Molecular transition probabilities for time-dependent, bilinear Hamiltonians in many dimensions: A recursive procedure

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(Received 19 September 1988; revised manuscript received 20 March 1989)

Vibrational transitions in collisions of two polyatomic systems are described in terms of a Hamiltonian bilinear in momentum and position operators, for several degrees of freedom. The relative motion is assumed to be classical and leads to time-dependent coefficients in the Hamiltonian. The present treatment employs a simple procedure that does not require the construction of the time-evolution operator and leads to recursion relations for transition amplitudes, suitable for numerical applications. As examples, we consider the special cases of a single degree of freedom, and of the linearly driven harmonic oscillator.

I. INTRODUCTION

The interaction of two molecular systems at thermal or hyperthermal relative velocities results in transitions among their vibrational levels. The corresponding transition probabilities are needed, for example, in the modeling of the kinetics of energy transfer in gases, and of the scattering of molecules by adsorbates on solid surfaces.

These and many other physical processes, such as those involving charge- and spin-density fluctuations and nonlinear optical effects, can be described in terms of position coordinates X_j and their conjugate momenta P_{X_j}, where $1 \leq j \leq f$, and f is the number of degrees of freedom of the system. The corresponding Hamiltonians can be expanded around average values $\langle X_j \rangle_t$ and $\langle P_{X_j} \rangle_t$ of these variables, keeping only up to bilinear terms in $x_j = X_j - \langle X_j \rangle_t$ and $P_{x_j} = P_{X_j} - \langle P_{X_j} \rangle_t$.

Transition probabilities can then be obtained in principle from the time-dependent Schrödinger equation using a basis of vibrational states. However, for systems with large total energy E, such as highly excited ones or extended systems, that approach is not practical because it would involve too many basis functions. Hence there have been several alternative treatments in the literature to avoid expansions in basis sets. Some of them rely on path-integral methods to calculate propagators and then transition amplitudes;[1] some others solve the equation of motion for the time-evolution operator,[2-5] or use operator algebras to construct the time-evolution operator.[6,7] A solution based on wave packets[8] has also been developed.[9-11] These treatments have been available for a single degree of freedom. For several degrees of freedom, they are more involved and have been developed only within certain approximations,[6,12] with two exceptions.

One of the general treatments for multidimensional Hamiltonians relies heavily on results of the theory of Lie algebras to construct the time-evolution operator and then its matrix elements between vibrational states;[13] the other one takes a more direct approach to calculate transition probabilities directly from the equations of motion of position and momentum operators.[14,15] In this contribution we expand on the second approach to obtain recurrence relations for transition amplitudes. These recurrence relations are well suited for computational work and can be applied to a large variety of problems.

In what follows we concentrated on collisional excitation of molecular vibrations. We treat the relative position $\mathbf{R}$ as a classical variable, dependent on the time t. The X_j are vibrational coordinates whose average values can be extracted from the wave function $\Psi(X_1, \ldots, X_f, t)$ as $\langle X_j \rangle_t = \langle \Psi(t) | X_j | \Psi(t) \rangle$. The averages need not be equilibrium values. Provided the dispersion of values of the X_j is small during the duration of the transition, we can expand the potential energy $V(R, X_1, \ldots, X_f)$ in the form

$$V(R,X)\Psi(X,t) = \left[V_0(t) + \sum_j V^{(j)}(t)x_j \right.$$
$$\left. + \tfrac{1}{2} \sum_{j,k} V^{(jk)}(t)x_j x_k \right] \Psi(X,t) , \qquad (1.1)$$

where we have kept only second-order terms in the $x_j = X_j - \langle X_j \rangle_t$. Adding to this the kinetic-energy operator times Ψ, we can identify a bilinear Hamiltonian, valid even when the average vibrational coordinates depart significantly from equilibrium values. In the present study, however, we assume that a linear transformation has been made from the x_j to the usual normal vibration coordinates Q_j, describing displacements from equilibrium positions of bond lengths and angles. This transformation maintains the bilinear form of the Hamiltonian.

The Schrödinger equation for a bilinear Hamiltonian has been solved in several other ways[16-18] in addition to those mentioned above. Transition probabilities have been exactly calculated for one degree of freedom.[3,4,6,7,11,17] The purpose of this paper is to present an alternative way of obtaining transition probabilities. The present method is based on the integration of equations of motion and avoids calculations of either the time-evolution operation or the propagator. As a result it is

easily applied to a bilinear Hamiltonian with many degrees of freedom, yielding recurrence relations for the transition probabilities which are most suitable for computational purposes.

