hat{X}_i$ under the commutator be of finite dimension [29].

This theorem implies that if we can express the interaction potential $\hat{V}_I(t)$ as in (100), then the solution for the evolution operator will be given in the form (101). The algebraic space in our hybrid model corresponds to an SU(2) Lie algebra and thus the potential $V(t)$ [Eq. (89)] is given in terms of a linear combination of the SU(2) generators. The approximations we propose in the following sections linearize the interaction potential $\hat{V}_I(t)$ in the SU(2) algebraic space in order for (101) to remain valid.

4. SUDDEN APPROXIMATION

The simplest way to obtain an interaction potential $\hat{V}_I(t)$ linear in the $\hat{J}_{\xi,1}$ corresponds to the sudden approximation, in which the interaction time is so short that $\hat{V}(t)$ can be taken as a pulse ($\Delta t \to 0$) in time. If this is the case the expansion of (98)

$$\hat{V}_I(t) = \hat{V}(t) + \frac{i}{\hbar}[H_0, \hat{V}(t)]\Delta t + \ldots \tag{102}$$

gives $\hat{V}_I(t) = \hat{V}(t)$, which is equivalent to assume a null commutator between $\hat{H}_0$ and $\hat{V}(t)$. In this approximation the differential equation to be solved reduces to

$$i\hbar \frac{\partial U_I(t,t_0)}{\partial t} = \hat{V}(t) U_I(t,t_0), \tag{103}$$

which has the form (99). The time evolution operator is then given by

$$U_I(t) = e^{-\frac{i}{\hbar}g_1(t)\hat{J}_x} e^{-\frac{i}{\hbar}g_2(t)\hat{J}_y} e^{-\frac{i}{\hbar}g_3(t)\hat{J}_z} e^{-\frac{i}{\hbar}g_4(t)}, \tag{104}$$

where we have deleted the subindex 1 in $\hat{J}_{\xi,1}$ to simplify the notation.

Substituting (104) into (103) we find the differential equations satisfied by the functions $g_i(t)$. By means of the modified Baker-Campbell-Hausdorff formula [26]

$$e^{\hat{A}} B e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!}[\hat{A}, [\hat{A}, \hat{B}]] + \frac{1}{3!}[\hat{A}, [\hat{A}, [\hat{A}, \hat{B}]]] + \ldots \tag{105}$$

they can be written as

$$\begin{pmatrix} \dot{g}_1(t) \\ \dot{g}_2(t) \\ \dot{g}_3(t) \\ \dot{g}_4(t) \end{pmatrix} = \begin{pmatrix} 1 & \sin(g_1(t)/\hbar)\tan(g_2(t)/\hbar) & -\cos(g_1(t)/\hbar)\tan(g_2(t)/\hbar) & 0 \\ 0 & \cos(g_1(t)/\hbar) & \sin(g_1(t)/\hbar) & 0 \\ 0 & -\sin(g_1(t)/\hbar)/\cos(g_2(t)/\hbar) & \cos(g_1(t)/\hbar)/\cos(g_2(t)/\hbar) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ V_3(t) \\ V_1(t) \\ V_2(t) \end{pmatrix}. \tag{106}$$

The solution of this system of differential equations leads to the time evolution operator $U(t)$. The vibrational transition probabilities $P(|jm\rangle \to |jm'\rangle)$ of the diatomic molecule can in turn be obtained from $U(t, t_0)$ by means of the scattering matrix

$$\hat{S} = \hat{U}(-\infty, +\infty) \tag{107}$$

as

$$P(|jm\rangle \to |jm'\rangle) = |\langle jm'|\hat{S}|jm\rangle|^2. \tag{108}$$

Explicitly,

$$P(|jm\rangle \to |jm'\rangle) = |\langle jm'|e^{-\frac{i\beta_1}{\hbar}\hat{j}_z} e^{-\frac{i\beta_2}{\hbar}\hat{j}_y}|jm\rangle|^2, \tag{109}$$

where the parameters

$$\begin{aligned} \beta_1 &= g_1(-\infty, +\infty)/\hbar, \\ \beta_2 &= g_2(-\infty, +\infty)/\hbar, \end{aligned} \tag{110}$$

correspond to the asymptotic values of the functions $g_i(t)$ in (106). A closed expression for (109) in terms of Wigner's D-functions can be found by inserting a complete set of states $|jm\rangle$:

$$P(|jm\rangle \to |jm'\rangle) = \left| \sum_{\tau\alpha} e^{-i\beta_1\tau} d^{j\dagger}_{\tau m'}\left(-\frac{\pi}{2}\right) d^{j}_{\tau\alpha}\left(-\frac{\pi}{2}\right) d^{j}_{\alpha m}(\beta_2) \right|^2. \tag{111}$$

In general the system of equations (106) is difficult to solve analytically and the functions must be calculated numerically. However, there are two cases, which we discuss in the next subsections, where analytic solutions can be found both for the classical trajectories and for the functions $g_i(t)$.

4.1. Exponential interaction potential

If the Hamiltonian (71) contains only the potential $\hat{V}_3(x)$,

$$\hat{H} = \hat{H}_0 + \hat{V}_3(x), \tag{112}$$

the total energy is given by

$$E = \frac{1}{2}\mu\dot{x}^2 + \gamma p e^{-bx/a_0}, \tag{113}$$

where we have defined

$$p \equiv e^{\frac{bx_e}{a_0}}. \tag{114}$$

The evolution operator takes the simple form

$$U(t) = e^{-\frac{ig_2(t)}{\hbar}\hat{j}_y}, \tag{115}$$

where $g_2(t)$ satisfies the equation

$$\dot{g}_2 = \gamma p e^{-bx/a_0}. \tag{116}$$

The solution for the classical trajectories is well known [10] and is given by

$$e^{-bx/a_0} = \frac{E}{\gamma p}\operatorname{sech}^2\left(\sqrt{\frac{E}{2\mu}}\,\frac{bt}{a_0}\right), \tag{117}$$

which leads to the solution

$$g_2(t_0,t) = \sqrt{2E\mu}\,\frac{a_0}{b}\left[\tanh\left(\sqrt{\frac{E}{2\mu}}\,\frac{bt}{a_0}\right)\right]_{t_0}^{t}, \tag{118}$$

for (116). In the limit $t \to \infty$ and $t_0 \to -\infty$ we have

$$g_2(-\infty,+\infty) = \frac{2a_0}{b}\sqrt{2E\mu} \tag{119}$$

and the scattering matrix takes the form

$$\hat{S} = e^{-\frac{2ia_0\sqrt{2E\mu}}{b\hbar}\hat{j}_y}. \tag{120}$$

According to (108) the transition probability from state $|jm\rangle$ to $|jm'\rangle$ is given by

$$P(|jm\rangle \to |jm'\rangle) = |d^j_{mm'}(\beta_I)|^2, \tag{121}$$

where we have introduced the $d^j_{mm'}$ functions [30] and

$$\beta_I = \frac{2a_0}{b\hbar}\sqrt{2E\mu}. \tag{122}$$

Expression (121) was obtained previously by Levine and Wulfman [12] for the vibrational energy transfer between an atom and a Morse oscillator in a linear collision as well as by Frank et al [17] in the one-dimensional limit of the three dimensional algebraic approach to atom-diatom collisions.

