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Exponential time-dependent perturbation theory in rotationally inelastic scattering

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An exponential form of time-dependent perturbation theory (the Magnus approximation) is developed for rotationally inelastic scattering. A phase-shift matrix is calculated as an integral in time over the anisotropic part of the potential. The trajectory used for this integral is specified by the diagonal part of the potential matrix and the arithmetic average of the initial and final velocities and the average orbital angular momentum. The exponential of the phase-shift matrix gives the scattering matrix and the various cross sections. A special representation is used where the orbital angular momentum is either treated classically or may be frozen out to yield the orbital sudden approximation. Calculations on Ar + N_2 and Ar + TlF show that the theory generally gives very good agreement with accurate calculations, even where the orbital sudden approximation (coupled-states) results are seriously in error.

INTRODUCTION

The calculation of cross sections for inelastic scattering is sufficiently simple that accurate values can be obtained for simple systems.[1,2] However, the calculations are sufficiently complicated that they are expensive even for simple systems and prohibitive for even moderately complex ones. We therefore need approximate methods for most cases, but these can be tested against the accurate calculations for simple systems and then used for more complicated ones. There are several directions to take. One of these is perturbation theory. We split the potential into a piece giving elastic scattering $V_0(R)$, and the remainder ΔV which is treated as a perturbation. From formal scattering theory one can derive a first-order perturbation theory known as the distorted-wave approximation (DWA).[1] A faster and simpler method is time-dependent perturbation theory (TDPT). From the elastic part of the potential we can calculate a trajectory $R(t)$ so that the inelastic part of the potential becomes a time-dependent perturbation on the internal energy states of the colliding molecules.

For most cases both types of perturbation theory fail because the perturbation is usually large enough to cause higher-order terms to be important. In addition, TDPT suffers from the added problem that the trajectory is not uniquely defined. A very simple way around the first problem is to use an exponential perturbation theory.[3,4] In the case of the DWA, we calculate a phase-shift matrix,[4]

$$\Delta\eta_{ij} = -(\mu/\hbar^2)\int_0^\infty u_i(R)\langle i|\Delta V|j\rangle u_j(R)\,dR\ , \tag{1}$$

where R is the distance between the centers-of-mass of the colliding molecules and $|i\rangle$ and $|j\rangle$ represent the collected internal states of the molecules and the orbital angular momentum eigenstates. The reduced mass is μ, and u_i and u_j are the unperturbed radial wave functions corresponding to the elastic scattering from $V_0(R)$ at energies and orbital angular momenta appropriate to states i and j. The scattering matrix is then given by

$$\mathbf{S} = \exp(i\eta_0)\exp(2i\Delta\eta)\exp(i\eta_0)\ , \tag{2}$$

where η_0 is the *diagonal* matrix of the phase shifts corresponding to V_0. The exponentiation of $\Delta\eta$ may be done by using a power series or by diagonalizing $\Delta\eta$, exponentiating the eigenvalues, and transforming back to the original representation. The usual DWA can be obtained by taking the zero order and linear terms in the expansion of the exponential. Since $\Delta\eta$ is Hermitian, $\mathbf{S}$ is unitary as it should be to conserve transition probability. The exponential perturbation theory (EPT) is strictly accurate only to first order. However, several calculations[3,4] have demonstrated a high degree of accuracy even for transitions between states which are only coupled to high order. EPT is very much faster than an accurate close-coupled (CC) calculation. The calculation of Eq. (1) is not easy because one must calculate u_i using the WKB approximation or an acuurate integration of Schrödinger's equation for $V_0(R)$. The integrand in Eq. (1) usually oscillates rapidly in R and thus the integration is often difficult.

