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Collinear inelastic collisions of an atom and a diatomic molecule using operator methods

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We calculate transition probabilities between vibrational levels of a diatomic molecule induced by an incident atom. Our prototype model is constructed treating the relative translation of the colliding species as a classical variable. The vibrational states of the diatomic molecule are treated quantum mechanically in terms of the evolution operator without involving wave functions. The corresponding equations of motion are coupled quasi-classically. For illustration purposes we present applications to the time dependence of transition probabilities for different initial and final states as well as a canonical ensemble of initial conditions.

Keywords: Inelastic; collisions; Lie; algebraic; harmonic; oscillator

Calculamos probabilidades de transición entre estados vibracionales de una molécula diatómica inducidas por un átomo incidente. El modelo prototipo trata el movimiento de traslación relativo como una variable clásica. Los estados vibracionales de la molécula diatómica se tratan cuánticamente en términos del operador de evolución, sin involucrar funciones de onda. Las ecuaciones de movimiento correspondientes se acoplan cuasi-clásicamente. A manera de ilustración presentamos aplicaciones a la dependencia temporal de probabilidades de transición para diferentes estados inicial y final así como para un ensamble canónico de condiciones iniciales.

Descriptores: Colisiones; inelásticas; álgebras; Lie; oscilador; armónico.

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1. Introduction

The analytical foundation for energy transfer in molecular collisions is laid with a collinear triatomic system [1-5]. In this system, a single collinear dimension is used for the relative motion of an atom and a diatomic molecule. The translational degree of freedom can be treated classically to a good approximation. It is indeed sufficient to deal with the relative molecular distance as a classical translational coordinate. However, it is essential to quantize the vibrational motion of the diatomic molecule. Therefore, we adapt quasi-classically this formalism to the response of a diatomic molecule treated as a harmonic oscillator to an external atomic interaction with an implicit time dependence.

There are two key features in our approach distinguishing it from earlier calculations [3-9]. The first one is the coupling between Hamilton equations for translation and the quantum equations of motion involving the diatomic molecular vibrations. Instead of solving the translational equation of motion independent of the vibrational motion [3-5,7,8] we solve the whole set of equations simultaneously. The second one is the appearance of an effective time dependent frequency [10] adapting the vibrational motion to the evolution during the inelastic collision.

Given that there is a natural way of separating the quantum Hamiltonian into an unperturbed part (the harmonic oscillator) and a perturbation due to the incoming atom, it has been customary to think in terms of time dependent perturbation theory and introduce the interaction representation for the quantum part. Our calculations instead are performed nonperturbatively in the Schrodinger picture exploiting the algebraic properties of the system. Higher order transitions are easily calculated with the Lie algebraic approach from a finite number of ordinary differential equations [7-9,11]. We consider a model Hamiltonian where both the oscillator and the atomic interaction terms contain trajectory dependent coefficients. The quantum part of the Hamiltonian is then reinterpreted in terms of Lie algebra elements while the translational part involves classical equations of motion. The chosen algebra is closed under commutation and we can express the time evolution operator $\hat{U}(t, t_0)$, as a product of exponentials, each corresponding to a single basis element of the algebra [12,13]. Within this scheme the time dependence is concentrated into c-number functions $\{\alpha_i(t)\}$, where $i = 1, ..., 4$. These appear as Lie group parameters for the time evolution operator, as will become evident in what follows. The Schrodinger equation satisfied by the evolution operator $\hat{U}(t)$ is replaced by a set of coupled ordinary differential equations for the α's that can be solved numerically. Armed with these solutions, we reconstruct the explicit time evolution operator $\hat{U}(t)$ and easily obtain

(a) time dependent transition probabilities between two of the oscillator states induced by the incoming atom, and

(b) time dependent expectation values of the position and momentum operators.

In deriving the quantum Hamiltonian we also allow for a shift in the oscillator frequency resulting in a coefficient that depends on the distance between the incoming atom and the center of mass of the diatomic molecule. This is the result of a coupling between the classical equation for translation and the quantum equation for the oscillator. Previous work assumes a precalculated incoming classical trajectory for the atom [3-9]. As mentioned above it also has been customary in this kind of problems to proceed to the interaction representation as the first step [7-9,11,14,15]. Although this step seems to be appropriate in perturbation theory, it can be obviated in our instance using the Schrodinger representation instead. In practice, the difference between these two approaches is an unobservable phase factor but the time dependence of the resulting model unperturbed effective Hamiltonian makes the interaction representation awkward.