4.2. Exponential and Morse interaction potentials

When the Morse potential (74) is added to (112) it is still possible to find a closed expression for the transition probabilities. In this case the Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{V}_2(x) + \hat{V}_3(x), \tag{123}$$

with classical total energy

$$E = \frac{1}{2}\mu\dot{x}^2 + \gamma p e^{-bx/a_0} + \beta p^2 e^{-2bx/a_0} - 2\beta p e^{-bx/a_0}, \tag{124}$$

with p given by (114). The evolution operator now has the form

$$U(t) = e^{-\frac{ig_2(t)}{\hbar}\hat{J}_y} e^{-\frac{ig_4(t)}{\hbar}}, \tag{125}$$

leading to the differential equations

$$\dot{g}_2 = \gamma p e^{-bx/a_0}, \tag{126}$$

$$\dot{g}_4 = \beta p(p e^{-2bx/a_0} - 2e^{-bx/a_0}). \tag{127}$$

In order to obtain the classical trajectories we rewrite (124) as

$$z^2 - 1 = \frac{\mu a_0^2 \dot{z}^2}{2Eb^2}, \tag{128}$$

where

$$z = \left(y + \frac{2\beta - \gamma}{2E}\right) \Big/ \sqrt{\frac{\beta}{E} + \frac{(2\beta-\gamma)^2}{4E^2}}$$

and

$$yp = e^{bx/a_0}.$$

The solution to (128) is then given by

$$\cosh\left(\sqrt{\frac{2E}{\mu}}\frac{bt}{a_0} + C\right) = \left(\frac{e^{bx/a_0}}{p} + \frac{2\beta-\gamma}{2E}\right) \Big/ \sqrt{\frac{\beta}{E} + \frac{(2\beta-\gamma)^2}{4E^2}}, \tag{129}$$

where C is a constant to be determined. At the classical turning point $t = 0$ and $x = \delta$ (maximal approximation), there is no kinetic energy and (124) becomes

$$E = \gamma p e^{-b\delta/a_0} + \beta p^2 e^{-2b\delta/a_0} - 2\beta p e^{-b\delta/a_0} \tag{130}$$

or

$$2\beta - \gamma = \beta p e^{-b\delta/a_0} - \frac{E}{p} e^{b\delta/a_0}, \tag{131}$$

while (129) reduces to

$$\cosh(C) = \left(\frac{2E}{p} e^{b\delta/a_0} + 2\beta - \gamma \right) \Big/ \sqrt{4E\beta + (2\beta - \gamma)^2}. \tag{132}$$

The substitution of (131) into (132) leads to the condition

$$\cosh(C) = 1,$$

which implies that $C = 0$. From (129) we find

$$\frac{e^{bx/a_0}}{p} = -\frac{2\beta - \gamma}{2E} + \sqrt{\frac{\beta}{E} + \frac{(2\beta - \gamma)^2}{4E^2}} \cosh\left(\sqrt{\frac{2E}{\mu}} \frac{bt}{a_0} \right), \tag{133}$$

which can be introduced into (126) to obtain

$$\dot{g}_2(t) = \gamma \left[-\frac{2\beta - \gamma}{2E} + \sqrt{\frac{\beta}{E} + \frac{(2\beta - \gamma)^2}{4E^2}} \cosh\left(\sqrt{\frac{2E}{\mu}} \frac{bt}{a_0} \right) \right]^{-1}$$

with solution

$$g_2(t_0, t) = \frac{\gamma a_0}{b\sqrt{A_1 A_2}} \sqrt{\frac{2\mu}{E}} \left[\arctan\left(\sqrt{\frac{A_2}{A_1}} \tanh\left(\sqrt{\frac{E}{2\mu}} \frac{bt}{a_0} \right) \right) \right]_{t_0}^{t}, \tag{134}$$

where we have defined

$$A_1 = \sqrt{\frac{\beta}{E} + \frac{(2\beta - \gamma)^2}{4E^2}} + \frac{\gamma - 2\beta}{2E} = \frac{e^{b\delta/a_0}}{p}, \tag{135}$$

$$A_2 = \sqrt{\frac{\beta}{E} + \frac{(2\beta - \gamma)^2}{4E^2}} - \frac{\gamma - 2\beta}{2E} = \frac{\beta p}{E} e^{-b\delta/a_0}. \tag{136}$$

Taking the limit $t \to \infty$ and $t_0 \to -\infty$ we obtain for (134)

$$g_2(-\infty, +\infty) = \frac{2\gamma a_0}{b} \sqrt{\frac{2\mu}{A_1 A_2 E}} \arctan\sqrt{\frac{A_2}{A_1}}. \tag{137}$$

We note that for $\beta \to \infty$ we recover the function (119). An analogous procedure leads to

$$g_4(-\infty, +\infty) = \frac{2\beta a_0}{b}\sqrt{\frac{2\mu}{EA_1A_2}}\left(\frac{A_1 - A_2}{2A_1A_2} - 2\right)\arctan\sqrt{\frac{A_2}{A_1}} + \frac{a_0\beta}{bA_1A_2}\sqrt{\frac{2\mu}{E}}. \tag{138}$$

Finally, from (125) we obtain the transition probabilities

$$P(|jm\rangle \to |jm'\rangle) = |d^j_{m,m'}(\beta_I)|^2, \tag{139}$$

where

$$\beta_I = \frac{2\gamma a_0}{b\hbar}\sqrt{\frac{2\mu}{A_1A_2E}}\arctan\sqrt{\frac{A_2}{A_1}}. \tag{140}$$

5. INTERACTION POTENTIAL

Although the use of the sudden approximation simplifies the analysis, much of the molecular identity is lost. The Hamiltonian $\hat{H}_0$ is not present in Eq. (103) and thus cannot influence the probability distribution, since the sudden approximation neglects the molecular vibrational energy when compared with the collision energy, turning the vibrational structure of the molecule irrelevant.

Even though these high energy collision processes are suitable to describe some limiting physical situations, it is clear that a more general approach is required if we want to describe the collision in greater detail. In this section we rewrite the interaction potential in a way that will allow us to go beyond the sudden approximation.

We first note that taking into account the commutation relations

$$\begin{aligned}
[\hat{J}_z^2, \hat{J}_y] &= -\hat{J}_y - 2i\hat{J}_z\hat{J}_x, \\
[\hat{J}_z^2, \hat{J}_x] &= -J_x + 2i\hat{J}_z\hat{J}_y,
\end{aligned}$$

and (105), it is possible to rewrite the interaction potential (98) in the form (see Appendix A)

$$\hat{V}_I(t) = \frac{iV_3(t)}{\sin(2At/\hbar)}\left[e^{-\frac{iAt}{\hbar}}\hat{J}_y\cos\left(\frac{2At\hat{J}_z}{\hbar}\right) - e^{\frac{iAt}{\hbar}}\cos\left(\frac{2At\hat{J}_z}{\hbar}\right)\hat{J}_y\right] + V_1(t)\hat{J}_z + V_2(t). \tag{141}$$

This expression is not a linear function of the SU(2) generators and consequently (104) ceases to be valid. We next proceed to obtain an appropriate linear approximation for (141).