These problems are not present in TDPT. Here we have,[4,5]

$$\Delta\eta_{ij} = -(2\hbar)^{-1}\int_{-\infty}^{\infty}\langle i|\Delta V[R(t)]|j\rangle \times\exp(i\omega_{ij})\exp[-i\Delta l\,\theta(t)]\,dl\ . \tag{3}$$

Here, the time $t(R)$ is given by,

$$t(R) = \mp(\mu/\hbar)\int_{R_c}^{R} dR/p(R)\ , \tag{4}$$

$$\theta(R) = \mp(l+1/2)\int_{R_c}^{R} dR/[R^2 p(R)]\ , \tag{5}$$

$$p_i(R) = +[k_i^2 - l_i(l_i+1)/R^2 - 2\mu V_0(R)/\hbar^2]^{1/2}\ . \tag{6}$$

The top signsof Eqs. (4) and (5) hold for the incoming half of the trajectory ($t<0$) and the bottom sign for the outgoing half. R_c is the classical turning point, the outermost zero of $p(R)$, $\omega_{ij} = (E_i - E_j)/\hbar$, and $\Delta l = l_i - l_j$. Except for the factor involving Δl, Eq. (3) is equivalent to the usual TDPT. The exponential form of TDPT is known as the Magnus approximation[6] and has been known for many years. Equation (3) can be derived from

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Eq. (1) by a series of semiclassical approximations[4,5] which, in many cases, are of dubious accuracy. The biggest problem in using Eq. (3) is that $t(R)$ and $\theta(R)$ depend on the kinetic energy and orbital angular momentum used in evaluating $p(R)$, and these, in turn, depend on the quantum states. There are several possible recipes: use the initial or final energies, or the arithmetic or geometric averages of the initial and final energies or velocities, or take the average of $\Delta\eta$ calculated for each energy. The results depend drastically on the choice if the two states differ appreciably in energy or orbital angular momentum. Calculations for several systems involving vibrationally and rotationally inelastic scattering[5,7] have shown that the correct choice is to use the arithmetic averages of v_i and v_j and of l_i and l_j. With this choice very good agreement is obtained between Eqs. (1) and (3) even if the two velocities are different by factors of 3 or more. This is true even though the integrands of Eqs. (1) and (3) are very different.

For an exact calculation the accuracy does not depend on which representation is used. However, a perturbation theory will generally become more accurate if the diagonal elements of **V** can be made as large as possible, since these can be treated exactly rather than as a perturbation. In the following section we develop the theory for the rotationally inelastic scattering of an atom and a rigid linear rotor and find a useful representation which gives both accurate results and a simple picture of the scattering. We then use the theory to obtain cross sections for several systems and show that the method is quite accurate even for fairly highly anisotropic potentials, and yet it is some 45 times faster than a CC calculation.

DETAILED THEORY

We consider the use of an exponential time-dependent perturbation theory (Magnus approximation) to the scattering of a rigid linear rotor. The addition of vibrational degrees of freedom and/or more complicated rotors is not difficult but tends to clutter up the theory. The potential can be expanded,

$$V(R,\gamma)=\sum_{\lambda=0}^{\infty} v_\lambda(R)P_\lambda(\cos\gamma)\,, \tag{7}$$

where γ is the angle between **R** and the molecular axis and P is a Legendre polynomial. $V_0(R)$ includes $v_0(R)$ and the diagonal matrix elements of the higher terms. The matrix elements of V are,[8]

$$\langle j'm_j'l'm_l'|\,V\,|jm_jlm_l\rangle = \sum_{\lambda=0}^{\infty} v_\lambda(R)(-1)^{\mu}\left(\frac{[l][j]}{[l'][j']}\right)^{1/2} C(l\lambda l';000) \tag{8}$$

$$C(j\lambda j';000)C(l\lambda l';m_l-\mu m_l')C(j\lambda j';m_j\mu m_j')\,,$$

where $[x]=2x+1$ and C is a Clebsch–Gordan coefficient.[8] The rotational eigenfunctions are $|jm_j\rangle$, and the orbital eigenfunctions are $|lm_l\rangle$. The usual procedure is to couple j and l.

