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Time-dependent perturbation theory for inelastic scattering

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We show by numerical integration that the first-order, time-dependent, Magnus approximation agrees with the first-order, exponential, distorted-wave approximation to within a few percent, *provided* that the trajectory used for the time-dependent calculation is characterized by the arithmetic mean of the initial and final velocities and the arithmetic mean of the initial and final orbital angular momenta. Calculations are done for rotational energy transfer from an exponentially repulsive potential characteristic of $He + H_2$ and for a Lennard-Jones potential characteristic of $Ar + N_2$.

INTRODUCTION

Rotationally and vibrationally inelastic scattering are important in a number of experiments; however, the current accurate theories are far too expensive for many applications.[1] This situation mandates the development of simple yet accurate approximations.[1-3] Among the various approximations are several variations on perturbation theory, including time-dependent perturbation theory (TDPT).[4,5] We wish to explore the accuracy of TDPT because it is a fast and simple approximation which is easy to visualize. If r is the distance between the colliding molecules and R the set of internal coordinates, then we can separate the potential $V(r, R)$ into a spherically symmetric $V_0(r)$ and a perturbation $\Delta V(r, R) = V - V_0$. Simple, first-order perturbation theories like the Born and distorted-wave approximations seldom work because ΔV is too big. However, if we exponentiate the result, very good agreement is often obtained.[2,3] We define the phase-shift matrix,[3]

$$\Delta \eta_{ij} = - (\mu/\hbar^2) \int_0^\infty u_{0i}(r) \langle i | \Delta V | j \rangle u_{0j}(r) \, dr , \qquad (1)$$

where μ is the reduced mass of the colliding molecules, i and j are the various internal and orbital (l, m) quantum numbers, and u_0 is the radial wave function for the unperturbed problem, the solution of Schrödinger's equation for $V = V_0(r)$. The phase-shift matrix is then exponentiated to give the scattering matrix

$$S = \exp(i\eta_0) \exp(2i\Delta\eta) \exp(i\eta_0) , \qquad (2)$$

where η_0 is the diagonal matrix of the elastic phase shifts obtained from V_0. Given S, one can calculate the various differential and integral cross sections, rate constants, etc.[1-3]

A second perturbation procedure is time-dependent perturbation theory.[3-5] Given $V_0(r)$ and a velocity and orbital angular momentum, we can compute a trajectory $r(t)$. $\langle i | \Delta V | j \rangle$ then becomes a time-dependent perturbation on the internal motions of the colliding molecules. The usual first-order TDPT does not work well because ΔV is usually too big, but the exponential, Magnus form of it does much better. In general, the internal and final states have different $k = \mu v/\hbar$ and different $l [l(l + 1)\hbar^2 = L^2 = (\mu v b)^2]$. This is nicely taken care of in Eq. (1), since each u_0 has a different k and l. However, the TDPT requires a single k and l to obtain

the trajectory. Various possibilities suggest themselves: an arithmetic or geometric average of the initial and final k and l, an average kinetic energy, or an average of the results calculated for each k and l. Most of these have been proposed at one time or other,[5] but there is no sound *a priori* reason for choosing one over the other. The situation becomes murkier when one derives TDPT from Eq. (1). Gordon[5] argues on semiclassical grounds that the arithmetic mean velocity is the proper choice. Although his arguments may be questioned, his result is correct. We add to this that, when the orbital angular momentum changes, one must take the arithmetic mean of the initial and final l's.

One can use the WKB approximation for u. The classical local wave vector is p,

$$p_i^2 = k_i^2 - 2\mu V_0/\hbar^2 - l_i(l_i + 1)/r^2 , \qquad (3)$$

where $\hbar p = \mu \dot{r}$ is the radial momentum. The classical phase is

$$\xi_i = \left| \int_{r_{ci}}^r p_i(r') \, dr' \right| , \qquad (4)$$

where r_c is the classical turning point, the outermost zero of p_i. Then

$$u_{0i} = (2\pi)^{1/2} |p_i|^{-1/2} |z_i|^{1/4} \text{Ai}(z_i) , \qquad (5)$$

where Ai is the Airy function[6] and

$$z_i = \pm \left| \tfrac{3}{2} \xi_i(r) \right|^{2/3} , \qquad (6)$$

with the $(+)$ sign for $r \leq r_c$ and the $(-)$ sign for $r \geq r_c$. Using the asymptotic form for $r \gg r_c$ gives

$$u_{0i} = (2/p_i)^{1/2} \sin(\xi_i + \pi/4) . \qquad (7)$$

Now, if one uses Eq. (7) in Eq. (1), using a common r_c, letting $(p_i p_j)^{1/2} = p_0$, neglecting the high-frequency contributions from $(\xi_i + \xi_j)$, and approximating the slowly oscillating difference term $(\xi_i - \xi_j)$, one gets[3]

$$\Delta\eta_{ij} = -\hbar^{-1} \int_0^\infty \langle i | \Delta V | j \rangle \cos[\omega_{ij} t - (l_i - l_j)\theta] \, dt , \qquad (8)$$

