SEMICLASSICAL ALGEBRAIC APPROACH TO TRANSLATIONAL-VIBRATIONAL ENERGY TRANSFER IN MOLECULAR COLLISIONS

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Translational-vibrational energy transfer in molecular collisions is studied by means of a semiclassical approach. The trajectory for the relative motion is obtained from the classical equations of motion for an effective interaction potential. The problem is then reduced to solving the Schrödinger equation for a harmonic oscillator with a time-dependent perturbation. Further simplification is achieved by expanding the interaction potential in a Taylor series around the quantum-mechanical expectation value of the vibrational coordinate. The advantage of using Lie algebraic methods is illustrated. Energy conservation and detailed balance within this approximate scheme are discussed. Results are shown for a simple atom-diatom collision model.

The semiclassical approximation [1] poses a simple and reasonably accurate way of calculating translational-vibrational energy transfer in molecular collisions. This approach is based on the assumption that some degrees of freedom, usually translational and rotational ones, can be described by means of classical mechanics. As a result of introducing the classical trajectories into the interaction potential a time dependent Hamiltonian operator is obtained for the vibrational degrees of freedom.

If the displacement of the vibrational coordinates from properly chosen reference values is found to be small, the interaction potential can be replaced by its Taylor expansion around them. Usually, terms of order larger than the second one are neglected (harmonic approximation) in which case the Schrödinger equation for the vibrational motion can be treated by means of Lie algebraic methods [2-6]. This fact greatly facilitates the calculation and allows one to treat systems with many degrees of freedom [5].

The equilibrium position is most often chosen to be the reference coordinate value [2, 4, 5] though remarkably more accurate results are certainly obtained by using either the classical vibrational trajectory [3] or the expectation value of the vibrational coordinate [7, 8].

Several effective potentials have been proposed for the classical relative motion [1, 9, 10] (see also Ref. [11] for the case of rotational transitions). Accurate results come from the expectation value of the interaction potential in the time-dependent semiclassical state [9]. As far as we know this effective potential has not been used together with the harmonic approximation and the Lie algebraic methods which enable one to easily generalize the approach to many degrees of freedom [5].

The purpose of the present communication id to show that the harmonic approximation and the Lie algebraic methods are most suitable for introducing improved features into the semiclassical approach such as the expansion of the interaction potential about the expectation value of the vibrational coordinate and the use of an effective potential for the classical relative motion.

For the sake of simplicity we consider here a simple model for the collinear collision between an atom A and a diatomic molecule BC. If the vibrational potential for the diatomic molecule is assumed to be harmonic then the hamiltonian operator can be written [1, 12]

$$H(q, R) = P^2/2\mu + H_0 + V(q, R), \quad H_0 = 1/2(p^2 + q^2), \quad (1)$$

where $\mu = m_A m_C/[m_B(m_A + m_B + m_C)]$, q is the displacement from equilibrium of the vibrational coordinate, R is the distance from A to the center of mass of BC, $p = -i\partial/\partial q$ and $P = -i\partial/\partial R$. Units are chosen so that the reduced mass of the oscillator, its frequency and $\hbar$ equal unity.

In the semiclassical approximation a trajectory for the relative motion is obtained from the classical equations

$$dR/dt = P/\mu, \quad dP/dt = -\partial V(R, t)/\partial R \quad (2)$$

where $V(R, t)$ is an appropriate potential that vanishes at $\pm\infty$ (the explicit time dependence comes from the vibrational motion). It is then introduced in Eq. (1) to obtain the semiclassical Hamiltonian $H_{sc}(q, t) = H_0 + V[q, R(t)]$. If the oscillator was in the vibrational state $|m\rangle$ at $t = t_0$, where $|m\rangle$ is an eigenstate of H_0 with eigenvalue $m + 1/2$, then the probability of finding it in the state $|n\rangle$ at the time t is given by $P_{m-n} = |\langle n|\Psi_m(t)\rangle|^2$, where $\Psi_m(t)$ is a solution of the Schrödinger equation

$$d\Psi_m(t)/dt = -iH_{sc}\Psi_m(t), \quad (3)$$

with the initial condition $\Psi_m(t_0) = |m\rangle$.