$$|JMjl\rangle=\sum_{m_jm} C(jlJ;m_jm_lM)\,|jm_j\rangle\,|lm_l\rangle \tag{9}$$

to get

$$\langle j'l'|\,V\,|jl\rangle_J=\sum_\lambda v_\lambda(R)\left(\frac{[l][j]}{[l'][j']}\right)^{1/2} C(l\lambda l';000)C(j\lambda j';000)$$

$$\times\sum_{m_jm_j',m_lm_l'}(-1)^{\mu}C(l\lambda l';m_l-\mu m_l')C(j\lambda j';m_j\mu m_j')\,C(jlJ;m_jm_lM)\,C(j'l'J;m_j'm_l'M) \tag{10}$$

$$=\sum_{\lambda=0}^{\infty} v_\lambda(R)\,\{[l][j]\}^{1/2}(-1)^{j-l'-J}\,C(j\lambda j';000)\,C(l\lambda l';000)\begin{Bmatrix} j'\lambda j\\ lJl'\end{Bmatrix}\,, \tag{11}$$

where $\{\ \}$ is a $6-j$ coefficient.[9] The advantage of Eq. (11) is that the potential is diagonal in J and M and independent of M. A useful semiclassical approximation to Eq. (11) may be obtained by using the semiclassical limit of C.

$$C(l\lambda l';m-\mu m_l')=d^{\lambda}_{-\mu\Delta l}(\theta_1)\,, \tag{12a}$$

$$\cos\theta_1=m_l\{l(l+1)\}^{-1/2}\,, \tag{12b}$$

where d is the central part of the rotation matrix. The formula is from Edmonds,[9] but we have used the sign conventions of Rose.[8] Equation (12) is valid for $l\gg\lambda$. Using Eq. (12) for all the C coefficients in Eq. (10) which contain l and l' gives

$$\langle j'l'|\,V\,|jl\rangle_J=\sum_{\lambda=0}^{\infty} v_\lambda(R)\left(\frac{[j]}{[j']}\right)^{1/2}$$

$$\times C(j\lambda j';000)C(j\lambda j';\delta-\Delta l\delta')(-1)^{\Delta l}d^{\lambda}_{0\Delta l}(\pi/2)\,, \tag{13}$$

where $\delta=J-l$ and $\delta'=J-l'$. This result is convenient because Δl appears as a projection quantum number, and thus $d\exp(-i\Delta l\theta)$ is proportional to the spherical harmonic $Y_{\lambda\Delta l}[\pi/2,\pi-\theta(t)]$. Equation (13) can then be rewritten in terms of the integral of three spherical harmonics to give,

$$\langle j'l'|\,\Delta\eta\,|jl\rangle_J=-(2\hbar)^{-1}\int_{-\infty}^{\infty}\sum_{\lambda=1}^{\infty} v_\lambda[R(t)]\,\frac{4\pi}{[\lambda]}\,(-1)^{\Delta l}\,Y_{\lambda\Delta l}[\pi/2,\pi-\theta(t)]$$

$$\times\langle j'\delta'|\,Y_{\lambda-\Delta l}(\theta_m,\phi_m)\,|j\delta\rangle\exp(i\omega_{j'j}t)\,dt=-(2\hbar)^{-1}\int_{-\infty}^{\infty}\langle j'\delta'|\,\Delta V[R(t),\beta(t)]\,|j\delta\rangle\exp(i\omega_{j'j}t)dt\,. \tag{14}$$

Here, $(\theta_m, \phi_m) = \hat{r}$ is the orientation of the rotor and $\beta(t)$ is the angle between (θ_m, ϕ_m) and $[\pi/2, \pi - \theta(t)]$. Because of the use of Eq. (12), Eq. (14) is valid for $l \approx J \gg j$. It gives a simple interpretation of the effect of the orbital motion on the rotational part of the problem.