In what follows, Sec. II introduces the notation for the multidimensional problem and the interaction picture used to calculate transition probabilities. Section III describes the equations of motion and the procedure followed to derive the recurrence relations, with Sec. IV developing as special cases the problem with a single degree of freedom, applied to $He + H_2$, and the one with vanishing or small quadratic terms in the potential. The conclusions in Sec. V briefly describe how the same approach can be applied to the calculation of collisional time-correlation functions for the same problem.[14]

II. BILINEAR HAMILTONIAN
AND THE TIME-EVOLUTION OPERATOR

The vibrational Hamiltonian for the isolated molecules can be written

$$H_0 = \sum_{j=1}^{f} (P_j^2/m_j + k_j Q_j^2)/2 , \qquad (2.1)$$

where f is the total number of vibrational degrees of freedom, Q_j is the displacement from equilibrium of the jth normal coordinate, $P_j = i\hbar\partial/\partial Q_j$, and m_j and k_j are the mass and force constant for the jth normal mode of vibration. It is convenient to introduce dimensionless coordinates and momenta as follows:

$$q_j = (m_j\omega_j/\hbar)^{1/2} Q_j , \qquad (2.2a)$$

$$p_j = -i\frac{\partial}{\partial q_j} = (\hbar m_j\omega_j)^{1/2} P_j , \qquad (2.2b)$$

where $\omega_j = (k_j/m_j)^{1/2}$ is the jth normal frequency. Therefore the Hamiltonian operator reads

$$H_0 = \tfrac{1}{2}\hbar \sum_{j=1}^{f} \omega_j(p_j^2 + q_j^2) . \qquad (2.3)$$

The interaction potential is a function of the normal coordinates $Q = (Q_1, Q_2, \ldots, Q_f)$ and depends on time through the coordinates of the relative motion $R(t)$. As indicated by Eq. (1.1) it can be expressed as

$$V(t) = V(Q, R(t))$$

$$= V_0(t) + \sum_{j=1}^{f} V_j(t)q_j$$

$$+ \tfrac{1}{2}\sum_{j=1}^{f}\sum_{k=1}^{f} V_{jk}(t)q_j q_k + \cdots , \qquad (2.4)$$

where V_0, V_j, and V_{jk} have dimension of energy because of Eq. (2.2a). If the displacements Q_j are much smaller than the corresponding equilibrium bond lengths and angles then larger-order terms in the expansion (2.4) can be neglected.

Further simplification is obtained by selecting an arbitrary frequency ω (for instance, the largest in the set $\omega_1, \omega_2, \ldots, \omega_f$) and giving frequencies, time and energy

in unity of ω, ω^{-1} and $\hbar\omega$, respectively. This choice corresponds to setting $\hbar = 1$. Therefore the Schrödinger equation becomes

$$\frac{d}{dt}U(t,t_0) = -iH(t)U(t,t_0), \quad U(t_0,t_0) = I , \qquad (2.5a)$$

where I is the identity operator and

$$H(t) = H_0 + V(t) , \qquad (2.5b)$$

$$H_0 = \tfrac{1}{2}\sum_{j=1}^{f} \omega_j(p_j^2 + q_j^2) . \qquad (2.5c)$$

The vibrational states are

$$|N\rangle = |n_1, n_1, \ldots, n_f\rangle , \qquad (2.6)$$

where $n_j = 0, 1, \ldots$, is the jth vibrational quantum number. Therefore

$$H_0|N\rangle = E_N|N\rangle, \quad E_N = \sum_{j=1}^{f} \omega_j(n_j + \tfrac{1}{2}) . \qquad (2.7)$$

The transition probability from an initial state $|N\rangle$ to a final state $|N'\rangle$ is given by

$$P_{N\to N'} = |\langle N|S|N'\rangle|^2 , \qquad (2.8)$$

where $S = U_I(\infty, -\infty)$ and $U_I(t,t_0)$ is the time-evolution operator in the interaction picture

$$U_I(t,t_0) = U_0^\dagger U(t,t_0), \quad U_0 = \exp[-i(t-t_0)H_0] . \qquad (2.9)$$