We also include a temperature dependent case of a canonical ensemble of initial conditions with mixed states. We calculate the translation-vibration transitions for a heat bath of collinear triatomic collisions. With an initial Boltzmann distribution we see time resolved regions where the energy distribution is far from thermal equilibrium.

Apart from its intrinsic value in understanding inelastic collisions, this work is motivated by the idea of applying similar methods to more general cases. Replacing the harmonic oscillator by a more realistic Morse potential requires an extension of the Lie algebra [10,16]. The reactive collinear case uses a similar approach to the present paper in terms of reaction coordinates [1,16]. Including rotational motion in two and three dimensions calls for the extension of the vibron model [17] which has already proven to be so valuable in the case of molecular structure [18].

The paper is organized as follows. Section 2 lays the foundation for the separation of the classical and quantum parts of the Hamiltonian and the corresponding coupling of the two subsystems. In Sec. 3 we present the operator methods applicable to the transformation of the quantum equation into a set of four coupled ordinary differential equations. In Sec. 4 we develop these ideas into a working model and find the expressions for the transition probabilities as a function of time, as well as the time evolution of the average position and momentum for a simple case. Section 5 is a short discussion of the methods employed and the results obtained.

2. Collinear formulation of the atom-diatomic molecule interaction

We set up the following coordinates for the nuclear positions of atoms A, B, and C as seen in Fig. 1(a). The Hamiltonian for this system is considered as a one-dimensional system with three degrees of freedom initially. In the laboratory frame the Hamiltonian is given by

$$\hat{H}_1 = \frac{p_{\mathrm{A}}^2}{2m_{\mathrm{A}}} + \frac{p_{\mathrm{B}}^2}{2m_{\mathrm{B}}} + \frac{p_{\mathrm{C}}^2}{2m_{\mathrm{C}}} + V_{\mathrm{BC}}(x_{\mathrm{B}} - x_{\mathrm{C}}) + V_{\mathrm{AB}}(x_{\mathrm{A}} - x_{\mathrm{B}}), \qquad (1)$$

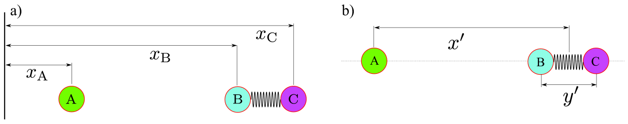

FIGURE 1. The system is reduced to an incoming atom disturbing an oscillator constrained to a wall, where the dotted vertical line is the oscillator equilibrium position.

where p's are the momenta, m's the masses for the three atoms. We consider the atoms B and C to be bound, the interaction between A and B to be repulsive, and the interaction between A and C to be negligible. We then reduce the problem to two dimensions using reduced mass coordinates [2] as seen in Fig. 1(b).

The resulting Jacobi coordinates [2] are y', the distance between the nuclei in the diatomic molecule and x', the distance between the atom A and the center of mass of B and C thus eliminating the center of mass. A further transformation [2] to dimensionless variables x and y allows us to construct a potential energy surface for the dynamics of the collision. The potential appropriate for the harmonic motion of the diatomic system is given in terms of the natural oscillation frequency ω_0 and the reduced mass μ_{BC} as

$$V_{\mathrm{BC}} = \frac{1}{2}\hbar\omega_0 y^2, \qquad (2)$$

where

$$y = \sqrt{\frac{\omega_0 \mu_{\mathrm{BC}}}{\hbar}}(y' - y_0). \qquad (3)$$

For the potential representing the collision we choose a repulsive exponential of strength V_0 and inverse range β:

$$V_{AB} = \hbar\omega_0 V_0 e^{-\beta(x-y)}. \qquad (4)$$

Together these two functions form a potential energy surface for the collinear collision. The system takes on a new interpretation: it is now reduced to a particle of dimensionless reduced mass

$$m = \frac{m_A m_C}{m_B\,(m_A + m_B + m_C)} \qquad (5)$$

at position x and a particle of unit mass at y.