An effective and popular approximate method is the orbital sudden (OS) approximation in which the orbital quantum number l is replaced by a parameter l_0.[10] This procedure diagonalizes the problem in l and thus reduces its dimensionality. The result is a decrease in computation time by over an order of magnitude. When used in a numerical solution of the coupled Schrödinger equations, the method is commonly called the coupled-states (CS) approximation. In the case of TDPT two approximations are involved. First, we neglect the factor $\exp(-i\Delta l\theta)$ in Eq. (3). This has the same effect as forcing $\theta \equiv 0$. Second, we use a common l_0 in calculating the trajectories $R(t)$ used in Eq. (3). The effect on Eq. (14) is to force $\beta(t)$ to a constant.

The potential matrix in Eq. (11) can be diagonalized by the transformation,[11]

$$|j\nu\rangle_J = \sum \left(\frac{[l]}{[J]}\right)^{1/2} C(ljJ;0\nu\nu)(-1)^{l-j} \,|\, jl\rangle_J \,. \tag{15}$$

When applied to Eq. (11), it gives,

$$\langle j'\nu' | V | j\nu\rangle_J = \sum_{\lambda=0}^{\infty} v_\lambda(R) \left(\frac{[j]}{[j']}\right)^{1/2} \times C(j\lambda j';000)\, C(j\lambda j';\nu 0\nu)\delta_{\nu',\nu} \,. \tag{16}$$

Using Eq. (12) converts Eq. (15) to

$$|j\nu\rangle_J = \sum (-1)^{l-j} D^J_{0\nu}(0, -\pi/2, 0)\, |j\delta\rangle_J \,. \tag{17}$$

The effect of Eq. (17) on Eq. (14) is to rotate the coordinates by $(0, -\pi/2, 0)$ to give

$$\langle j'\nu' | \Delta\eta | j\nu\rangle_J = -(2\hbar)^{-1} \int_{-\infty}^{\infty} \langle j'\nu' | \Delta V[R(t), \alpha(t)] | j\nu\rangle \exp(i\omega_{j',j}t)dt \,, \tag{18}$$

where $\alpha(t)$ is the angle between (θ_m, ϕ_m) and $(-\theta, 3\pi/2)$. Note that Eq. (18) retains the factor $\exp(-i\Delta l\theta)$ but uses a common l_0 in the trajectory. Now, Eq. (18) is obtained by using a semiclassical approximation valid only for $l \gg j$. Yet Eq. (18) is exact in the orbital sudden limit for *all* l. To see this we expand Eq. (18),

$$\langle j'\nu' | \Delta\eta | j\nu\rangle_J = -(2\hbar)^{-1} \sum_{\lambda=1}^{\infty} \left(\frac{4\pi[j]}{[\lambda][j']}\right)^{1/2} (-1)^{\mu} C(j\lambda j';000) \times C(j\lambda j';\nu\mu\nu') \int_{-\infty}^{\infty} \Delta v_\lambda(R)\, e^{i\omega t}\, Y_{\lambda,-\mu}[-\theta(t), 3\pi/2]\, dt \,. \tag{19}$$

In the orbital sudden approximation $\theta \equiv 0$ and Y is zero except for $\mu = \Delta\nu = 0$. In this case

$$\langle j'\nu' | \Delta\eta | j\nu\rangle_J = -(2\hbar)^{-1} \sum_{\lambda=1}^{\infty} \left(\frac{[j]}{[j']}\right)^{1/2} C(j\lambda j';000) C(j\lambda j';\nu 0\nu) \times \int_{-\infty}^{\infty} \Delta v_\lambda[R(t)] \exp(i\omega_{j',j})\, dt\, \delta_{\nu',\nu} \tag{20}$$

which is exactly what is obtained using Eq. (16) in Eq. (3).