6. HARMONIC LIMIT

An straightforward way to obtain a linear expansion for $\hat{V}_I(t)$ is to consider the harmonic limit. This limit was analyzed in Sect. 2, and implies taking the limit $N \to \infty$. From (34) we have that in this limit $2J_z/N$ becomes the identity operator.

Applying this result to the non linear part of the interaction potential (141) we obtain

$$\lim_{N\to\infty} \hat{V}_I(t) = \cos(\omega_0 t)V_3(t)\hat{J}_y + V_1(t)\hat{J}_z + V_2(t), \tag{142}$$

where we introduced the harmonic constant defined by

$$\omega_0 \equiv \frac{\omega_e}{\hbar}. \tag{143}$$

The potential (142) is linear in the SU(2) generators and consequently (104) is valid. Substitution of (104) and (142) in (97) leads to the set of differential equations

$$\begin{pmatrix} \dot{g}_1(t) \\ \dot{g}_2(t) \\ \dot{g}_3(t) \\ \dot{g}_4(t) \end{pmatrix} = \begin{pmatrix} 1 & \sin(g_1(t)/\hbar)\tan(g_2(t)/\hbar) & -\cos(g_1(t)/\hbar)\tan(g_2(t)/\hbar) & 0 \\ 0 & \cos(g_1/\hbar) & \sin(g_1(t)/\hbar) & 0 \\ 0 & -\sin(g_1(t)/\hbar)/\cos(g_2(t)/\hbar) & \cos(g_1(t)/\hbar)/\cos(g_2(t)/\hbar) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ V_{31}(t) \\ V_1(t) \\ V_2(t) \end{pmatrix} \tag{144}$$

where we have defined

$$V_{31}(t) \equiv \cos(\omega_0 t)V_3(t). \tag{145}$$

Once we know the solution of (144) the transition probabilities can be computed using (109). For a general Hamiltonian of the type (71) the solutions to (144) are obtained numerically, but again it is possible to find closed expressions for particular interactions, as we now show.

6.1. *Exponential interaction potential*

When the dipole and Morse interactions do not contribute to the atom-diatom interaction, the energy of the system is again given by (113)–(114) with classical trajectories (117). The evolution operator, however, should now satisfy

$$i\hbar\frac{d\hat{U}(t)}{dt} = V_{31}(t)\hat{J}_y\hat{U}(t), \tag{146}$$

the solution of which is given by

$$U(t) = e^{-\frac{ig_2(t)}{\hbar}\hat{J}_y}. \tag{147}$$

Introducing (147) in (146) we obtain the asymptotic solution

$$g_2(-\infty,+\infty) = \hbar\frac{k_1}{k_2}, \tag{148}$$

where

$$k_1 = \frac{2\mu\omega_0\pi a_0^2}{\hbar}, \tag{149}$$

$$k_2 = \sinh(k_0), \tag{150}$$

and

$$k_0 = \omega_0 a_0 \pi\sqrt{\frac{\mu}{2E}}. \tag{151}$$

The transition probabilities are then given by (121)

$$P(|jm\rangle \to |jm'\rangle) = |d^j_{mm'}(\beta_2)|^2, \tag{152}$$

with

$$\beta_2 = \frac{g_2(-\infty,+\infty)}{\hbar} = \frac{k_1}{k_2}. \tag{153}$$

We note that this expression reduces to (122) in the large E limit

$$\lim_{E\to\infty}\beta_2 = \frac{2a_0}{b\hbar}\sqrt{2E\mu}, \tag{154}$$

since it then corresponds to the sudden approximation.

The transition probabilities (152) can be simplified to the expression

$$P(|Nv\rangle \to |Nv'\rangle) = \binom{v_f}{v}\binom{N-v}{v'-v}\frac{\rho^{v'-v}}{(1+\rho^2)^N}, \tag{155}$$

with

$$\rho = \tan^2\left(\frac{\beta_2}{2}\right), \tag{156}$$

where we have used the number of quanta v instead of m.

6.2. Exponential and Morse interaction potentials

When a Morse interaction is introduced in addition to the exponential potential, again closed expressions can be found. In this case the energy is given by (130), with classical trajectory (133)

$$\frac{2e^{bx/a_0}}{p} = A_1 - A_2 + (A_1 + A_2)\cosh\left(\sqrt{\frac{2E}{\mu}}\frac{bt}{a_0}\right), \tag{157}$$

where A_1 and A_2 are defined by (135)–(136). On the other hand, in the harmonic approximation we find the interaction potential

$$\hat{V}_I(t) = \cos(\omega_0 t)\hat{J}_y \gamma p e^{-bx(t)/a_0} + \beta p^2 e^{-2bx(t)/a_0} - 2\beta p e^{-bx(t)/a_0}. \tag{158}$$

Substitution of (158) and (115) in (97) gives rise to the differential equation

$$\dot{g}_2(t) = \frac{2\gamma\cos(\omega_0 t)}{A_1 - A_2 + (A_1 + A_2)\cosh\left(\sqrt{\frac{2E}{\mu}}\frac{t}{a_0}\right)} \tag{159}$$

with asymptotic solution

$$\beta_2 \equiv \frac{g_2(-\infty, +\infty)}{\hbar} = \frac{\gamma\pi a_0}{\hbar k_2}\sqrt{\frac{2\mu}{A_1 A_2 E}}\sinh\left(\frac{k_0}{\pi}\arctan\left(\frac{2\sqrt{A_1 A_2}}{A_1 - A_2}\right)\right). \tag{160}$$

Finally, the transition probabilities are obtained by means of (152), with β_2 given by (160) and approximated by (155) for systems where β_2 is small.

7. $\hat{J}_z$ AS A VARIATIONAL PARAMETER

Since in the harmonic limit $2\hat{J}_z/N$ becomes unity, a simple possibility is to consider this operator as a free parameter. If this is the case we can linearize $V_I(t)$ substituting the $\hat{J}_z$ operator by $2P$ in the nonlinear part of (141) and treat P as a variational parameter. In this way the interaction potential (141) becomes linear in the SU(2) generators while the parameter P is fixed by fitting the transition probabilities to the ones calculated with other methods. This leads to the potential

$$\hat{V}_I(t) = \frac{\cos(\omega_0 t P)}{\cos(x_0\omega_0 t)}V_3(t)\hat{J}_y + V_1(t)\hat{J}_z + V_2(t), \tag{161}$$

where we have introduced the anharmonicity parameter $x_0\omega_0$, which is related to the Morse potential parameter through $x_0\omega_0 = \frac{x_e\omega_e}{\hbar} = -A/\hbar$ [see Eq. (13)]. The operator $U(t)$ is again given by (104) but now the functions $g_i(t)$ also depend on the (fixed) parameter P. The differential equations satisfied by $g_i(t)$ are given by (147), where (148) is modified to

$$V_{31} = \frac{\cos(\omega_0 t P)}{\cos(x_0 \omega_0 t)} V_3(t) \tag{162}$$

and the transition probabilities are in general computed using (111). This procedure still relies on the harmonic limit, where $\hat{J}_z$ is taken to be a scalar, but introduces anharmonic contributions in a simple fashion in terms of the modified potential (162).