We now proceed to break the two remaining coordinates up into classical and quantum degrees of freedom [3-5,7,9]. We first choose x to be the classical translation coordinate. The oscillator coordinate is quantized, $\hat{y}$. The full Hamiltonian is divided out by $\hbar\omega_0$ resulting in the final dimensionless workable Hamiltonian:

$$\hat{H} = \frac{1}{2m}p_x^2 + \frac{1}{2}\hat{p}_y^2 + \frac{1}{2}\hat{y}^2 + V_0 e^{-\beta(x-\hat{y})}. \qquad (6)$$

In this new system, the classical equation becomes

$$m\frac{d^2x}{dt^2} = \beta V_0 e^{-\beta x} e^{\beta\langle\hat{y}(t)\rangle}. \qquad (7)$$

Equation (7) couples to the quantum part through the expectation value of the vibrational distance $\langle\hat{y}(t)\rangle$.

3. The algebraic approach and the quantum dynamics

In general, the diatomic molecule has a well established vibrational energy spectrum. It is usually anharmonic in nature requiring high order terms to be accurately modeled. In a first approximation we treat the molecule as a harmonic oscillator. Since the vibration of the diatomic molecule is quantized and the relative translation of the two colliding species is considered as a classical degree of freedom we get a quasi-quantum/classical coupled system. The result is a classical equation being coupled to quantum equations through the time dependent expectation value of the harmonic oscillator's position $\langle \hat{y}(t) \rangle$.

We will now simplify the quantum part of the Hamiltonian expanding the exponential in Eq. (6) to second order in $\hat{y}$. This introduces a new quadratic term thus redefining the oscillator frequency to be $\Omega^2(x) = 1+\beta^2 V_0 e^{-\beta x}$. The linear term in $\hat{y}$ acts as an effective "dipole" driving term inducing transitions in the vibrational spectrum. We hence take advantage of the quasi-classical variable separation and focus on the quantum Hamiltonian,

$$\hat{H}_q = \frac{1}{2}\hat{p}_y^2 + \frac{1}{2}\Omega^2(x)\hat{y}^2 + \beta\hat{y}V_0 e^{-\beta x} + V_0 e^{-\beta x}. \tag{8}$$

In terms of the number operator $\hat{N}$ for the parametric harmonic oscillator Eq. (8) becomes,

$$\hat{H}_q = \Omega\left(x\right)\left(\hat{N} + \frac{1}{2}\right) + \beta\hat{y}V_0 e^{-\beta x} + V_0 e^{-\beta x}. \tag{9}$$

In order to find the evolution operator in closed form we introduce the Lie algebra generated by $\{\hat{a}, \hat{a}^\dagger, \hat{N}, I\}$ including the harmonic oscillator ladder operators $\hat{a}$ and $\hat{a}^\dagger$, the number operator $\hat{N}$ and the identity I. The corresponding non-trivial commutators are the usual $[\hat{a}, \hat{a}^\dagger] = I$, $[\hat{a}, \hat{N}] = \hat{a}$, and its Hermitian conjugate $[\hat{a}^\dagger, \hat{N}] = -\hat{a}^\dagger$. The Hamiltonian $\hat{H}_q$ is an element of the Lie algebra with

$$\hat{y} = \sqrt{\frac{1}{2\Omega}}\left(\hat{a} + \hat{a}^\dagger\right). \tag{10}$$

The operators can be exponentiated to form a Lie group [16] and the time evolution operator $\hat{U}(t)$ is part of this group with the Lie group parameters being functions of time [11-13]. The quantum dynamics can then be rewritten matching the coefficients of the Lie algebra basis in the Schrodinger equation:

$$i\left(\frac{d}{dt}\hat{U}\left(t\right)\right)\hat{U}\left(t\right)^{-1} = \hat{H}. \tag{11}$$

In this equation the dimensionless time requires a scaling of $t = t'\omega_0$ to stay consistent with the scaled energy units.