The effective potential $V[R, t)$ is often chosen to be $V(0, R) [1 - 6]$. However, better results are obtained from the effective potential [9]

$$V(R, t) = \langle\Psi_m|V(q, R)|\Psi_m\rangle. \quad (4)$$

From a practical point of view, the classical equations (2) are integrated from t_0 to t_f chosen so that $V[R(t_0), t_0]$ and $V[R(t_f), t_f]$ are both small enough. At the same time one has to solve the Schrödinger equation (3) because V depends on $\Psi_m(t)$ as shown in Eq. (4). This composite calculation can be carried out by expanding $\Psi_m(t)$ in the basis set of states of H_0. The potential for the relative motion depends on the trajectory $R(t)$ and therefore on the initial kinetic energy.

If E is the total energy the initial momentum is $P_m = [2\mu(E - E_m)]^{1/2}$ where $E_m = m + 1/2$ is the vibrational energy of the oscillator in the initial state. On the other hand, the initial momentum for the calculation of the probability P_{n-m} is P_n, so that we would use two different time-evolution operators in the calculation of those transition probabilities. To overcome this difficulty, which arises from the approximate nature of the method, the initial value of the classical momentum is commonly chosen to be [2]

$$P(t_0) = (P_m + P_n)/2. \quad (5)$$

The energy transferred to the oscillator is $\Delta E = \langle\Psi_m(t_f)|H_0|\Psi_m(t_f)\rangle - \langle m|H_0|m\rangle$.

The calculation is greatly simplified by means of the harmonic approximation which consists of expanding the perturbation potential in a Taylor series around a given reference value of the coordinate (say q_0). If terms of order larger than the second one are neglected then the problem reduces to solving the Schrödinger equation $\partial U(t, t_0)/\partial t = -iH_H U(t, t_0)$, where $U(t_0, t_0) = I$ is the identity operator,

$$H_H = H_0 + V_H,$$

$$V_H = W_0(t) + W_1(t)q + \frac{1}{2}W_2(t)q^2, \quad (6a)$$

and

$$W_0 = V[q_0, R(t)] - V^{(1)}[q_0, R(t)]q_0 + (1/2)V^{(2)}[q_0, R(t)]q_0^2$$

$$W_1 = V^{(1)}[q_0, R(t)] - V^{(2)}[q_0, R(t)]q_0,$$

$$W_2(t) = V^{(2)}[q_0, R(t)], \quad (6b)$$

with $V^{(n)}(q, R) = \partial^n V(q, R)/\partial q^n$. We omit $W_0(t)$ as well as $P^2(t)/2\mu$ in the treatment below because they contribute only to a phase factor which does not appear in the transition probabilities.

Although the differential equation for the time evolution operator is simpler in the Schrödinger picture than in the interaction one, the latter is preferable from the computational point of view [2, 5]. The time-evolution operator in the interaction picture satisfies the differential equation

$$\partial U_I(t, t_0)/\partial t = -iH_I U_I(t, t_0), \quad U_I(t_0, t_0) = I, \quad (7)$$

where $U_I = U_0^+ U$, $U_0 = \exp(-i\tau H_0)$, and $\tau = t - t_0$. The Hamiltonian in this picture, namely, $H_I = U_0^+ V_H U_0$, is found to be

$$H_I = \frac{1}{2}[A(t)(a^+)^2 + A^*(t)a^2 + B(t)(a^+a + aa^+)] + C(t)a + C^*(t)a^*, \quad (8)$$

where + stands for adjoint and * for complex conjugation, $a = 2^{-1/2}(q + ip)$ and $a^+ = 2^{-1/2}(q - ip)$ are the annihilation and creation operators, respectively, $A = W_2 e^{-2i\tau}/2$, $B = W_2/2$, and $C = 2^{-1/2}W_1 e^{-i\tau}$.

Since H_I belongs to the sixth-dimensional Lie algebra spanned by $\{1, a, a^+, a^2, (a^+)^2, a^+a + aa^+\}$, the time-evolution operator U_I can be written as a product of simple exponential operators [13] which greatly facilitates the calculation of transition probabilities [2-4] and other physical properties of the system. However,

In order to obtain transition probabilities, which in terms of U_I read $P_{n\to m} = |\langle n|U_I|n\rangle|^2$, it is convenient to proceed in a different way that avoids giving U_I any particular form and yields simple and computationally advantageous recurrence relations for the matrix elements $\langle n|U_I|n\rangle$ [5, 14].