This way to linearize the potential $\hat{V}_I(t)$ has been included for the sake of completeness, but we do not explore it any further. Since the basic aim of this work is to analyze a new methods to go beyond the sudden and harmonic approximations, we now proceed to study this problem.

8. THE EVOLUTION OPERATOR AS A FUNCTION OF THE INITIAL STATE

We now turn our attention to a more general method of approximating the interaction potential $\hat{V}_I(t)$ which still allows the solution of (97).

To search for a linear approximation to (141) we first apply $\hat{V}_I(t)$ to a Morse eigenfunction $|jm\rangle$ and then insert a complete set of states $\sum_\mu |j\mu\rangle\langle j\mu|$ in the resulting expression. Taking into account the selection rules for $\hat{J}_y$, which imply $\mu = m \pm 1$, we readily find

$$\hat{V}_I(t)|jm\rangle \equiv \hat{V}_m(t)|jm\rangle,$$

where

$$\begin{aligned} \hat{V}_m(t) = {} & \frac{iV_3(t)}{\sin(2At/\hbar)} \left\{ e^{-iAt/\hbar} \hat{J}_y \cos\left(\frac{2Atm}{\hbar}\right) \right. \\ & - e^{iAt/\hbar} \left[\cos\left(\frac{2At(m+1)}{\hbar}\right) |jm+1\rangle\langle jm+1| \right. \\ & \left. \left. + \cos\left(\frac{2At(m-1)}{\hbar}\right) |jm-1\rangle\langle jm-1| \right] \right\} \hat{J}_y \\ & + V_1(t)\hat{J}_z + V_2(t). \end{aligned} \tag{163}$$

It is not apparent, however, whether the m-dependent operator $\hat{V}_m(t)$, is hermitian. To assure Hermiticity we thus define the potential

$$\hat{V}_I^m(t) = \tfrac{1}{2}(\hat{V}_m^\dagger(t) + \hat{V}_m(t)), \tag{164}$$

which takes the form

$$\begin{aligned} \hat{V}_I^m(t) = \frac{V_3(t)}{\cos(At/\hbar)} \Big\{ & \cos(2Atm/\hbar) + \cos(2At(m+1)/\hbar)|jm+1\rangle\langle jm+1| \\ & + \cos(2At(m-1)/\hbar)|jm-1\rangle\langle jm-1| \Big\} \hat{J}_y \\ & + V_1(t)\hat{J}_z + V_2(t). \end{aligned} \tag{165}$$

We now use the fact that the m-dependent cosine functions in (165) are essentially identical for small values of the diatom phonon numbers v (large m values) so the error is small if we average the excitation of the two possible states $\mu = m \pm 1$. This leads to the simple m-dependent potential

$$\begin{aligned} \hat{V}_I^m(t) &= \cos(2x_0\omega_0 tm)\cos(x_0\omega_0 t)V_3(t)\hat{J}_y \\ &\quad + V_1(t)\hat{J}_z + V_2(t), \end{aligned} \tag{166}$$

which has the form (100). Formally, we can consider the time evolution of the component wave function $\langle\psi(t)|jm\rangle$:

$$\begin{aligned} -i\hbar\frac{d}{dt}\langle\psi(t)|jm\rangle &= -i\hbar\frac{d\langle\psi(t)|}{dt}|jm\rangle \\ &= \langle\psi(t)|\hat{V}_I(t)|jm\rangle, \end{aligned} \tag{167}$$

and introduce the adjoint of the time evolution operator

$$\left\langle \psi(t_0) \left| \left(-i\hbar\frac{d\hat{U}^\dagger(t)}{dt} \right) \right| jm \right\rangle = \langle\psi(t_0)|\hat{U}^\dagger(t)\hat{V}_I(t)|jm\rangle. \tag{168}$$

If we now substitute (166) for the action of $\hat{V}_I(t)$ on the state $|jm\rangle$, we find

$$-i\hbar\frac{dU_m^\dagger(t)}{dt} = \hat{U}_m^\dagger(t)\hat{V}_I^m(t) \tag{169}$$

when we consider that the initial state of the molecule is $|jm\rangle$. We can now propose an m-dependent evolution operator whose adjoint is given by

$$U_m^\dagger(t) = e^{\frac{i}{\hbar}g_3(m,t)\hat{J}_z} e^{\frac{i}{\hbar}g_2(m,t)\hat{J}_y} e^{\frac{i}{\hbar}g_1(m,t)\hat{J}_z} e^{\frac{i}{\hbar}g_4(m,t)}. \tag{170}$$

where the functions g_i also depend on the initial state m. The differential equations satisfied by the functions $g_i(m,t)$ are

$$\begin{pmatrix} \dot{g}_1(t) \\ \dot{g}_2(t) \\ \dot{g}_3(t) \\ \dot{g}_4(t) \end{pmatrix} = \begin{pmatrix} 1 & \sin(g_1/\hbar)\tan(g_2/\hbar) & -\cos(g_1/\hbar)\tan(g_2/\hbar) & 0 \\ 0 & \cos(g_1/\hbar) & \sin(g_1/\hbar) & 0 \\ 0 & -\sin(g_1/\hbar)/\cos(g_2/\hbar) & \cos(g_1/\hbar)/\cos(g_2/\hbar) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ V_{32}(m,t) \\ V_1(t) \\ V_2(t) \end{pmatrix}, \tag{171}$$

where

$$V_{32}(m,t) = \cos(2x_0\omega_0 tm)\cos(x_0\omega_0 t)V_3(t). \tag{172}$$

The transition probabilities are again evaluated using (111), but closed expressions can be found only for the particular interactions considered before.

8.1. *Exponential interaction potential*

For the exponential interaction the evolution operator acquires a closed form. This case is particularly interesting since an exponential potential was assumed by Clark and Dickinson in their quantum mechanical description of the transition probabilities for the scattering of an atom from a one dimensional Morse oscillator [11]

When $V_1(t) = V_2(t) = 0$ the time evolution operator takes the form

$$\hat{U}_m(t) = e^{-\frac{i}{\hbar} g(m,t)\hat{J}_y}, \tag{173}$$

which for the potential (166) leads to

$$\dot{g}(m,t) = \cos(2x_0\omega_0 mt)\cos(x_0\omega_0 t)V_3(t), \tag{174}$$

where $V_3(t)$ is again given in terms of the classical trajectory (117)

$$V_3(t) = \gamma p e^{-bx(t)/a_0} = E\mathrm{sech}^2\left(\sqrt{\frac{E}{2\mu}}\,\frac{bt}{a_0}\right), \tag{175}$$

with $\gamma = -\frac{1}{2}DN\mathcal{J}_{y,1}$. To obtain the scattering matrix we integrate (174)

$$\beta(m) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} g(m,t)\,dt = \frac{\omega_0\pi\mu a_0^2}{b^2\mathcal{J}_y\hbar}\left\{\frac{(2m-1)x_0}{\sinh[(2m-1)x_0k_0]} + \frac{(2m+1)x_0}{\sinh[(2m+1)x_0k_0]}\right\}, \tag{176}$$

where k_0 is given by (154) and $x_0 = 1/(N+1)$.