The time dependence for $\hat{U}$ is transferred completely into four Lie group parameters α_1, α_2, α_3, and α_4 corresponding to the four basis elements of the Lie algebra. After determining the evolution operator we can get infinite order transition probabilities of the oscillator by only having to solve four ordinary differential equations. The Ansatz of choice for approaching Eq. (11) is a product of normal ordered exponentials

$$\hat{U}\left(t\right) = e^{\alpha_1(t)\hat{a}^\dagger} e^{\alpha_2(t)\hat{a}} e^{\alpha_3(t)\hat{N}} e^{\alpha_4(t)I}. \tag{12}$$

The Wei-Norman [12,13] form for the time evolution operator is preferred since it simplifies its application to the number operator eigenkets. This particular form also reveals a consistency with the interaction picture given that the unperturbed oscillator eigenvalues are retreivable from the last two terms $e^{\alpha_3\hat{N}}e^{\alpha_4 I}$ acting on the corresponding ket. Equation (12) defines the general quantum solution we will work with. Inverting the Wei-Norman result in Eq. (12) isolates the Hamiltonian as seen in Eq. (11). This is the landmark form in quantum dynamics as it is a general and explicit solution for the generator of time evolution. The explicit form of the quantum Hamiltonian appropriate for the algebraic approach is thus

$$\begin{aligned}\hat{H}_q &= \beta\sqrt{\frac{1}{2\Omega(x)}}V_0 e^{-\beta x}\left(\hat{a} + \hat{a}^\dagger\right)\\ &\quad + \Omega(x)\hat{N} + V_0 e^{-\beta x} + \frac{\Omega(x)}{2}.\end{aligned} \tag{13}$$

The left hand side of Eq. (12) is evaluated applying the Baker-Hausdorff formula [10,20]. The details are worked out in the Appendix.

$$\begin{aligned}i\left(\frac{d}{dt}\hat{U}\right)\hat{U}^{-1} &= \left(i\dot{\alpha}_3\right)\hat{N} + \left(i\dot{\alpha}_1 - i\dot{\alpha}_3\alpha_1\right)\hat{a}^\dagger\\ &\quad + \left(i\dot{\alpha}_2 + i\dot{\alpha}_3\alpha_2\right)\hat{a}\\ &\quad + \left(i\dot{\alpha}_4 - i\dot{\alpha}_2\alpha_1 - i\dot{\alpha}_3\alpha_2\alpha_1\right)I.\end{aligned} \tag{14}$$

Equating Eqs. (13) and (14) yields four ordinary differential equations for the α's. The resulting coupled equations of motion for each Lie parameter are:

$$\begin{aligned}&\dot{\alpha}_1 = -i\left(f_1 + \Omega(x)\alpha_1\right), \quad \dot{\alpha}_2 = -i\left(f_1 - \Omega(x)\alpha_2\right), \\ &\dot{\alpha}_3 = -i\Omega(x), \quad \dot{\alpha}_4 = -i\left(f_1\alpha_1 + V_0 e^{-\beta x} + \frac{\Omega(x)}{2}\right).\end{aligned} \tag{15}$$

where

$$\Omega(x) = \sqrt{1+\beta^2 V_0 e^{-\beta x}}, \quad f_1 = \beta\sqrt{\frac{1}{2\Omega}}V_0 e^{-\beta x}. \tag{16}$$

Meanwhile, the translation equation of motion,

$$m\ddot{x}\left(t\right) = \beta V_0 e^{-\beta x} e^{\beta\langle\hat{y}(t)\rangle}, \tag{17}$$

becomes quasi-classically coupled to Eqs. (15) resulting in a system of six first order differential equations which may be solved numerically. Once these equations are solved, the time evolution operator can tell us everything about the system at any given time t using the Wei-Norman result.

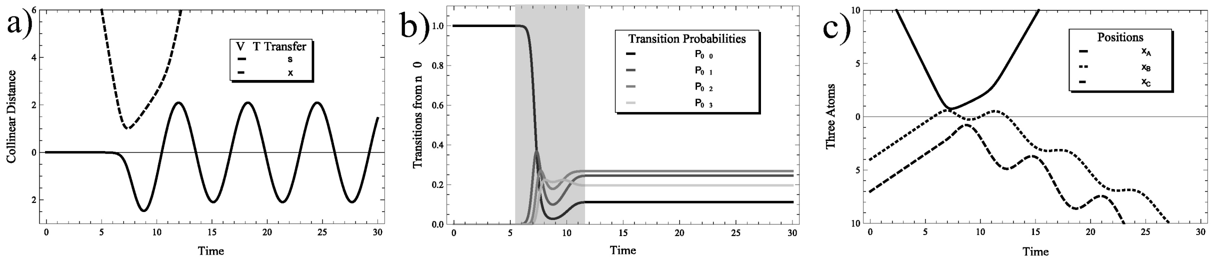

FIGURE 2. Initial state with expectation value of position at $x = 0$. a) The collinear trajectories show that coupling the coordinates results in asymmetric atomic trajectories unlike the usual precalculated trajectories in the previous literature. b) The transition probabilities from ground state are calculated continuously. The interaction region is shown to be strongest in the gray area. c) Conversion back to the real motion of the atoms in the laboratory frame.