Equations (18) and (19) are a convenient representation. We can do a calculation with and without the OS approximation in the same representation. The approximation is a uniform one in that at small l it is correct because the OS approximation is accurate. This has been demonstrated by the success of numerous CS calculations. At $l = 0$ we can see from Eq. (5) that $\theta = 0$ (i.e., direct backscattering). At large l the OS approximation breaks down because θ gets larger, but then Eqs. (18) and (19) are still valid. The representation gives a simple picture of the OS approximation. Finally, the representation is good for a perturbation treatment. At small l where the perturbation is largest, the elastic scattering ($j' = j$) occurs mainly for diagonal elements of V since the contribution for $\nu' \neq \nu$ is small. Since the diagonal part of V can be put into V_0, it can be treated exactly, rather than as a perturbation. In the $|jl\rangle_J$ representation much of the elastic scattering occurs for $l \neq l'$, and this contribution must be treated as a perturbation. In earlier calculations using the $|jl\rangle_J$ representation we found that the results were appreciably less accurate than those for the OS approximation which used the $|j\nu\rangle_J$ representation.

There are two further simplifications of Eqs. (18) and (19). We can use the basic symmetry of the integrand in Eq. (19) about $t = 0$ to convert the integral to a real integral from 0 to ∞. We can also break up the problem into blocks of odd and even parity which are then uncoupled to each other. Let

$$|j0_+\rangle = |j0\rangle \,, \quad |j\nu_\pm\rangle = 2^{-1/2}[|j\nu\rangle \pm |j-\nu\rangle] \,. \tag{21}$$

We then obtain

$$\langle j'\nu_\pm | \Delta\eta | j\nu_\pm\rangle = -\hbar^{-1} B^{\pm} \int_0^{\infty} \sum_{\lambda=1}^{\infty} \Delta v_\lambda[R(t)] \times \cos(\omega_{j',j}t)\, dt \quad (\Delta\nu \text{ even}) \tag{22a}$$

$$= -\hbar^{-1} i B^{\pm} \int_0^{\infty} \sum_{\lambda=1}^{\infty} \Delta v_\lambda[R(t)] \sin(\omega_{j',j}t)\, dt \quad (\Delta\nu \text{ odd}) \,, \tag{22b}$$

$$B^{\pm} = a_\nu a_{\nu'} C(j\lambda j';000)[i^{\nu'-\nu} C(j\lambda j';\nu\Delta\nu\nu') Y_{\lambda\Delta\nu}[-\theta(t), 0] + i^{-\nu-\nu'} C(j\lambda j';\nu, -\nu-\nu', -\nu') Y_{\lambda,-\nu'-\nu}[-\theta(t), 0] \,, \tag{22c}$$

where $a_0 = 2^{-1/2}$ and $a_\nu = 1$ ($\nu \neq 0$). Note that $\Delta\eta$ is real in spite of all the i's in Eq. (22). It is also easily seen to be Hermitian. In calculating $t(R)$ and $\theta(R)$ we use Eqs. (4)–(6) and the arithmetic average velocity and orbital angular momentum of the initial and final states in $\Delta\eta$. V_0 is the diagonal part of the potential matrix (which includes the spherically symmetric part of V). Thus $V_0(R)$ depends slightly on the quantum state, and, therefore, we use the arithmetic mean of V_0 for the two states. With this set of definitions, $\Delta\eta$ has no diagonal elements.

In an earlier paper, a result equivalent to Eq. (14) was obtained.[12] The recipe for calculating $\theta(t)$ was to use the average of θ for the two states. Fitz and Kouri[13] used the method in several calculations using the energy sudden approximation and found in some cases an improvement over the OS approximation. However, they reported two difficulties. First, the calculations took much more computer time than those using the OS

approximation. This is largely inherent in the method because a sudden approximation requires fewer variables to describe the system than any other representation, and, thus, the averaging is easier. Second, they found difficulty in evaluating $\theta(R)$ where R was between the classical turning points of the two states, and thus θ was undefined. In the present formulation the second difficulty is avoided by using a simple trajectory at the average velocity. The use of a representation compatible with the OS approximation helps in that one can use the OS at small l and then change over to the more accurate case at large l without changing representations.