The transition probabilities are thus

$$\begin{aligned} P(|jm\rangle \to |jm'\rangle) &= |\langle jm'|e^{i\beta(m)\hat{J}_y}|jm\rangle|^2 \\ &= |d^j_{m',m}(\beta(m))|^2. \end{aligned} \tag{177}$$

which are compared in the next section with the results of Clark and Dickinson.

8.2. Exponential and Morse interaction potential

We now consider the effect of the Morse potential together with the exponential interaction. In this case the total energy is given by (124) with classical trajectory

$$\frac{2e^{bx/a}}{p} = A_1 - A_2 + (A_1 + A_2)\cosh\left(\sqrt{\frac{2E}{\mu}}\frac{bt}{a_0}\right), \tag{178}$$

where A_1 and A_2 were defined in (135)–(136). The interaction potential is then

$$V_I^m(t) = \cos(2x_0\omega_0 mt)\cos(x_0\omega_0 t)V_3(t)\hat{J}_y + V_2(t) \tag{179}$$

and the time evolution operator takes the form

$$U_m(t) = e^{-\frac{i}{\hbar}g_2(t)J_y}\ e^{-\frac{i}{\hbar}g_4}.$$

Substitution in (169) gives rise to the differential equation

$$\dot{g}_2(t) = \frac{\gamma[\cos(\omega_0 x_0 t(2m+1)) + \cos(\omega_0 x_0 t(2m-1))]}{A_1 - A_2 + (A_1 + A_2)\cosh\left(\sqrt{\frac{2E}{\mu}}\frac{bt}{a_0}\right)}, \tag{180}$$

whose solution can be found in closed form

$$\begin{aligned}\beta_2(m) = \frac{g(-\infty, +\infty)}{\hbar} &= \frac{\pi\gamma\arctan\epsilon}{\sqrt{\frac{2\beta}{\mu}}\frac{b}{a_0}}\left\{\frac{\sinh(\Omega(2m+1))}{\sinh(\Omega(2m+1)\pi)}\right.\\ &\qquad\left. + \frac{\sinh(\Omega(2m-1))}{\sinh(\Omega(2m-1)\pi)}\right\},\end{aligned} \tag{181}$$

where

$$\epsilon = \frac{2\sqrt{\beta E}}{\gamma - 2\beta},$$

and

$$\Omega = \frac{\omega_0 x_0}{\sqrt{\frac{2E}{\mu}}\frac{b}{a_0}}.$$

The transition probabilities are again given by

$$P(|jm\rangle \to |jm'\rangle) = |d^j_{mm'}(\beta_2(m))|^2.$$

When the dipole interaction $\hat{V}_1(t)$ is taken into account it is not possible to obtain closed expressions for the transition probabilities, but a numerical analysis is straightforward.

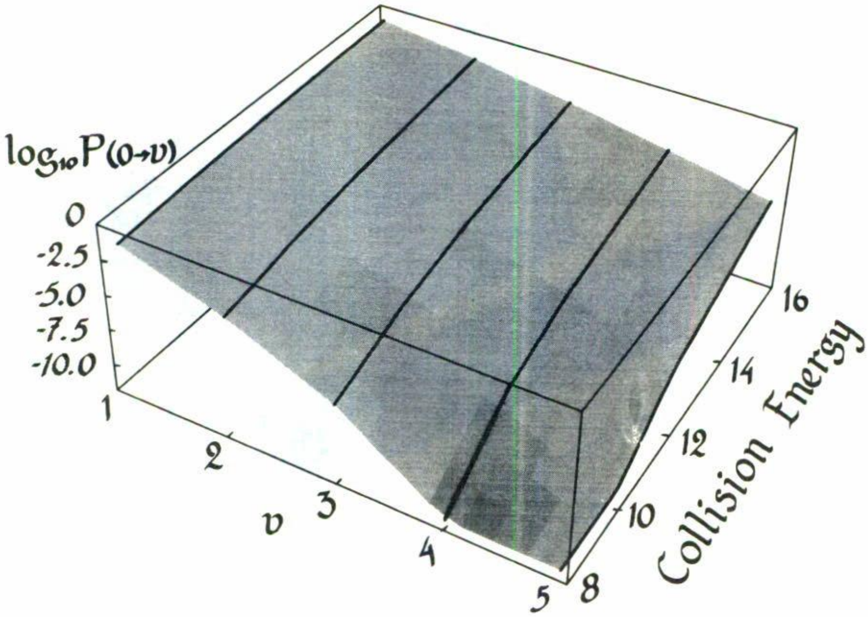

FIGURE 1. Three dimensional representation of the probability $P(0 \to v)$ as a function of the collision energy in units of $\hbar\omega_e/2$ according to the calculations of Clark and Dickinson [11]. The interaction parameter b is given by 0.314.

9. RESULTS

In this section we present the results of the different approximations we have considered, starting with the case where only the exponential interaction is taken into account and compare them with the analysis of Clark and Dickinson.

A convenient way to present the global results is to fix the initial state (to $v_i = 0$, for example) and to plot in a three dimensional figure the probabilities $P(0 \to v)$ as a function of both the energy and v. In Fig. 1 we show in this way the results of Clark and Dickinson for the $H_e - H_2$ system, where we only plot energies above $4\hbar\omega_e$, since we expect our approximations to break down for lower energies. In Fig. 2 we show the calculated probability surface corresponding to the sudden approximation, Eq. (121). In this case the probabilities depend only on the interaction parameter b, which was fitted to obtain the best agreement with the surface of Fig. 1. (In this approximation the probabilities are independent of the properties of the molecule). Note that it is possible to minimize this error for different values of b, as illustrated in Fig. 3 where we plot the deviation (defined as the sum of the probability differences between the ones given in Fig. 1 and those of Fig. 2) as a function of b. The global fit is clearly not satisfactory, and the oscillations observed are unphysical. We should mention the role of the equilibrium distance x_e in the description of the collision. When the triatomic system from which we start our model can give rise to a bound molecule, then x_e can be determined. When this is not the case (*e.g.*, for the $H_2 + H_e$ system), the parameter $p = p(x_e)$ is to be treated as an additional parameter. However, when only the exponential interaction is taken into