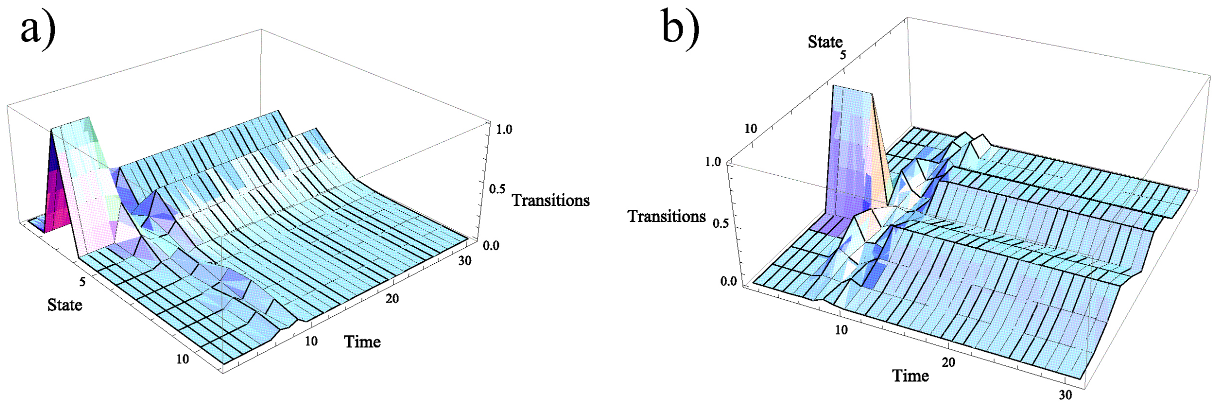

FIGURE 3. Landscape of transition to nearby states through time. a) Initial state chosen to be $n = 2$. Notice that first order transitions are strongest. b) The plot is rotated to show that for certain collisions, an initial state of $n = 5$ has a more rich transition landscape where the persistence of the intial state is significant.

4. Results

4.1. Quantum dynamics of a single collision

Arbitrary state-to-state $(n_i \to n_f)$ transitions become functions of the Lie parameters. Since these parameters are continuous functions of time, we may calculate the transition probabilities P from state n to m as continuous functions of time with

$$P_{n\to m}(t) = \left| e^{\alpha_3 n} e^{\alpha_4} \sqrt{m!}\sqrt{n!} \times \sum_{k=0}^{n} \frac{1}{k!} \frac{1}{(m-n+k)!\,(n-k)!} \alpha_1^{m-n+k} \alpha_2^{k} \right|^2 . \qquad (18)$$

The relative translational motion has been taken to be classical, so its trajectory is well defined. For the quantum coordinate we can calculate the position expectation value for an average oscillator trajectory. For any given single initial stationary state before the collision, the position expectation value is centered at the bottom of the harmonic well. This means $\langle \hat{y}(0) \rangle = 0$ as can be seen at the early times Fig. 2(a). It is also necessary that all Lie parameters be zero at $t = 0$ as well to fulfill the initial condition $\hat{U}(0) = I$. With these conditions, the evolution operator retains its unitarity through time. One powerful result of the Lie algebraic approach is that the time evolution of arbitrary state-to-state transitions is directly comparable to the evolution of the real atomic trajectories. The time resolution is fine enough that separate regions appear in both the trajectories and the transition probabilities.

For all of the following figures the triatomic mass ratio is 1:2:1. We have included calculations and figures for a simple case as an illustration of the methods. More examples will be shown for the more realistic anharmonic case [16].

When the quantum transitions and collision dynamics are simultaneously calculated, three distinct regions are revealed. This is most evident in Fig. 2(b) where the interaction region is in the gray box separating the other two regions. Fig. 2(b) shows a time interval in the interaction region where the population becomes inverted.