This operator satisfies

$$\frac{dU_I}{dt} = -iH_I U_I , \qquad (2.10a)$$

where

$$H_I = U_0^\dagger V(t)U_0 . \qquad (2.10b)$$

A straightforward generalization of the treatment for one degree of freedom shows that

$$H_I = \tfrac{1}{2}[\mathbf{p}^T\mathbf{A}(t)\mathbf{p} + \mathbf{q}^T\mathbf{B}(t)\mathbf{q} + \mathbf{p}^T\mathbf{C}(t)\mathbf{q} + \mathbf{q}^T C(t)^T\mathbf{p}]$$

$$+ \mathbf{D}(t)^T\mathbf{p} + \mathbf{F}(t)^T\mathbf{q} + V_0(t)\hat{I} , \qquad (2.11a)$$

where $\mathbf{p}$ and $\mathbf{q}$ are $f \times 1$ matrices with elements p_j and q_j, respectively, and the superscript T means the transpose. Here $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are $f \times f$ matrices, and $\mathbf{D}$ and $\mathbf{F}$ are $f \times 1$, matrices, with elements

$$A_{jk} = V_{jk}\sin[\omega_j(t-t_0)]\sin[\omega_k(t-t_0)] ,$$

$$B_{jk} = V_{jk}\cos[\omega_j(t-t_0)]\cos[\omega_k(t-t_0)] ,$$

$$C_{jk} = V_{jk}\sin[\omega_j(t-t_0)]\cos[\omega_k(t-t_0)] , \qquad (2.11b)$$

$$D_j = V_j\sin[\omega_j(t-t_0)] ,$$

$$F_j = V_j\cos[\omega_j(t-t_0)] .$$

It must be remembered that V_j and V_{jk} are given in units of $\hbar\omega$.

The method developed in what follows applies to any bilinear operator of the form (2.11a) with arbitrary real

time dependent matrices $\mathbf{A}(t)$, $\mathbf{B}(t)$, etc. The matrix elements (2.11b) are just a particular case. Clearly, the physical meaning of the transition probabilities in Eq. (2.8) requires that $H_I \rightarrow 0$ as $|t| \rightarrow \infty$.

III. EQUATIONS OF MOTION AND TRANSITION PROBABILITIES

The calculation of transition probabilities for the model in Sec. II is greatly simplified by considering the canonical transformation

$$\tilde{O} = U_I O U_I^\dagger , \tag{3.1}$$

where O is a linear operator. The rate of change of the operator $\tilde{O}$ is easily found to be

$$\frac{d\tilde{O}}{dt} = i[\tilde{O}, H_I] + U_I \frac{\partial O}{\partial t} U_I^\dagger . \tag{3.2}$$

The canonical transformation in Eq. (3.1) does not correspond to any of the well-known quantum-mechanical pictures. It becomes the identity transformation when the interaction potential V vanishes. We choose such an unusual transformation here because it simplifies the following calculations.

Since $[H_I, \mathbf{p}]$ and $[H_I, \mathbf{q}]$ are linear combinations of $\mathbf{p}$ and $\mathbf{q}$, the solution of Eq. (3.2) for these operators can be written

$$\tilde{\mathbf{p}} = \mathbf{u}_p(t) + \mathbf{u}_{pp}(t)\mathbf{p} + \mathbf{u}_{pq}(t)\mathbf{q} ,$$
$$\tilde{\mathbf{q}} = \mathbf{u}_q(t) + \mathbf{u}_{qp}(t)\mathbf{p} + \mathbf{u}_{qq}(t)\mathbf{q} , \tag{3.3}$$

where $\mathbf{u}_p$, and $\mathbf{u}_q$ are $f \times 1$ real matrices and $\mathbf{u}_{pp}$, $\mathbf{u}_{pq}$, $\mathbf{u}_{qp}$, and $\mathbf{u}_{qq}$ are $f \times f$ real matrices. Since $\tilde{\mathbf{p}}(t_0) = \mathbf{p}$ and $\tilde{\mathbf{q}}(t_0) = \mathbf{q}$ it follows immediately that

$$\mathbf{u}_p(t_0) = \mathbf{u}_q(t_0) = 0, \quad \mathbf{u}_{pq}(t_0) = \mathbf{u}_{qp}(t_0) = 0 ,$$
$$\mathbf{u}_{pp}(t_0) = \mathbf{u}_{qq}(t_0) = 1 , \tag{3.4}$$

where **1** is the identity matrix. Upon introducing Eq. (3.3) into Eq. (3.2) we obtain the equations of motion for the matrices **u**:

$$\begin{bmatrix} \dot{\mathbf{u}}_{pp} & \dot{\mathbf{u}}_{pq} \\ \dot{\mathbf{u}}_{qp} & \dot{\mathbf{u}}_{qq} \end{bmatrix} = \begin{bmatrix} \mathbf{u}_{pp} & \mathbf{u}_{pq} \\ \mathbf{u}_{qp} & \mathbf{u}_{qq} \end{bmatrix} \begin{bmatrix} \mathbf{C}^T & \mathbf{B} \\ -\mathbf{A} & -\mathbf{C} \end{bmatrix} ,$$
$$\begin{bmatrix} \dot{\mathbf{u}}_p \\ \dot{\mathbf{u}}_q \end{bmatrix} = \begin{bmatrix} \mathbf{u}_{pp} & \mathbf{u}_{pq} \\ \mathbf{u}_{qp} & \mathbf{u}_{qq} \end{bmatrix} \begin{bmatrix} \mathbf{F} \\ -\mathbf{D} \end{bmatrix} , \tag{3.5}$$

where the dot stands for time differentiation and the superscript T means transpose. It is not difficult to verify that these equations are closely related to Hamilton's equations of motion for the classical analog of (2.11a).