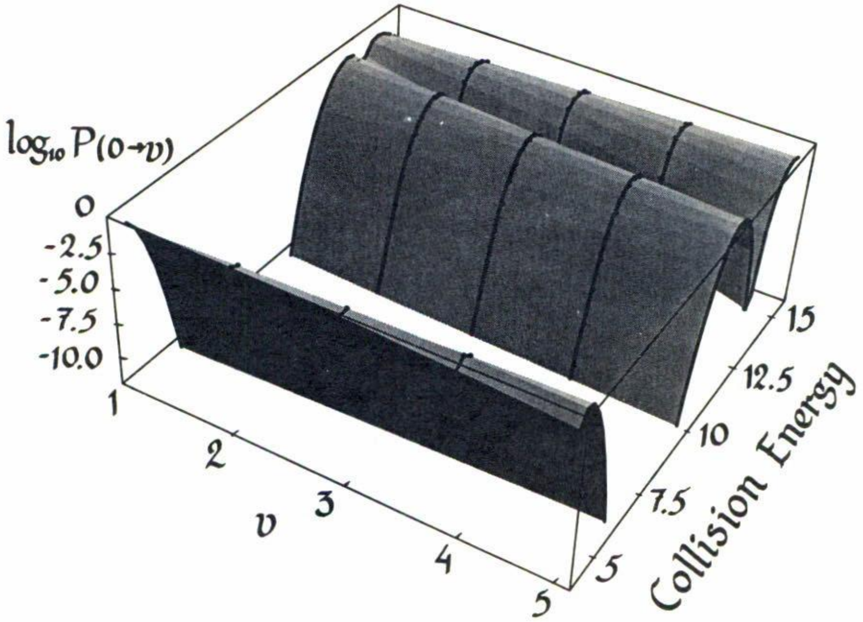

FIGURE 2. Probability $P(0 \to v)$ as a function of the collision energy (in units of $\hbar\omega_e/2$) in the sudden approximation. The fitted interaction parameter was found to be $b = 0.112$.

account the interaction γ can be renormalized to include p, making this parameter unnecessary. This is the case when we compare our model with the Clark and Dickinson results.

As shown in Sects. 5 and 6, the sudden approximation can be removed by making some approximations in the interaction potential given by (141). Taking the limit (144) we obtain the harmonic approximation, with transition probabilities given by (155). We remark that even though both (155) and (121) are given in terms of Wigner's d- function, their arguments are quite different. In this case we do obtain a dependence on the spectroscopic constant ω_e ($\omega_e = 4395$ cm^{-1}, $x_e\omega_e = 117$ cm^{-1} for H_2) which characterizes the molecule. In Fig. 4 we present the fit of the transition probability function (155) to the results of Clark and Dickinson of Fig. 1. Although the improvement with respect to the sudden approximation is evident and the unphysical oscillations disappear, strong discrepancies remain for low energies and for high values of v.

We finally turn our attention to the m-dependent approximation proposed in Sect. 8. In Fig. 5 we present the results of (176) and (177) with b as our only free parameter. The discrepancies for lower energies and higher quantum numbers v are drastically diminished. Even though these results differ slightly from the exact calculations of Clark and Dickinson, the general trend is reproduced remarkably well taking into account the semiclassical method and our other approximations. In Fig. 6 we present the transition probabilities $P(1 \to v)$ at fixed energy $E = 12\hbar\omega_e/2$, for the exact calculation of Ref. [11] and the three different approximations we have analyzed in this article. Again the agreement with Ref. [11] becomes closer as we move from the sudden approximation to the m-dependent approximation, with the harmonic limit in-between.

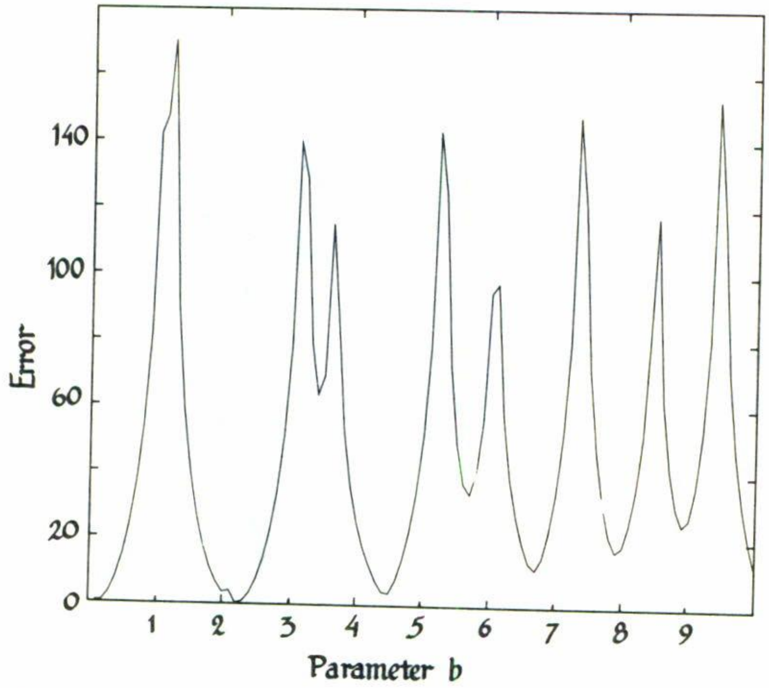

FIGURE 3. Plot of deviations between the probabilities calculated in the sudden approximation and those provided by Clark and Dickinson, as a function of the interaction parameter b.

The algebraic model we have presented provides three types of interactions between the atom and the molecule. Up to now we have only considered the exponential interaction since in this case exact calculations are available. However, the other two contributions —Morse and dipole interactions— can be easily included in order to study their effect on the transition probabilities.

The introduction of the dipole interaction is particularly interesting, since it distinguishes between homonuclear and heteronuclear diatomic molecules. Although in this case we cannot compare with exact calculations, we present in Fig. 7 the results of including the dipole interaction on the transition probabilities obtained with our m-dependent approximation. Note that we have considered both signs of the dipole interactions, which correspond to the two possible frontal collisions.

10. CONCLUSIONS

We have presented an algebraic approach to one-dimensional atom-molecule collisions, which seems to provide an attractive alternative to the standard integro-differential techniques. Although we have tested our approximations only for the case of an exponential interaction, the model naturally provides additional Morse and dipole potentials. The inclusion of the Morse potential together with the exponential one still leads to analytical expressions for the classical trajectories and transition probabilities. To our knowledge these are new solutions for this system. This is not the case for the dipole interactions,