RESULTS

Calculations were done using the exponential TDPT both with and without the OS approximations for several variations on the Ar + N_2 system and for Ar + TlF. Ar + N_2 has a fairly anisotropic potential and yet, due to the symmetry and large rotation constant, does not involve a large number of states. The potential used for the calculations is[14–16]

$$V(R,\gamma)=\epsilon\{(R_0/R)^{12}[1+\alpha_{12}P_2(\cos\gamma)] - 2(R_0/R)^6[1+\alpha_6 P_2(\cos\gamma)]\}. \quad (23)$$

TABLE I. Cross sections $Q_{j'\leftarrow j}$ for Ar+N_2 (short range) at $E=0.025\,85$ eV (300 K). Cross sections are given in Å^2. The results in descending order are: CC ($j_{max}=10$), CS ($j_{max}=10$), TDPT–CC, TDPT–CS, CC ($j_{max}=8$), CS ($j_{max}=8$).

j \ j'	0	2	4	6	8
0	•••	26.7	22.8	10.1	1.16
		21.7	21.5	9.51	1.02
		22.6	23.5	10.4	1.25
		22.1	24.4	10.7	1.26
		26.7	23.0	10.2	0.86
		21.7	21.7	9.66	0.72
2	5.67	•••	27.6	12.9	2.28
	4.87		25.8	11.0	1.76
	4.80		25.0	15.3	2.80
	4.70		26.0	15.7	2.82
	5.66		27.8	13.3	1.59
	4.88		22.3	11.3	1.18
4	3.14	17.9	•••	17.7	5.04
	3.35	20.7		15.0	3.85
	3.23	16.2		19.6	6.46
	3.36	16.9		19.2	6.36
	3.17	18.0		18.7	3.45
	3.39	16.8		16.2	2.55
6	1.31	7.87	16.6	•••	13.2
	1.48	8.98	17.6		10.3
	1.35	9.30	18.4		16.8
	1.39	9.54	18.1		15.9
	1.32	8.11	17.5		10.1
	1.50	9.03	19.3		7.77
CPU[a] Time (min)	1713				
	79				
	9				
	0.8				
	406				
	35				

[a]The calculations were done an a DEC VAX750 with a floating-point accelerator, using the operating system VMS V3.0.