According to Eq. (3.3) the operators $\tilde{\mathbf{p}}$ and $\tilde{\mathbf{q}}$ are defined by $4f^2 + 2f$ functions of time. However, not all of them are independent since $[\tilde{p}_j, \tilde{p}_k] = [\tilde{q}_j, \tilde{q}_k] = 0$ and $[\tilde{q}_j, \tilde{p}_k] = i\delta_{jk}$, which lead to

$$\mathbf{u}_{qq} \mathbf{u}_{pp}^T - \mathbf{u}_{qp} \mathbf{u}_{pq}^T = 1 ,$$
$$\mathbf{u}_{pq} \mathbf{u}_{pp}^T - \mathbf{u}_{pp} \mathbf{u}_{pq}^T = 0 , \tag{3.6}$$
$$\mathbf{u}_{qq} \mathbf{u}_{qp}^T - \mathbf{u}_{qp} \mathbf{u}_{qq}^T = 0 .$$

The number of these equations is $2f^2 - f$ and, for this reason, there are only $2f^2 + 3f$ independent functions. Equation (3.6) can be used as a test for the numerical solution of Eq. (3.5).

In order to obtain the recurrence relations for the transition probabilities it is convenient to introduce the occupation number representation given by the column matrices of annihilation and creation operators

$$\mathbf{a} = \frac{1}{\sqrt{2}} (\mathbf{q} + i\mathbf{p}) = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_f \end{bmatrix} ,$$
$$\mathbf{a}_+ = \frac{1}{\sqrt{2}} (\mathbf{q} - i\mathbf{p}) = \begin{bmatrix} a_1^\dagger \\ a_2^\dagger \\ \vdots \\ a_f^\dagger \end{bmatrix} . \tag{3.7}$$

They satisfy

$$a_j | n_1, \ldots, n_j, \ldots, n_f \rangle$$
$$= (n_j)^{1/2} | n_1, \ldots, n_j - 1, \ldots, n_f \rangle , \tag{3.8}$$
$$a_j^\dagger | n_1, \ldots, n_j, \ldots, n_f \rangle$$
$$= (n_j + 1)^{1/2} | n_1, \ldots, n_j + 1, \ldots, n_f \rangle .$$

It follows immediately from Eqs. (3.3) that

$$\tilde{\mathbf{a}} = \mathbf{G}_0 + \mathbf{G}_- \mathbf{a} + \mathbf{G}_+ \mathbf{a}_+, \quad \mathbf{a}_+ = \mathbf{G}_0^* + \mathbf{G}_-^* \mathbf{a}_+ + \mathbf{G}_+^* \mathbf{a} , \tag{3.9}$$

where

$$\mathbf{G}_0 = 2^{-1/2} (\mathbf{u}_q + i\mathbf{u}_p) ,$$
$$\mathbf{G}_- = 2^{-1} [\mathbf{u}_{pp} + \mathbf{u}_{qq} + i(\mathbf{u}_{pq} - \mathbf{u}_{qp})] , \tag{3.10}$$
$$\mathbf{G}_+ = 2^{-1} [\mathbf{u}_{qq} - \mathbf{u}_{pp} + i(\mathbf{u}_{qp} + \mathbf{u}_{qp})] .$$

Besides, according to Eqs. (3.4) and (3.6) we have

$$\mathbf{G}_0(t_0) = 0, \quad \mathbf{G}_-(t_0) = 1, \quad \mathbf{G}_+(t_0) = 0 , \tag{3.11}$$

and

$$\mathbf{G}_- \mathbf{G}_-^\dagger - \mathbf{G}_+ \mathbf{G}_+^\dagger = 1, \quad \mathbf{G}_- \mathbf{G}_+^T - \mathbf{G}_+ \mathbf{G}_-^T = 0 , \tag{3.12}$$

respectively.