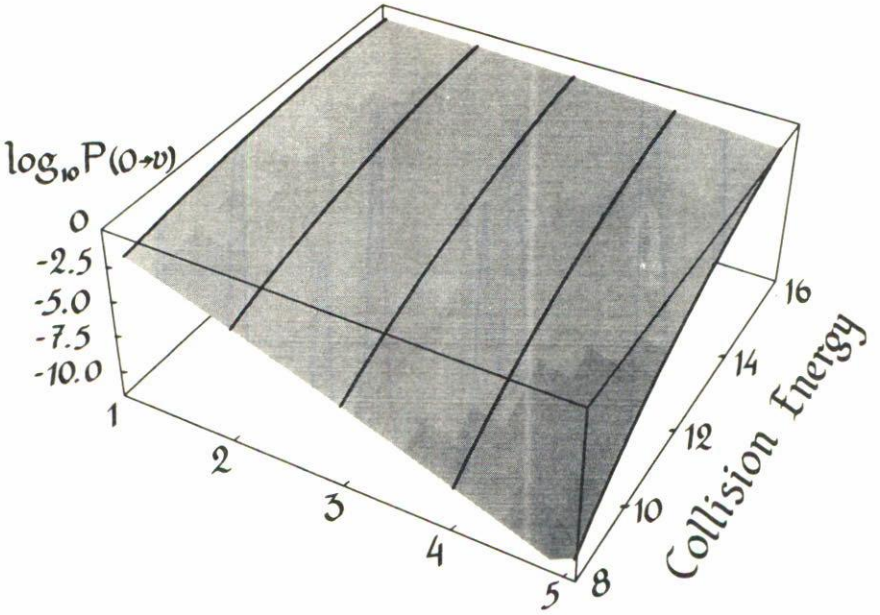

FIGURE 4. Probability $P(0 \to v)$ as a function of the collision energy (in units of $\hbar\omega_e/2$) in the harmonic approximation. The fitted interaction parameter was found to be $b = 0.137$.

where only numerical solutions for the classical trajectories can be obtained. Through these potentials, however, it is possible to study collisions involving heteronuclear molecules, as shown in Fig. 7.

It is important to note that the m-dependent averaged potential (166) can be obtained directly from (98) without going through the one-dimensional interaction potential (141). These results suggest that the approximation method developed in this work can be extended to three dimensional systems. We can obtain an m-dependent three dimensional interaction potential (linear in the generator of the U(4) algebra) by carrying out an average over the three dimensional matrix elements equivalent to (165). We are thus in a position where we can develop the three-dimensional algebraic model without the stringent restrictions implied by the sudden approximation and apply it to real atom-molecule collision processes. This work is currently in progress.

ACKNOWLEDGMENTS

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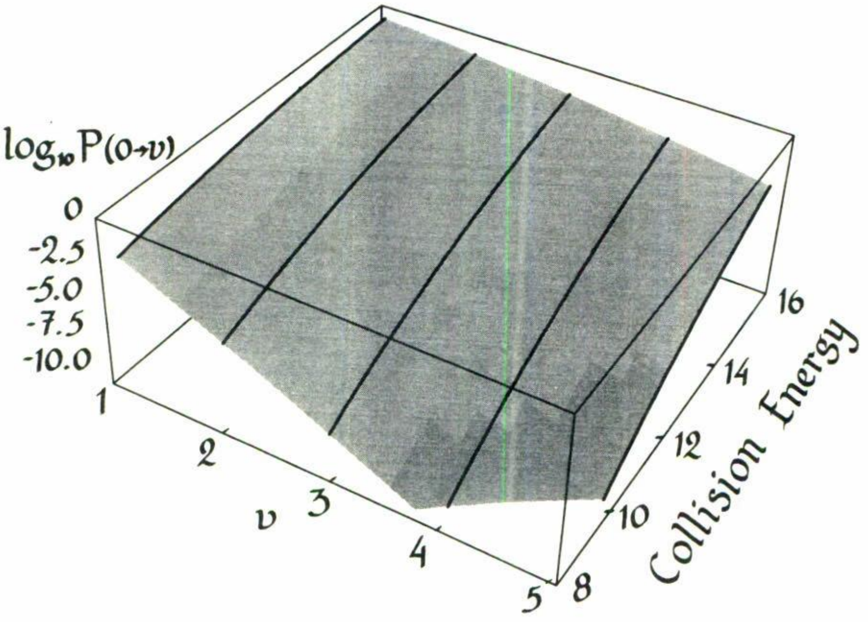

FIGURE 5. Probability $P(0 \to v)$ as a function of the collision energy (in units of $\hbar\omega_e/2$) in the approximation with m-dependence in the interaction potential [Eq. (177)]. The interaction parameter is $b = 0.122$.

APPENDIX A

In this appendix we derive the interaction potential (141) starting from (98).

The Hamiltonian $\hat{H}_0$ only depends on the J_z operator (see Eq. (72)). On the other hand the potential $\hat{V}(t)$ includes contributions of the operators $\hat{J}_z$ and $\hat{J}_y$ as indicated in (89) and (90)–(93). Since $\hat{H}_0$ commutes with $\hat{J}_z$, we only need to analyze the contribution

$$\hat{V}_I^{[3]} \equiv e^{iq\hat{J}_z^2} \hat{J}_y e^{-iq\hat{J}_z^2} \tag{182}$$

in the interaction potential (98), where $q = A(t - t_0)/\hbar$.

Applying to (182) the Baker-Campbell-Hausdorff formula (105) we obtain

$$\hat{V}_I^{[3]} = \sum_{n=0}^{\infty} \frac{(iq)^n}{n!} [\hat{J}_z^2, [\hat{J}_z^2, \ldots, [\hat{J}_z^2, J_y] \ldots], \tag{183}$$

where the number of commutators corresponds to the summation index n. Taking into account the commutation relations

$$[\hat{J}_z^2, J_y] = -\hat{J}_y - 2_i \hat{J}_z \hat{J}_x, \tag{184}$$

$$[\hat{J}_z^2, J_x] = -J_x + 2_i \hat{J}_z \hat{J}_y, \tag{185}$$

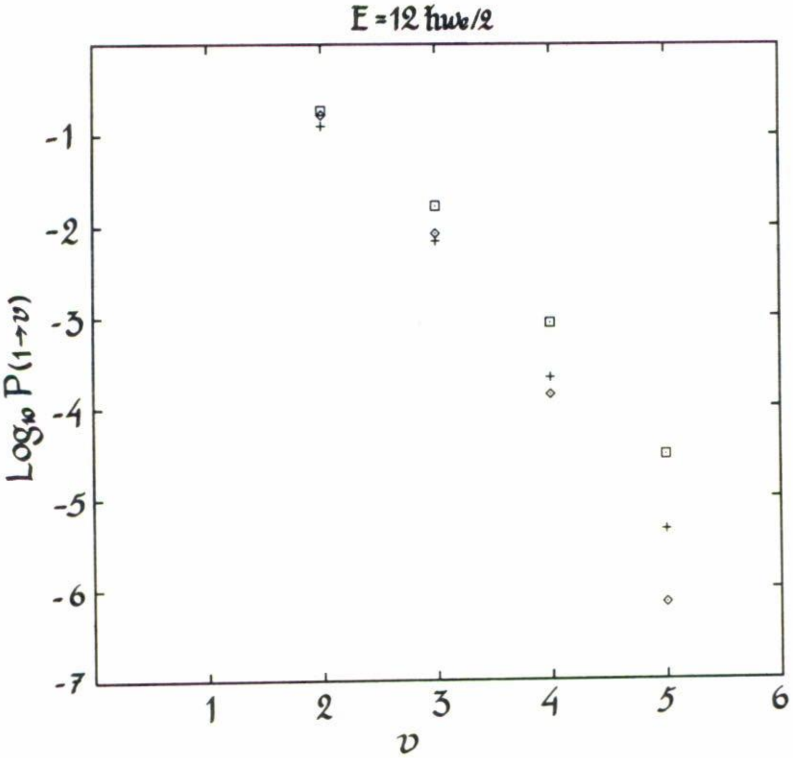

FIGURE 6. Transition probabilities $P(1 \rightarrow v)$ for a fixed collision energy $E = 12\hbar\omega_e/2$ using (a) the exact results of Clark and Dickinson (◇), (b) the harmonic limit (□) and (c) the m-dependence approximation (+). The points corresponding to the sudden approximation do not appear in the plot.