The method is based on the equations of motion

$$d\hat{O}/dt = U_I^+\{\partial O/\partial t + i[H_I, O]\}U_I,$$

where $\hat{O} = U_I^+ O U_I$. In particular, for the annihilation and creation operators it is found that

$$\hat{a} = C_0(t) + G_-(t)a + G_+(t)a^+,$$

and

$$\hat{a}^+ = C_0^*(t) + G_+^*(t)a + G_-^*(t)a^+$$

where the complex-valued functions of time C_0, G_- and G_+ are solutions of the differential equations

$$dG_0/dt = -i(C'G_0 + AG_0^* + D^*),$$ (9a)

$$dG_-/dt = -i(CG_- + G_+^*),$$ (9b)

$$dG_+/dt = -i(CG_+ + AG_-),$$ (9c)

with the initial conditions $G_0(t_0) = G_+(t_0) = 0$, and $G_-(t_0) = 1$.

Since $\hat{a}U_I = U_I\hat{a}$ and $\hat{a}^+U_I + U_I(\hat{a})^+$, it follows from the form of $\hat{a}$ and $(\hat{a})^+$ and the well-known properties of the annihilation and creation operators that [5, 14]

$$\langle n|U_I|m+1\rangle = G_+^{*-1}(m+1)^{-1/2}\{-G_0^*\langle n|U_I|m\rangle + n^{1/2}\langle n-1|U_I|m\rangle$$
$$-G_+^*m^{1/2}\langle n|U_I|m-1\rangle\},$$ (10a)

$$\langle n+1|U_I|m\rangle = G_-^{-1}(n+1)^{-1/2}\{G_0\langle n|U_I|m\rangle - G_+G_0^*\langle n|U_I|m\rangle$$
$$+G_+^*n^{1/2}\langle n-1|U_I|m\rangle, + m^{1/2}\langle n|U_I|m-1\rangle\}.$$ (10b)

These recurrence relations are easily programmed and yield all the ratios $r_{m,n} = \langle n|U_I|m\rangle/\langle 0|U_I|0\rangle$ hierarchically starting from $m = n = 0$. The recurrence relations (10) do not give us the transition amplitude $\langle 0|U_I|0\rangle$. In order to calculate $P_{m\to n} = |r_{m,n}|^2 P_{0\to 0}$ we need $P_{0\to 0} = |\langle 0|U_I|0\rangle|^2$ which can be obtained either directly [14] or from the completeness relation that can be rewritten $P_{0\to 0} = (r_{0,0} + r_{1,0} + \ldots)^{-1}$ [5].

When $\langle \Psi_m|q|\Psi_m\rangle$ deviates largely from zero during the collision, results obtained from the semiclassical algebraic treatment with $V = V(0, R)$ and $q_0 = 0$ are not sufficiently accurate. In such cases it is convenient to expand the interaction potential around $q_0 = u(t) = \langle m|U^+qU|m\rangle$ [8] and to use the effective potential $V = \langle m|U^+V_H U|m\rangle$, which is the harmonic approximation to Eq. (4). The algebraic procedure proposed in this paper is particularly useful because it allows writing all the equations in terms of the functions G. For instance

$$u(t) \equiv \langle m|U^+qU|m\rangle = 2^{1/2}\text{Re}(e^{-i\tau}G_0),$$ (11)

where Re stands for real part of a complex number. Besides, the effective potential for the classical trajectory becomes

$$V(R, t) = V[u(t), R] + (1/2)V^{(2)}[u(t), R]\sigma^2$$ (12a)

where

$$\sigma^2 = \langle m|U^+(q - u)^2U|m\rangle$$
$$= \{(m+1/2)[2\text{Re}(e^{-2i\tau}G_-^*G_+) + |G_-|^2 + |G_+|^2] + 2[\text{Re}(e^{-i\tau}G_0)]^2\}^{1/2}$$ (12b)

which shows that classical equations of motion (2) and the quantum-mechanical ones (9) are to be integrated simultaneously from t_0 to t_r. The initial relative momentum is given by Eq. (5) and the final values of G_0, G_+ and G_- are used to obtain the transition probabilities through the recurrence relations (10).

From now the semiclassical algebraic procedures based on the choices ($V = V(0, R)$, $q_0 = 0$) and ($V = \langle m|U^+V_H U|m\rangle$, $q_0 = u$) are called methods A and B respectively. The quantities A, C and D in (9) are functions of q_0. In method B $q_0 = u$ depends on G_0 so that (9) is a set of nonlinear coupled differential equations which one integrates using standard numerical algorithms.