Upon taking matrix elements $\langle N' | \, | N \rangle$ on both sides of $U_I \mathbf{a} = \tilde{\mathbf{a}} U_I$ and $U_I \mathbf{a}_+ = \tilde{\mathbf{a}}_+ U_I$ we have, after solving for $\langle N' | \mathbf{a} U_I | N \rangle$ in the former,

$$\langle N' | \mathbf{a} U_I | N \rangle = \mathbf{G}_-^{-1} [\langle N' | U_I \mathbf{a} | N \rangle - \mathbf{G}_0 \langle N' | U_I | N \rangle$$
$$- \mathbf{G}_+ \langle N' | \mathbf{a}_+ U_I | N \rangle] , \tag{3.13a}$$
$$\langle N' | U_I \mathbf{a}_+ | N \rangle = \mathbf{G}_0^* \langle N' | U_I | N \rangle + \mathbf{G}_-^* \langle N' | \mathbf{a}_+ U_I | N \rangle$$
$$+ \mathbf{G}_+^* \langle N' | \mathbf{a} U_I | N \rangle , \tag{3.13b}$$

respectively, where the following notation is used:

$$\langle N'|U_I\mathbf{a}|N\rangle = \begin{pmatrix} \langle N'|U_I a_1|N\rangle \\ \langle N'|U_I a_2|N\rangle \\ \cdots \\ \langle N'|U_I a_f|N\rangle \end{pmatrix} , \tag{3.14}$$

etc. Notice that the elements of the column vectors $\langle N'|U_I\mathbf{a}|N\rangle$, etc., are the desired transition amplitudes, except for coefficients that can be easily determined. Besides, since the eigenvalues of $\mathbf{G}_+\mathbf{G}_+^\dagger$ are larger than or equal to zero, it follows from Eq. (3.12) that those of $\mathbf{G}_-\mathbf{G}_-^\dagger$ will be larger than or equal to unity and $|\det\mathbf{G}_-|\geq 1$. Therefore $\mathbf{G}_-^{-1}$ exists for all t values.

Equation (3.13b) can be rewritten in a more convenient way by introducing Eq. (3.13a) into it and using Eq. (3.12). The result is

$$\langle N'|U_I\mathbf{a}^\dagger|N\rangle = (\mathbf{G}_0^* - \mathbf{G}_+^*\mathbf{G}_-^{-1}\mathbf{G}_0)\langle N'|U_I|N\rangle$$

$$+ \mathbf{G}_+^*\mathbf{G}_-^{-1}\langle N'|U_I\mathbf{a}|N\rangle$$

$$+ (\mathbf{G}_-^{-1})^T\langle N'|\mathbf{a}_+ U_I|N\rangle . \tag{3.13b'}$$

The starting point of the recursive process is $|N'\rangle = |0\rangle$, $|N\rangle = |0\rangle$, where $|0\rangle = |n_1 = 0, n_2 = 0, \ldots, n_f = 0\rangle$ is the ground state of H_0. In the first step we obtain

$$\langle 0|\mathbf{a}U_I|0\rangle = -\mathbf{G}_-^{-1}\mathbf{G}_0\langle 0|U_I|0\rangle ,$$
$$\langle 0|U_I\mathbf{a}_+|0\rangle = (\mathbf{G}_0^* - \mathbf{G}_+^*\mathbf{G}_-^{-1}\mathbf{G}_0)\langle 0|U_I|0\rangle , \tag{3.15}$$

which yield all the transition amplitudes for $|0\rangle \to a_j^\dagger|0\rangle$, and $a_j^\dagger|0\rangle \to |0\rangle$, $j = 1, 2, \ldots, f$, respectively. Strictly speaking, the recurrence relations (3.13) provide the transition probabilities divided by $\langle 0|U_I|0\rangle$, which can be easily calculated as shown below.

Since $\mathbf{a}|0\rangle = 0$ we have $\tilde{\mathbf{a}}U_I|0\rangle = 0$ which, because of Eqs. (3.7) and (3.9), is a first-order partial differential equation for $U_I|0\rangle$. The solution is easily found to be

$$\langle \mathbf{q}|U_I|0\rangle = N\exp(-\mathbf{g}_1^T\mathbf{q} - \tfrac{1}{2}\mathbf{q}^T\mathbf{g}_2\mathbf{q}) , \tag{3.16a}$$

$$\mathbf{g}_1 = 2^{1/2}(1 - \mathbf{G}_-^{-1}\mathbf{G}_+)^{-1}\mathbf{G}_-^{-1}\mathbf{G}_0 , \tag{3.16b}$$

$$\mathbf{g}_2 = (1 - \mathbf{G}_-^{-1}\mathbf{G}_+)^{-1}(1 + \mathbf{G}_-^{-1}\mathbf{G}_+) , \tag{3.16c}$$

where

$$|N| = [\pi^{-f}\det(\mathrm{Re}\,\mathbf{g}_2)]^{1/2}$$

$$\times \exp[-\tfrac{1}{3}(\mathrm{Re}\,\mathbf{g}_1)^T(\mathrm{Re}\,\mathbf{g}_2)^{-1}(\mathrm{Re}\,\mathbf{g}_1)] . \tag{3.17}$$