we find for the n consecutive commutators in (183) the result

$$[\hat{J}_z^2, \hat{J}_z^2, \dots, [\hat{J}_z^2, J_y], \dots] = (-)^n \left[\sum_{r=0}^{[n/2]} \binom{n}{2r} (2\hat{J}_z)^{2r} \hat{J}_y + i \sum_{r=0}^{\left[\frac{n-1}{2}\right]} \binom{n}{2r+1} (2\hat{J}_z)^{2r+1} J_x \right], \tag{186}$$

where $[z]$ denotes the integer part of z. Expression (186) is now substituted in (183) to obtain

$$\hat{V}_I^{[3]} = S_1\, \hat{J}_y + i S_2\, \hat{J}_x, \tag{187}$$

where

$$S_1 = \sum_{n=0}^{\infty} \sum_{r=0}^{\left[\frac{n}{2}\right]} \frac{(-iq)^n}{(n-2r)!(2r)!} (2\hat{J}_z)^{2r}, \tag{188}$$

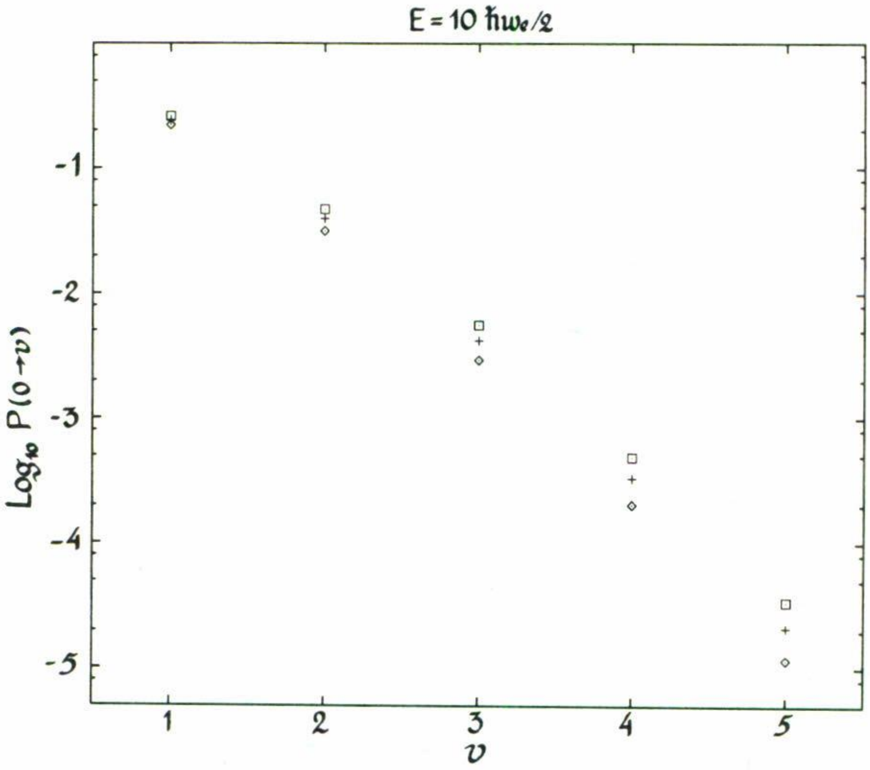

FIGURE 7. Effect of the dipole interaction on the transition probabilities in the m-dependent approximation. The energy was taken to be $E = 10\hbar\omega_e/2$. We have denoted by (□) and (◇) this effect for positive ($\alpha = 0.02$) and negative ($\alpha = -0.02$) values of the dipole parameter, respectively.

$$S_2 = \sum_{n=0}^{\infty} \sum_{r=0}^{\left[\frac{n-1}{2}\right]} \frac{(-iq)^n}{(2r+1)!(n-2r-1)!} (2\hat{J}_z)^{2r+1}. \tag{189}$$

We now proceed to simplify the first sum. The second one can be simplified in the same way.

The sum S_1 can be split in two parts, corresponding to n even ($n = 2u$) and n odd ($n = 2u+1$), respectively:

$$\begin{aligned} S_1 = & \sum_{u=0}^{\infty} \sum_{r=0}^{u} \frac{(-)^u q^{2u}}{(2u-2r)!(2r)!} (2\hat{J}_z)^{2r} \\ & - i \sum_{u=0}^{\infty} \sum_{r=0}^{u} \frac{(-)^u q^{2u+1}}{(2u+1-2r)!(2r)!} (2\hat{J}_z)^{2r}. \end{aligned} \tag{190}$$

This double sum can be written in a more convenient form by interchanging the sums over u and r, and identifying the series expansion of the functions $\cos(q)$ and $\sin(q)$. We thus obtain

$$\begin{aligned} S_1 &= \sum_{r=0}^{\infty} \frac{(-)^r q^{2r}}{(2r)!} (2\hat{J}_z)^{2r} [\cos(q) - i \sin(q)] \\ &= e^{-iq} \cos(2q\hat{J}_z). \end{aligned} \tag{191}$$

Following the same procedure for the second sum S_2, we find

$$\begin{aligned} S_2 &= i \sum_{r=0}^{\infty} \frac{(-1)^{r+1} q^{2r+1}}{(2r+1)!} (2\hat{J}_z)^{2r+1} e^{-i\alpha} \\ &= -ie^{-iq} \sin(2q\hat{J}_z). \end{aligned} \tag{192}$$

With these results the contribution (187) takes the final form

$$\hat{V}_I^{[3]} = \frac{i}{\sin(2q)} \left[e^{-iq} \hat{J}_y \cos(2q\hat{J}_z) \hat{J}_y + e^{iq} \cos(2q\hat{J}_z) \hat{J}_y \right], \tag{193}$$

which allows to rewrite the interaction potential (98) in the form

$$\begin{aligned} \hat{V}_I(t) = \frac{iV_3(t)}{\sin(2At/\hbar)} & \left[e^{-\frac{iAt}{\hbar}} \hat{J}_y \cos\left(\frac{2At\hat{J}_z}{\hbar} \right) \right. \\ & \left. - e^{\frac{iAt}{\hbar}} \cos\left(\frac{2At\hat{J}_z}{\hbar} \right) \hat{J}_y \right] + V_1(t)\hat{J}_z + V_2(t). \end{aligned}$$

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