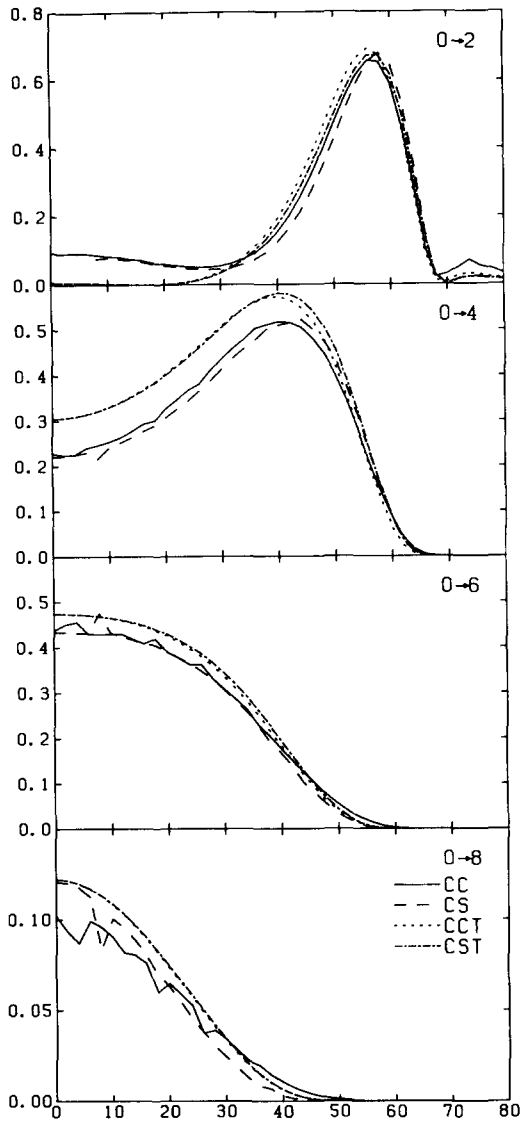

FIG. 1. The curves show the m-averaged transition probabilities defined by Eq. (24) as a function of the total J for Ar+N_2 (short ranged) at a total energy of 0.025 85 eV. The curves are CC (close coupled, $j_{max}=10$), CS (coupled states, $j_{max}=10$), TDPT–CC, and TDPT–CS. The data correspond to the top four rows in Table I.

The well depth of v_0 is $\epsilon=0.010\,297$ eV $=83.05$ cm^{-1} and the minimum in v_0 is at $R_0=3.929$ Å. Two choices of α's were used. The conventional choice, referred to here as short-ranged (SR), is $\alpha_{12}=0.50$ and $\alpha_6=0.13$. This is the original potential of Pattingill.[15] A second choice, termed long-range (LR) is $\alpha_{12}=\alpha_6=0.315$, and was used by dePristo and Alexander.[16] Results for the short-ranged potential at a total energy of 0.025 85 eV are given in Table I. Because the original CC calculations by Tsien, Parker, and Pack[14] are a decade old and include only $j=0$–6, we redid them. The CC and CS calculations were done on a slightly rewritten version of the program VIVAS (variable interval, variable step) written by Parker, Lill, and Light[17] and obtained from the now defunct National Resource for Computational Chemistry at Berkeley. The calculations included all open chan-

TABLE II. Cross sections $Q_{j'\leftarrow j}$ for Ar^*N_2 (short range) at $E = 0.06619$ eV (768 K). Cross sections are given in Å^2. The results in descending order are: CC ($j_{max}=12$) (from Ref. 18), CS ($j_{max}=14$) (from Ref. 19), TDPT-CC, TDPT-CS.

j \ j'	0	2	4	6	8	10	12	14
0	•••	15.7	11.4	10.8	5.7	1.15	0.055	•••
		15.2	11.9	11.2	5.82	1.17	0.078	0.001
		14.9	12.8	12.0	5.77	1.12	0.076	0.001
		14.3	12.9	12.4	5.96	1.15	0.077	0.001
2	3.2	•••	14.4	10.5	6.6	1.86	0.119	•••
	3.18		14.8	11.0	6.64	1.87	0.172	0.035
	3.04		14.9	12.7	7.78	2.12	0.196	0.004
	2.96		15.2	13.2	8.05	2.17	0.198	0.004
4	1.37	8.4	•••	12.8	7.9	3.5	0.320	•••
	1.43	8.70		13.0	7.74	3.33	0.480	0.014
	1.53	8.73		13.2	8.81	3.90	0.571	0.018
	1.55	8.94		13.5	8.98	3.95	0.573	0.018
6	0.99	4.7	9.7	•••	11.0	5.9	0.81	•••
	1.02	4.91	9.88		10.7	5.50	1.26	0.06
	1.10	5.68	10.0		11.5	6.62	1.57	0.07
	1.14	5.90	10.2		11.3	6.60	1.56	0.07
8	0.46	2.59	5.3	9.7	•••	10.8	2.08	•••
	0.470	2.62	5.20	9.45		9.54	3.11	0.213
	0.465	3.07	5.92	10.1		10.8	3.92	0.291
	0.481	3.17	6.03	10.0		10.5	3.84	0.282

nels ($j=0$–8) and one closed channel ($j=10$). They were done for J up through $J=92$, where the inelastic probabilities were negligible. The step size in J was 2. The elastic scattering probability oscillates sufficiently rapidly to require $\Delta J=1$ and extends to much larger J so that we did not calculate elastic cross sections. These are largely determined by the spherically symmetric part of the potential, and therefore we did not think it worth the added expense to calculate the elastic cross sections. The calculations using TDPT include only the open channels. The derivation of EPT[4] shows that to first order only open channels should be included so that the transition probability to closed channels is identically zero as it should be. Second- and higher-order terms in the EPT include the closed channels as intermediate, virtual states. To see if the differences were due to the closed channels, we repeated the CC and CS calculations including only the open channels. Figure 1 shows the detailed transition probabilities $P_{j'j}$,