In this last equation Re stands for the real part of a complex number. Finally, since $|0\rangle = \pi^{-f/4}\exp(\mathbf{q}^T\mathbf{q}/2)$ we have

$$\langle 0|U_I|0\rangle = |N|[\pi^f\det(1 - \mathbf{G}_-^{-1}\mathbf{G}_+)]^{1/2}$$

$$\times \exp[-\tfrac{1}{2}(\mathbf{G}_-^{-1}\mathbf{G}_0)^T(1 - \mathbf{G}_-^{-1}\mathbf{G}_+)^{-1}\mathbf{G}_-^{-1}\mathbf{G}_0$$

$$+ i\theta] , \tag{3.18}$$

where θ is a phase factor that is immaterial for the present purposes.

In actual applications, one first integrates the equations of motion (3.5) from an initial time t_0 before the interaction to a final time t_1 after the interaction. The matrices $\mathbf{u}$, calculated at time t_1, are used to construct the matrices $\mathbf{G}$ in Eq. (3.10). Finally, the transition probabilities are obtained from the recurrence relations in Eqs. (3.13). The time dependence of the matrices $\mathbf{u}$ is asymptotically smoother in the interaction picture (described in Sec. II) than in the Schrödinger picture. For this reason, choosing the former picture facilitates both the integration process and the determination of the final time t_1 for which convergence is achieved up to the desired accuracy.

IV. TWO EXAMPLES FOR MOLECULAR COLLISIONS

In order to illustrate more plainly how the recurrence relations (3.13) work, two simple particular cases are discussed below. To begin with, consider an atom-diatom collision. Since there is only one vibrational degree of freedom then $f = 1$ and Eqs. (3.13a) and (3.13b') reduce to

$$I_{n'+1,n} = G_-^{-1}(n'+1)^{-1/2}(n^{1/2}I_{n',n-1} - G_0 I_{n',n}$$

$$- G_+ n'^{1/2}I_{n'-1,n}) , \tag{4.1a}$$

$$I_{n',n+1} = (n+1)^{-1/2}G_-^{-1}[(G_0^*G_- - G_+^*G_0)I_{n',n}$$

$$+ n^{1/2}G_+^* I_{n',n-1}$$

$$+ n'^{1/2}I_{n'-1,n}] , \tag{4.1b}$$

where $I_{n',n} = \langle n'|U_I|n\rangle$ and G_0, G_-, and G_+ are complex numbers. Given $I_{n',n}$, $I_{n'-1,n}$, and $I_{n',n-1}$, the recurrence relations (4.1a) and (4.1b) proceed rightwards and upwards yielding $I_{n'+1,n}$ and $I_{n',n+1}$, respectively. The calculation of $I_{5,3}$ is shown in Fig. 1. The transition amplitudes can be written $I_{n',n} = J_{n',n}I_{0,0}$ where $\{J_{n',n}; n'n, = 0, 1, \cdots\}$ is a solution of Eqs. (3.13) with the initial condition $J_{0,0} = 1$. The transitions probability $|I_{0,0}|^2$ can be obtained either from Eq. (3.18) or from

$$|I_{0,0}|^2 = (1 + |J_{0,1}|^2 + |J_{0,2}|^2 + \cdots)^{-1}$$

because $|I_{0,0}|^2 + |I_{0,1}|^2 + \cdots = 1$. This series is found to converge quickly enough so that only a few terms are re-
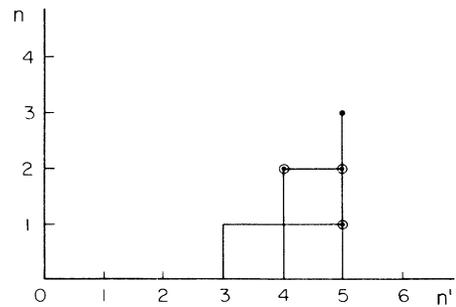
FIG. 1. Example for the calculation of the transition amplitude $I_{5,3}$. Equations (4.1a) and (4.1b) are used to move rightwards and upwards, respectively. Circles indicate the input into $I_{5,3}$. The points are generated in the order $(n,n') = (0,1)$, $(0,2)$, $(0,3)$, $(0,4)$, $(0,5)$, $(1,3)$, $(1,4)$, $(2,4)$, $(1,5)$, $(2.5,)$, and finally (3.5).