The total energy defined according to the harmonic approximation, $E_H = \langle m|U^+H_H U|m\rangle + P^2/(2\mu)$ is not conserved during the collision. In fact since $\partial P/\partial t = -\partial V/\partial R$ it follows that

$$dE_H/dt = (dR/dt)\frac{\partial}{\partial R}\left[V^{(1)}(R, 0)u + V^{(2)}(R, 0)(u^2 + \sigma^2)\right]$$ (13a)

for method A and

$$dE_H/dt = \langle m|U^+(\partial V_H/\partial t)U|m\rangle + (P/\mu)\partial P/\partial t$$
$$= \langle m|U^+(\partial V_H/\partial R)U|m\rangle\partial R/\partial t + \langle m|U^+(\partial V_H/\partial u)U|m\rangle du/dt$$
$$+ (P/\mu)\partial P/\partial t$$
$$= (\partial V/\partial R + \partial P/\partial t)P/\mu + \langle m|U^+(\partial V_H/\partial u)U|m\rangle du/dt$$
$$= \langle m|U^+(\partial V_H/\partial u)U|m\rangle du/dt$$
$$= (1/2)(du/dt)V^{(3)}(R, u)\sigma^2(t)$$ (13b)

for method B. One can convince oneself that the magnitude of the change of E_h with time is a measure of the inaccuracy of the harmonic approximation which requires that both $V(3)$ and σ^2 be small. It is worth mentioning that even though dE_H/dt may be large for certain t values, the difference $E_H(\infty) - E_H(-\infty)$ is frequently small because R and u values are nearly symmetric around the turning point t_c, where $P(t_c) = 0$.

Because of the symmetry of the collision process about the turning point t_c one expects that $P_{m\to n} = P_{n\to m}$. This equality, often called detailed balance, is satisfied by method A because $R(t_c - t) = R(t_c + t)$ but not by method B because as V is given by Eq. (12) the relative trajectory is no longer symmetric around t_c, and, which is more important, because different semiclassical Hamiltonian are used in the calculation of $P_{m\to n}$ and $P_{n\to m}$ (notice that $V[q, R(t)]$ depends on the initial vibrational state). Therefore, in the latter case the average of $P_{m\to n}$ and $P_{n\to m}$ is considered to be the actual transition probability.

It is usually assumed that intermolecular potentials are relatively well described by Lennard-Jones, Morse or Buckingham functions. However, since the vibrational energy transfer is extremely sensitive to the slope of the repulsive branch of the interaction it is customary to chose the exponential repulsive potential $V(q, R) = \exp[-\alpha(R - q)]$ in most calculations [1]. Here we also choose it to test the accuracy of the harmonic approximation because of the large amount of "exact" and approximate results available. The system is characterized by two independent parameters, namely α and μ. Systems for which exact quantum-mechanical calculations exist [12] can be arbitrarily divided into two classes one for small and the other one for large reduced masses [9]. Two examples, one of each class, are considered here which are called system 1 and system II, respectively, from now on.
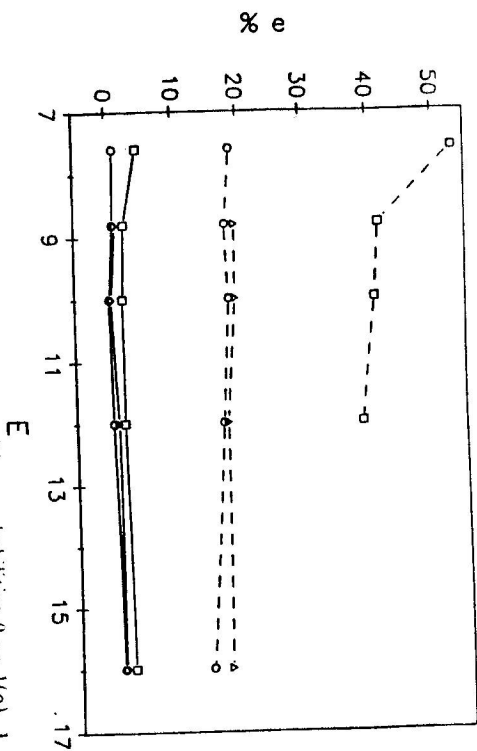
Table 1

Transition probabilities obtained by methods A and B and exact results from ref. [12]. The model parameters are $\alpha = 0.114$, $\mu = 1/2$ for system I and $\alpha = 0.2973$, $\mu = 5/4$ for system II. E is the total energy in units of the ground-state vibrational energy $\bar{\omega}/2$. The number in brackets is the negative power of ten.