In Figs. 3 we present a time dependent transition probability "landscape" which can be visualized in a 3D plot with the number states as the third dimension. In Fig 3(a) the initial single state is taken to be $n_i = 2$. In the landscape plot the inversion through the interaction region is even more pronounced as states above $n_f = 10$ have non-vanishing transition probabilites. In the final state only the transitions $\triangle v = \pm 1$ are significant. In Fig. 3(b) the initial state is $n_i = 5$ and the landscape is rotated to see the detail of the

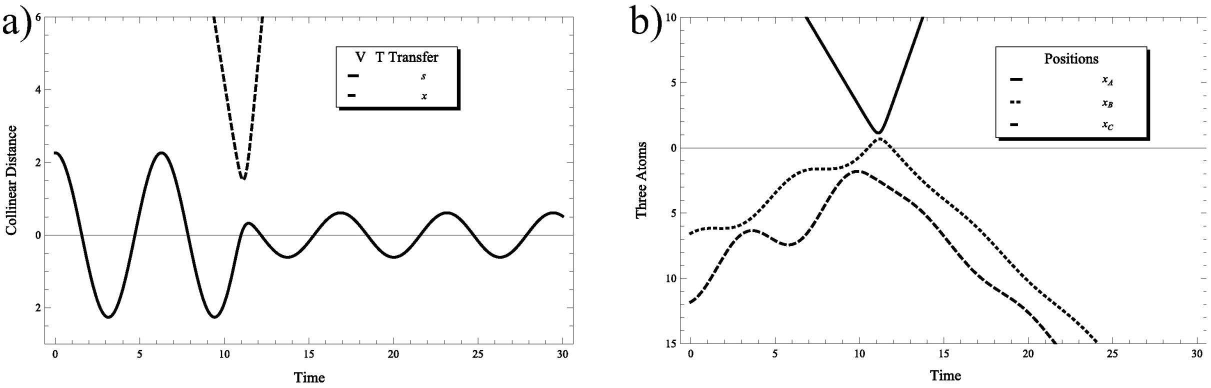

FIGURE 4. Initial state as a linear combination of time-dependent states. a) Coherence is seen in the incoming diatomic molecule. This produces an incoming vibrational phase condition which in this case relaxes the molecule and results in V-T energy transfer b) The mass of the middle atom is three times greater than the other two. The real nuclear trajectories in the laboratory frame show the assymetric motion in the diatomic molecule.

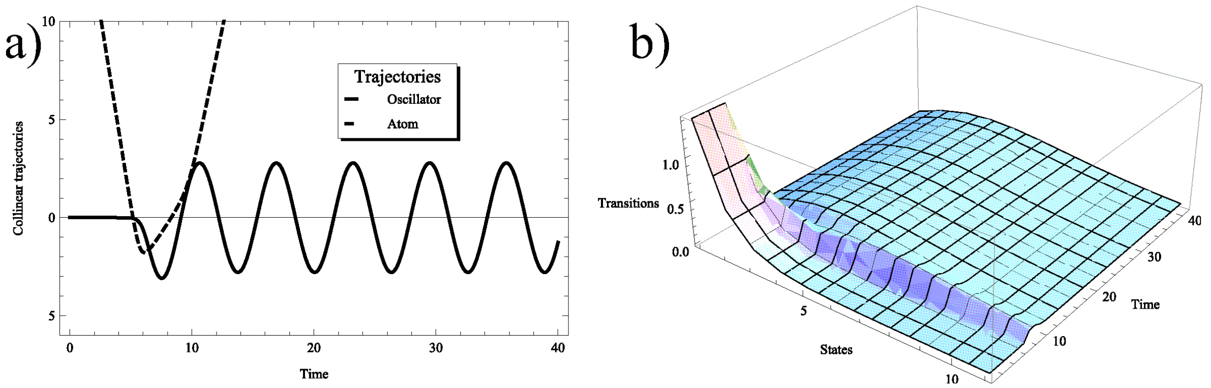

FIGURE 5. A heat bath of Boltzmann weighted oscillators initially in thermal equilibrium undergo collisions into non-equilibrium. a) The initial conditions for the incoming atom and molecule are based off average velocities and maximal entropy. b) The Boltzmann distribution is shown to be distrusted after the collision.

final two regions. Note that at any slice of constant time the sum of the probabilities, $\sum P_{if} \approx 1$.