TABLE I. Transition probabilities $P_{n \rightarrow n'}$ for the He-H$_2$ collision ($m_A = 4$, $m_B = m_C = 1$, $a = 0.2$ Å, and $\alpha = 0.3$) (Ref. 14) calculated with the recurrence relations (RR) and with the basis-set expansion (BSE) for $M = 10$. The total energy is chosen to be $5\hbar\omega$.

n	n'	RR	CPU time (sec)	BSE	CPU time (sec)
0	1	0.2317	31	0.2317	1741
0	2	0.016 78	32	0.016 79	1534
1	2	0.1979	32	0.1982	2554

quired to obtain $|I_{0,0}|^2$ accurately. However, Eq. (3.18) is preferable when there are many vibrational degrees of freedom. In order to show the computational advantages of the present method we consider the collision between an atom A and a diatomic molecule BC; i.e.,

$$A + BC(n) \rightarrow A + BC(n') \ . \tag{4.2}$$
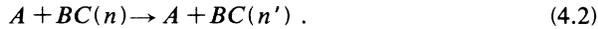
The most widely used interaction potential V between an atom and a diatom is an exponential function

$$V(r_{AB}) = D \exp(-r_{AB}/a) \ , \tag{4.3}$$

where D and a are potential parameters and r_{AB} is the distance between A and B. This potential can be written as $V(R,q)$, where R is the distance between A and the center of mass of BC and q is the dimensionless displacement of the harmonic oscillator BC from equilibrium.

Since the purpose of the present paper is to illustrate the use of recurrence relations for the transition amplitudes we choose, for the sake of simplicity, $R(t)$ to be the solution of the classical equations of motion for the potential $V(R,0)$. Upon expanding $V(R(t),q)$ as $V_1(t)q + V_{11}(t)q^2/2$ we find[14]

$$V_1(t) = (\hbar m^{-1}\omega^{-1})^{1/2}\gamma a^{-1}E \ \text{sech}^2[(E/2\mu)^{1/2}a^{-1}t] \ , \tag{4.4a}$$

$$V_{11}(t) = [(\hbar m^{-1}\omega^{-1})^{1/2}\gamma a^{-1}]V_1(t) \ , \tag{4.4b}$$

where $\gamma = m_C/(m_B + m_C)$, $m = \gamma m_B$, $\mu = (m_B + m_C)m_A/(m_A + m_B + m_C)$, and ω is the frequency of the harmonic vibrations of BC. The average relative kinetic energy E is given by

$$E = \tfrac{1}{2}\mu[\tfrac{1}{2}(v_i + v_f)]^2 \ , \tag{4.5}$$

where v_i and v_f are the initial and final relative velocities, respectively. It is also convenient to introduce the dimensionless parameter $\alpha = a^{-1}(\hbar m^{-1}\omega^{-1})^{1/2}$.

The calculation is very simple. First Eqs. (3.5) are integrated from $t_0 \ll 0$ to $t \gg 0$ in order to obtain the real

numbers $u_p(t)$, $u_q(t)$, $u_{pp}(t)$, $u_{qq}(t)$, $u_{pq}(t)$, and $u_{qp}(t)$. Next we calculate the complex numbers $G_0(t)$, $G_+(t)$, and $G_-(t)$ according to (3.10) and obtain $I_{n',n}/I_{0,0}$ for the desired n' and n values from Eqs. (4.1). Finally, $I_{0,0}$ is calculated as discussed before and $P_{n \rightarrow n'} = |I_{n',n}|^2$.

We also calculate the transition probabilities by means of the usual basis-set-expansion method:

$$U_I(t, -\infty)|n\rangle = \lim_{M \to \infty} \sum_{j=0}^{M} a_{jn}(t)\exp(-iE_j\hbar^{-1}t)|j\rangle \ , \tag{4.6}$$

where the expansion coefficients $a_{jn}(t)$ are solutions of an infinite set of first-order differential equations with the initial conditions $a_{jn}(-\infty) = \delta_{jn}$. Then, $P_{n \rightarrow n'} = |a_{n'n}(\infty)|^2$.

The transition probabilities for a model He-H$_2$ collision with the parameters given in Ref. 3 were calculated using both the present algorithm and the basis-set expansion. In both cases the interaction potential was expanded in a Taylor series up to second order as shown in Eqs. (4.4). Therefore results are expected to agree provided convergence is reached. Results are shown in Table I.

The differential equations were solved with the Richardson method of successive extrapolations. The recurrence relations are found to be about 60 times faster than the basis-set expansion. The larger the number of vibrational degrees of freedom, or the quantum numbers of the transition, the larger the difference in running times between both procedures. The recurrence relations enable one to obtain many transition probabilities very quickly. Some of them are shown in Table II for the same system and large quantum numbers, for which the basis-set-expansion method would be very time consuming. Numerical results are collected here for comparison purposes; for $n' = 8$ the transition probabilities are smaller than 10^{-5}.