System	E	Transition	Exact	Method A	Method B
I	7.6	0 → 1	4.30(5)	5.12(5)	4.25(5)
		0 → 2	1.28(11)	1.96(11)	1.34(11)
	8.8	0 → 1	2.03(4)	2.40(4)	2.01(4)
		1 → 2	2.23(5)	2.67(5)	2.20(5)
		0 → 2	1.13(9)	1.60(9)	1.10(9)
	10.0	0 → 1	6.58(4)	7.81(4)	6.55(4)
		1 → 2	1.52(4)	1.82(4)	1.51(4)
		0 → 2	9.43(7)	1.31(6)	9.20(7)
	12.0	0 → 1	2.85(3)	3.35(3)	2.83(3)
		1 → 2	1.32(3)	1.56(3)	1.30(3)
		0 → 2	2.51(8)	3.54(8)	2.45(8)
	16.0	0 → 1	1.92(2)	2.21(2)	1.89(2)
		1 → 2	1.66(2)	1.93(2)	1.63(2)
		0 → 2	8.12(5)	1.09(5)	7.86(5)
II	4.9455	0 → 1	1.12(4)	1.84(4)	1.12(4)
		1 → 2	2.30(4)	3.68(4)	2.28(4)
		0 → 2	1.69(7)	4.44(7)	1.67(7)
	6.9455	0 → 1	2.93(3)	4.76(3)	2.92(3)
		1 → 2	5.97(3)	9.47(3)	5.96(3)
		0 → 2	2.31(5)	5.94(5)	2.29(5)
	8.9455	0 → 1	1.53(2)	2.44(2)	1.53(2)
	16.7882	0 → 1	1.97(1)	2.58(1)	1.85(1)
		1 → 2	2.37(1)	2.95(1)	2.28(1)
		0 → 2	1.62(2)	3.39(2)	1.62(2)

Fig. 1. Percent relative error, %e, for the transition probabilities 0 → 1(o), 1 → 2(□) and 0 → 2(□) for system I ($\mu = 1/2$, $\alpha = 0.114$), calculated by means of methods A(- -) and B(—).
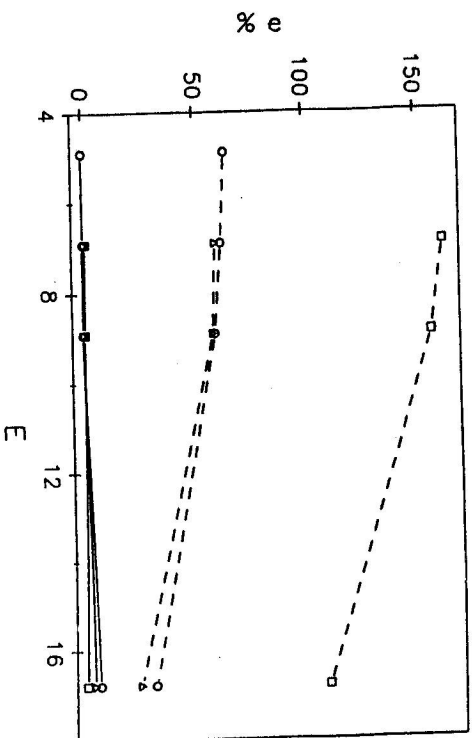
Fig. 2. The same as in Fig.1 for system II ($\mu = 5/4$, $\alpha = 0.2973$).

The transition probabilities calculated by means of methods A and B are compared with the exact quantum-mechanical ones [12] in Table 1, and the percent relative errors are shown in Figs. 1 and 2. As expected, method B gives better results than method A and the difference is larger for the large-mass system II for which the deviation of u from zero is much larger [8]. Both the results obtained by using the complete semiclassical potential (i.e. without the harmonic approximation) [9] and present method B are in remarkable agreement with the quantum-mechanical

ones, the relative error being less than 3%. However, it is preferable to use present algebraic method because the calculation is much simpler, requiring remarkably less computation memory and time [5]. It should be kept in mind that when the whole semiclassical potential $V(q, t)$ is used, the Schrödinger equation is solved by expanding the wave function in the basis of states of H_0 [9]. In such a case the basis dimension required to reach convergence, and thereby the number of differential equations, is proportional to the total relative energy. On the other hand, the number of differential equations when using the harmonic approximation remains constant. This advantage is even more noticeable in systems with a larger number of degrees of freedom. For instance in the case of the collision between two identical diatomic molecules the number of open channels increases with the square of the energy.

For all these reasons the harmonic approximation and the Lie algebraic methods discussed in this paper are most suitable for implementing improved versions of the semiclassical approach to study translational-vibrational energy transfer in collisions between large molecules.

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