All figures so far have considered a single initial state where $\langle \hat{y}(0) \rangle = 0$, a stationary state before the atomic collision. A second interesting case is one where the initial oscillator position expectation value is not zero, *i.e.* $\langle \hat{y}(0) \rangle \neq 0$. This corresponds to a wave packet and, although the time evolution is still unitary, its initial value is not necessarily the unit operator so we do not show transition probabilities in this case. The phase-space dynamics becomes more interesting as the oscillator now has an initial coherence of which the incoming atom quasi-classically couples to as it approaches the oscillator as seen in Fig. 4(a). The vibrational to translational energy transfer is noticed in the change of the oscillator amplitude as well as the increased slope of the translational coordinate. Notice that $m_{\rm B}$, the heavier atom, is barely oscillating after the collision in Fig. 4(b).

4.2. Quantum dynamics from a heat bath of collisions

To consider an ensemble of oscillators, we begin with a canonical ensemble of Boltzmann weighted initial states, a mixed state. The corresponding transition probability to a final state n_f is

$$P_{\beta \to f} = \sum_{i=0}^{n_f} |\langle n_f | \, U \, | n_i \rangle|^2 \, \frac{e^{-\beta E_i}}{Z}, \tag{19}$$

where $E_n = \omega \left(n + \frac{1}{2} \right)$ and $Z = \sum_{n=0} e^{-\beta\omega\left(n+\frac{1}{2}\right)}$ is the partition function. Considering the number of states in Eq. (19) to be $N = 10$ and assuming maximum initial entropy in the diatomic molecule [11], there is no coherence in the distribution of stationary states. We may take a single inelastic collision like in Fig. 5(a) and distribute it across these 10 states as initial conditions, with Boltzmann weights to model a canonical ensemble of oscillators. The initial distribution is seen in the early times of Fig. 5(b).

The interaction region shows the distribution to be much different than a Boltzmann distribution. Even in the final region, the bath of oscillators is not Boltzmannian. In practice, after this final region a relaxation of states back to a Boltzmann distribution is expected. This happens through a series of subsequent collisions on a different time scale.

5. Discussion

The Lie algebraic model proves to be a powerful and choice formulation in molecular dynamics. Finding the time evolution operator produces all the information we need for both average phase space and transitions. The Schrodinger equation in the form

$$i\left(\frac{d}{dt}\hat{U}\right)\hat{U}^{-1}=\hat{H}$$

can now be seen as a generalized tool one can tailor to a specific system. Time resolved, infinite order transition probability calculations are a powerful result of the operator approach. We are now able to see the transition probabilities continuously through the whole collision. In the algorithm developed here, we see a simplification in non-equilibrium quantum statistical analysis as the density matrix elements are easily calculated from previous code.

The next step is to apply this method to more general situations [10,16,17] including anharmonic properties in the oscillators as seen in previous energy transfer work, as well as to the reactive case [16].

Appendix

Evaluation of the left hand side of Eq.(13) needs the calculation of the following:

$$i\dot{\alpha}_2 e^{\alpha_1 a^\dagger} a e^{-\alpha_1 a^\dagger} + i\dot{\alpha}_3 e^{\alpha_1 a^\dagger} e^{\alpha_2 a} N e^{-\alpha_2 a} e^{-\alpha_1 a^\dagger}.$$

We use the Baker-Hausdorff formula

$$e^X Y e^{-X} = e^{X\times} Y.$$

where the cross-product stands for the commutator. This results in the more intuitive structure

$$i\dot{\alpha}_2 e^{\alpha_1 a^\dagger \times} a + i\dot{\alpha}_3 e^{\alpha_1 a^\dagger \times}\left(e^{\alpha_2 a\times} N\right).$$

Using the relation

$$a^\dagger \to -\frac{\partial}{\partial a}$$

we get

$$e^{-\alpha_1 \frac{d}{da}\times} a = a - \alpha_1.$$

This brings the expression to

$$i\dot{\alpha}_2\left(a-\alpha_1\right) + i\dot{\alpha}_3 e^{\alpha_1 a^\dagger \times}\left(e^{\alpha_2 a\times} N\right),$$

where

$$e^{\alpha_2 a\times} N = N + \alpha_2 a \times N = N + \alpha_2 a.$$

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