In the next example it is assumed that the quadratic terms in the Taylor expansion (2.4) for the interaction po-

TABLE II. Transition probabilities for the He-H$_2$ collision at the total energy of $10\hbar\omega$. The numbers in square brackets are powers of 10.

n'	$P_{0 \rightarrow n'}$	$P_{1 \rightarrow n'}$	n'	$P_{0 \rightarrow n'}$	$P_{1 \rightarrow n'}$
0	0.1029	0.2601	4	0.3990[−1]	0.1742
1	0.2601	0.1132	5	0.5950[−2]	0.5261[−1]
2	0.2659	0.1899[−1]	6	0.4109[−3]	0.6028[−2]
3	0.1400	0.1965	7	0.1011[−4]	0.2182[−3]

tential can be neglected, but we consider a general f, suitable for molecule-molecule collisions. Although this special case has been fully discussed in the literature, we will briefly consider it here in order to show the quite simple form of the recurrence relations (3.13). Since $A = B = C = 0$ then Eqs. (3.5) can be easily solved and the result is

$$\mathbf{u}_{pp} = \mathbf{u}_{qq} = 1, \quad \mathbf{u}_{pq} = \mathbf{u}_{qp} = 0 \; ,$$

$$\mathbf{u}_p(t) = \int_{t_0}^{t} \mathbf{F}(s)ds, \quad \mathbf{u}_q(t) = - \int_{t_0}^{t} \mathbf{D}(s)ds \; , \tag{4.7}$$

and

$$\mathbf{G}_0 = 2^{-1/2}(\mathbf{u}_q + i\mathbf{u}_p), \quad \mathbf{G}_- = 1, \quad \mathbf{G}_+ = 0 \; , \tag{4.8}$$

which clearly shows that the recurrence relations (3.13) do not couple the components of the transition-probability column vectors. In other words, we have $2f$ recurrence relations of the form

$$\langle N'|a_j U_I|N \rangle = \langle N'|U_I a_j|N \rangle - G_{0j}\langle N'|U_I|N \rangle \; ,$$

$$\langle N'|U_I a_j^{\dagger}|N \rangle = G_{0j}^{*}\langle N'|U_I|N \rangle + \langle N'|a_j^{\dagger} U_I|N \rangle \; ,$$

$$j = 1, 2, \ldots, f \tag{4.9}$$

and increases by unity can be made in each quantum number at a time (for instance, n_j and n_j') without altering the remaining ones.

V. CONCLUSIONS

The method just presented allows the calculation of transition amplitudes for general f-dimensional time-dependent quadratic Hamiltonians. The procedure is quite simple. First, the classical equations of motion (3.5) are integrated from t_0 to t and the matrices $\mathbf{u}$ are obtained. Second, they are used to calculate the matrices $\mathbf{G}$ and the integral $\langle 0|U_I|0 \rangle$. Finally, the recurrence relations (3.13) are used to obtain the desired transition amplitudes.

This procedure offers at least two advantages. First, the recurrence relations (3.13) are most appropriate for computational purposes because they only involve matrices. This is certainly very convenient when there are many degrees of freedom. Second, instead of the nonlinear differential equations for the parameters in the time-evolution operator we obtain linear differential equations which are closely related to the classical equations of motion.

It has been argued that the bilinear (or harmonic) approximation would not lead to acceptable results in some other cases involving different interaction potentials.[19] For the interaction potential and atomic masses used in the present paper we have verified here that the bilinear Hamiltonian gives very good results, in accordance with expectations.[3] We have further investigated our model for other masses introducing expansion around average trajectories.

In closing we add that the procedure just described is also useful in calculating time-correlation functions.[20] For instance, a diagonal matrix element of the form $C_N(t) = \langle N|S^{\dagger}S(t)|N \rangle$, where S is given in Eq. (2.3) and

$$S(t) = \exp(itH_0)S \exp(-itH_0) \; ,$$

can be written as $C_N(t) = \langle N|\Gamma|N \rangle \exp(-itE_N)$, where $\Gamma = S^{\dagger}\exp(itH_0)S = \exp(itS^{\dagger}H_0 S)$ defines a canonical transformation. Since $\Gamma a \Gamma^{\dagger}$ and $\Gamma a_+ \Gamma^{\dagger}$ are easily obtained, one can therefore apply the procedure of Sec. IV with U_I replaced by Γ to derive a recurrence relation for the matrix elements of Γ.

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