where $\omega_{ij} = (E_{\text{int } i} - E_{\text{int } j})/\hbar$ and

$$\theta = -(l + 1/2) \int_{r_c}^r (r^2 p_0)^{-1} \, dr , \qquad (9)$$

$$t = (\mu/\hbar) \int_{r_c}^r p_0^{-1} \, dr . \qquad (10)$$

Note that θ is related to the classical deflection angle. Equation (8) is the usual TDPT plus angular momentum terms. Unfortunately, with all of the approximations made, the result is a poor approximation to the integrand of Eq. (1). The figure shows the integrand of Eq. (1) for the exact u_0 and for the TDPT case. The Airy function approximation in Eq. (5) agrees closely with the exact result obtained by the numerical integration of the radial Schrödinger equation. The potential is exponentially repulsive and approximates $He + H_2$ with one state at a kinetic energy of 0.9 eV and the other at 0.45 eV. The TDPT uses an arithmetic average of k_i and k_j and $l_i = l_j = 0$. At $r \ll r_c$ the exact result goes exponentially to zero, while the TDPT one has an integrable singularity at r_{cav}, where $dr/dt = 0$. Note also the rapid oscillations in the exact expression which are absent in the TDPT. It is also apparent that the integrands in both cases oscillate about zero, resulting in cancellation of the positive and negative contributions. In the case shown here, the positive part of the integral is 93% of the negative part so that the cancellation is nearly complete. As the difference in the energies increases, the two curves oscillate more and more rapidly about zero, and the integral decreases roughly exponentially to zero. This behavior puts a high premium on the accuracy of the integrand. Given these considerations, one would expect that the TDPT would be accurate to at best a factor of 2 or so. Instead, the two integrals agree to within 1%, and even this difference may well be due largely to the numerical error in the integration of oscillating functions. Even when the two states differ in kinetic energy by a factor of 9, the error in TDPT is only 4%. This agreement is not by chance. We have tested TDPT for two potentials, an exponentially repulsive potential characteristic of $He + H_2$[7] and a Lennard-Jones (6, 12) potential characteristic of $Ar + N_2$.[8] The tests have been carried out over a range in E, l, ΔE, and Δl. Except for two cases TDPT is accurate to within a few percent. At a sufficiently large ΔE and/or Δl, $\Delta\eta$ becomes very small. Often, when it drops below about 10^{-3} of its value at $\Delta E = \Delta l = 0$, TDPT starts to fail. This corresponds to a drop of six orders of magnitude or more in the transition probability. It is not clear whether the discrepancy is due to a real failure or TDPT or to the errors in the numerical integration of rapidly oscillating functions. A second cause of failure occurs with $Ar + N_2$ at impact parameters near the potential minimum and a moderate or large ΔE. Then, the trajectory for the state of higher kinetic energy is largely repulsive and that for the lower state largely attractive. Here the errors approach 20%; however, the transitions involved have their maximum probability at smaller impact parameters where TDPT is accurate to a few percent, so that the errors do not seriously affect the cross sections for the process. Gordon[5] and Gentry and Giese[9] have done similar calculations for collinear vibrational energy transfer using the semiclassical INDECENT approximation.[9]

Time-dependent perturbation theory has an appealing simplicity and is also more easily evaluated than the exponential distorted-wave approximation. However, there is an ambiguity of what is to be used for TDPT. We have
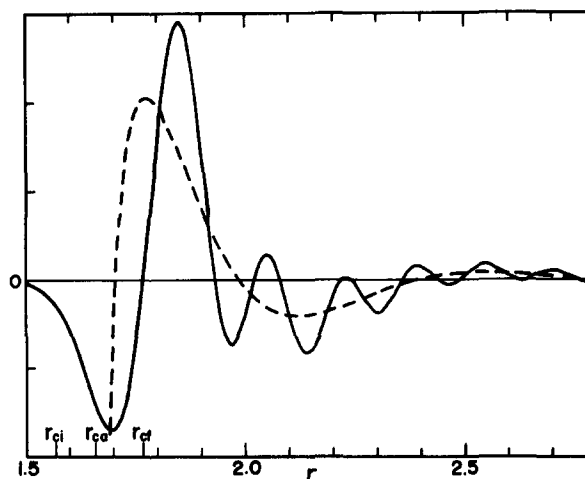

FIG. 1. The solid curve is the integrand (in arbitrary units) for the exponential distorted-wave approximation in Eq. (1). The dashed curve is the integrand for time-dependent perturbation theory (TDPT) (8) as a function of r (in Å). The calculations were done for an exponentially repulsive potential characteristic of $He + H_2$. The initial state has a kinetic energy of 0.9 eV and the final state 0.45 eV, $l_i = l_f = 0$. The trajectory for TDPT uses the arithmetic mean velocity. The two integrals agree to within 1%. The classical turning points for the initial, final, and averaged trajectories are shown.

demonstrated numerically, as have Gordon[5] and Gentry and Giese,[9] that if one uses the arithmetic mean velocity and orbital angular momentum, TDPT is highly accurate even for very large changes in velocity and angular momentum. It is quite clear from the derivation of TDPT given here and elsewhere—see Fig. 1—that one cannot easily justify this accuracy on theoretical grounds. Similar arguments pertain to the use of Miller's semiclassical mechanics.[10] The true classical trajectory starts and ends with different velocities and, in Miller's theory, may go through complex time. This is quite different from the trajectory used here for TDPT, and so one might logically expect very different results. We are left with a very useful result which is not well supported in theory.

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