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Exact Semiclassical Calculations of Translational-Vibrational Energy Transfer*

J. Daniel Kelley and Max Wolfsberg

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

We present "exact" calculations, by the semiclassical method, of vibrational excitation of a harmonic diatomic molecule A-B, in its ground vibrational state, upon collinear collision with an atom C. Results are compared with those of first-order quantum mechanical time dependent perturbation methods and those of purely classical methods.

The interaction here is exponentially repulsive between B and C so that $V(X,Y) \equiv A \exp\left[(\alpha Y - X)/L\right]$ where Y is the A-B distance, X is the distance between C and the A-B center-of-mass, and $\alpha = m_A/(m_A + m_B)$. In the usual semiclassical method[1] X(t) is obtained classically, assuming $Y = Y_0$, the equilibrium value, during collision and the interaction becomes V(t,Y). A solution is sought for $\left[H_0 + V(t,Y)\right]\Psi(t,Y) = i\hbar\dot{\Psi}(t,Y)$ with H_0 the unperturbed oscillator Hamiltonian. Expansion of Ψ in unperturbed functions φ_j $\left[\epsilon_j = (j + \frac{1}{2})\hbar\omega\right]$, $\Psi(t,Y) = \sum a_j(t)\,\varphi_j(Y)\exp(-i\epsilon_j t/\hbar)$, leads to the coupled equations

$$(i\hbar)\dot{a}_j = \sum_n a_n(t) V_{jn} \exp\left[i(j-n)\omega t\right] \tag{1}$$

where $V_{jn} = \int \varphi_j^* V \varphi_n d\tau$ and ω is the oscillator angular frequency.

Usual first order perturbation theory[1] (a approximation) assumes that $a_0(t) = 1$ (zero refers to ground vibrational state) and that only n = 0 contributes to rhs of eqs. (1) to obtain $(j \neq 0)$, $(i\hbar)\dot{a}_j = V_{j0} \exp\left[ij\omega t\right]$. Substituting $a_n(t) = c_n(t) \exp\left[(i\hbar)^{-1}\int_{-\infty}^{t} V_{nn} dt\right]$ in eq. (1), one obtains

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an improved first order result[2] (c-approximation) by setting $c_0(t) = 1$ and proceeding as above to find ($j \neq 0$), $(i\hbar)\dot{c}_j = V_{j0} \exp(ij\omega t) \exp\left[(i\hbar)^{-1} \int_{-\infty}^{t} (V_{00} - V_{jj})dt\right]$. This latter approximation has been employed by Mies.[3]

One can obtain numerical solutions of a set of eqs. (1), truncated at level j, on a computer using a Runge-Kutta-Gill procedure. Such results are considered "exact" if addition of extra levels does not alter the previous result. The average energy transferred to the oscillator (originally in ground state) after collision ($t = \infty$) is obtained from $\Delta E = \sum_n |a_n(\infty)|^2 n\hbar\omega$. In the calculations here, only $a_1(\infty)$ contributes non-negligibly to ΔE in the a- and the c-approximations. Table I shows ΔE_a, ΔE_c, ΔE_{exact}, and also $\Delta E_{0 \to 1}$, the contribution of $a_1(\infty)$ to ΔE_{exact}, for some systems. Table II lists $|a_j(t)|^2$ for $j = 1,\ldots,4$ for various cases at $t = 0$, the time of maximum $V(t,Y_0)$, and at $t = \infty$.

The classical equations of motion for an initially non-vibrating oscillator perturbed by $V(t,Y)$ were solved on a computer to obtain $\Delta E_{classical}$, the completely classical analogue of ΔE_{exact}, in Table I. For comparison, Table I lists ΔE, previously[4] obtained as the exact classical energy transfer to an initially non-vibrating oscillator interacting with atom C through the potential $V(X,Y)$. Also listed is ΔE_{ap}, previously[4] obtained classically as the energy transferred to the oscillator when the interaction potential is $(Y-Y_0)V'(t,Y_0)$ where $V' = (\partial V(t,Y)/\partial Y)$.

Table I shows that ΔE_c better approximates ΔE_{exact} than ΔE_a although for cases 5 ΔE_c is not too good an approximation. One notes from the Table that other states besides the 0 and 1 states can enter the exact calculations importantly, while in the a- and c-approximations only the 0 and 1 states so enter. The participation of higher states as intermediate and final states for systems like 3, with large energy transfer, confirms results of Sharp and

Rapp.[5] However, such participation in the systems 5 occurs in cases where final energy transfer is low. From classical calculations, participation of higher states was expected since large Y displacement was found[4] during such collisions. Comparison of ΔE_{exact} and $\Delta E_{classical}$ shows the smallness of quantum effects ($\Delta E_{exact} \cong \Delta E_{classical}$); small quantum effects are also shown by systems where the masses are uniformly scaled (3a,b,c and 5b,c) since mass scaling semi-classically is equivalent to scaling the time, as it is classically,[4] and similarly scaling h. Perturbing potentials linear in Y should show no quantum effect,[6] but comparison between $\Delta E_{classical}$ and ΔE_{ap} shows that the linear potential is not always a good approximation.[7] Comparison of ΔE and $\Delta E_{classical}$ gives some indication of the error inherent in substituting V(t,Y) for V(X,Y).

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Table I. Energy transfer in harmonic diatomic molecule-atom collisions.[a]

No.	System A-B C	ΔE_a (eV)	ΔE_c (eV)	ΔE_{exact} (eV)	$\Delta E_{0 \rightarrow 1}$ (eV)	$\Delta E_{classical}$ (eV)	ΔE_{ap} (eV)	ΔE (eV)
1a	1-12+13[b]	6.1^{-3}[d]	5.9^{-3}	5.8^{-3}	5.8^{-3}	5.8^{-3}	6.1^{-3}	5.8^{-3}
1b	1-12+13[c]	4.8^{-2}	4.6^{-2}	4.5^{-2}	4.0^{-2}	4.5^{-2}	4.8^{-2}	4.5^{-2}
2	12-12+2[b]	1.2	1.1	9.3^{-1}	1.3^{-2}	9.2^{-1}	1.1	1.0
3a	1-1 + 2[b]	1.8	1.0	8.5^{-1}	2.7^{-1}	8.4^{-1}	1.7	7.4^{-1}
3b	2-2 + 4[b]	1.8	1.0	8.5^{-1}	1.7^{-1}	8.4^{-1}	1.7	7.4^{-1}
3c	12-12+24[b]	1.7	9.9^{-1}	8.4^{-1}	1.7^{-1}	8.4^{-1}	1.7	7.4^{-1}
4	1-1 +24[b]	9.9^{-1}	3.3^{-1}	3.0^{-1}	2.0^{-1}	3.0^{-1}	9.6^{-1}	1.7^{-1}
5a	12-1+13[b]	9.5^{-1}	1.5^{-2}	7.8^{-5}	7.8^{-5}	1.3^{-4}	8.8^{-1}	2.3^{-4}
5b	12-1+13[c]	7.6	6.5^{-2}	1.4^{-2}	1.4^{-5}	1.6^{-2}	6.9	1.2^{-5}
5c	6-0.5+6.5[c]	8.0	5.8^{-2}	1.3^{-2}	1.3^{-2}	1.6^{-2}	6.9	1.2^{-5}

[a] Collision energy E_0 = 5.078 eV. All energy conversions carried out as in reference 4. In V(X,Y), L = 0.2214 and the calculations are independent of A.

[b] Force constant of diatomic molecule, k = 10.57 md/A°.

[c] k = 5.312 md/A°.

[d] 6.1^{-3} means 6.1×10^{-3}.

Table II. Values of $|a_j(t)|^2$ for $j=1,\ldots,4$.

No.[a]	Method	$a_1(0)$[b]	$a_1(\infty)$	$a_2(0)$	$a_2(\infty)$	$a_3(0)$	$a_3(\infty)$	$a_4(0)$	$a_4(\infty)$
1b	a approx	1.5^{-1}	1.2^{-1}	1.3^{-5}	2.2^{-7}	1.2^{-9}	1.5^{-13}	1.1^{-13}	5.9^{-20}
	c approx	1.5^{-1}	1.2^{-1}	1.3^{-5}	1.9^{-7}	1.2^{-9}	1.0^{-13}	1.1^{-13}	2.8^{-20}
	exact	1.3^{-1}	1.0^{-1}	9.0^{-3}	6.0^{-3}	4.1^{-4}	2.3^{-4}	1.3^{-5}	6.8^{-6}
3c	a approx	6.8	8.1	7.8^{-3}	8.8^{-4}	7.6^{-6}	3.6^{-8}	7.8^{-8}	8.9^{-13}
	c approx	5.7	4.6	5.0^{-3}	5.4^{-5}	4.6^{-6}	3.2^{-10}	5.1^{-9}	1.0^{-14}
	exact	4.2^{-2}	7.9^{-2}	1.0^{-1}	1.5^{-1}	1.6^{-1}	2.0^{-1}	1.9^{-1}	1.9^{-1}
5a	a approx	10.1	1.7	6.9^{-2}	2.1^{-5}	6.8^{-4}	9.1^{-4}	6.7^{-6}	2.7^{-16}
	c approx	2.5	2.7^{-2}	2.1^{-2}	2.7^{-8}	2.2^{-4}	9.6^{-15}	2.2^{-6}	8.8^{-19}
	exact	2.5^{-1}	1.4^{-4}	3.0^{-1}	5.6^{-9}	2.1^{-1}	4.0^{-14}	9.9^{-2}	1.4^{-14}

[a] The numbers correspond to those in Table I.

[b] The points do not correspond to t=0 exactly, but as closely as the calculation conveniently permitted.

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[1] See for instance K. Takanayagi, Prog. Theor. Phys. Supplement (Kyoto) #25, 1 (1963); D. Rapp, J. Chem. Phys. 40, 2813 (1964).

[2] D. R. Bates, Quantum Theory. I. Elements (Academic Press Inc., New York, 1961), pp. 252-253.

[3] F. H. Mies, J. Chem. Phys. 41, 903 (1964). Our calculations differ from Mies's in that we do not symmetrize the collision energy, but use the initial value.

[4] J. D. Kelley and M. Wolfsberg, J. Chem. Phys. 44, 324 (1966).

[5] D. Rapp and T. E. Sharp, J. Chem. Phys. 38, 2641 (1963).

[6] E. Kerner, Can. J. Phys. 36, 371 (1958); C. E. Treanor, J. Chem. Phys. 43, 532 (1965).

[7] Treanor[6] has shown that including the quadratic Y term in V(t,Y) should lead to $\Delta E_{exact} > \Delta E_{classical}$; he predicts a negligible quantum effect for systems 1-4, but not for systems 5.