$$P_{j'j}=[j]^{-1}\sum_{\nu\nu'}|\langle j'\nu'|S|j\nu\rangle|^2 . \tag{24}$$

The curves for the CC calculation show several resonances which apparently involve the closed channel $j=10$ since they are largely absent when this state is deleted from the calculation.

The close agreement between TDPT and the accurate CC calculation is quite remarkable when one considers the crudity of the TDPT. From Eq. (23) we see that the potential couples only those states for which $\Delta j=0,\pm2$ yet the theory predicts accurate values for the cross section from $j=0$ to 8. This is due to the exponentiation of $\Delta\eta$. The velocities for the various states range from 5.5×10^4 cm/s for $j=0$ to 3.0×10^4 cm/s for $j=8$ so that the trajectories for the initial and final states are quite different. Nevertheless, the use of the trajectory at the averaged velocity works quite well. Perhaps the best statement about the utility of TDPT is in the computer times shown in Table I. The CS version of TDPT is faster than the full CC calculation by a factor of 2000. Cross sections for $Ar+N_2$ (SR) at a total energy of 0.06619 eV are given in Table II. Here states through $j=14$ are open. The CC results are taken from Pack[18] and the CS results from McGuire.[19] Again, the agreement is good.

Results for $Ar+N_2$ (LR) at $E=0.02585$ eV are given in Table III. Although it is the same system as the SR potential, the results are very different. The anisotropy

TABLE III. Cross sections $Q_{j'\leftarrow j}$ for $Ar+N_2$ (long range) at $E=0.02585$ eV (300 K). Cross sections are given in Å^2. The results in descending order are: CC (j_{max} 8), CS ($j_{max}=8$), TDPT-CC, TDPT-CS.

j/j'	0	2	4	6
0	•••	59.1	15.3	0.32
		78.2	4.91	0.06
		58.2	2.07	0.03
		63.6	0.56	3.1–4[a]
2	12.6	•••	20.3	0.60
	18.1		12.2	0.21
	12.4		5.19	0.16
	13.5		1.22	2.2–3[a]
4	2.11	13.1	•••	5.00
	0.96	10.8		4.26
	0.28	3.37		5.29
	0.07	0.79		1.48

[a] 3.1–4 is 3.1×10^{-4}.

TABLE IV. Cross sections $Q_{j'\leftarrow j}$ for Ar+TlF at $E=0.1158$ eV (1344 K). Cross sections are given in Å^2. The results in descending order are: CC (from Ref. 14), CS, TDPT-CC, TDPT-CS, SA (from Ref. 13), IOS (from Ref. 13).

j \ j'	0	2	4	6	8	10	12	14	16	18
0	...	58.9	16.4	...	...	...	...	...	...	...
		68.8	26.8	10.8	6.44	5.79	5.45	3.79	2.10	1.24
		60.9	18.0	10.2	8.16	7.85	6.23	3.44	1.35	0.37
		72.6	28.9	12.0	7.84	7.44	5.96	3.31	1.31	0.36
		57.6	17.5	...	...	...	...	...	...	...
		65.0	28.9	...	...	...	...	...	...	...
2	...	...	...	...	...	...	...	...	...	...
	14.9		42.9	15.1	7.57	5.74	4.88	3.58	2.30	1.71
	12.2	...	37.1	13.2	9.81	8.66	7.06	4.55	2.22	0.73
	14.5		46.4	17.9	10.1	8.27	6.75	4.38	2.15	0.71

is such that the attractive and repulsive contributions to $\Delta\eta$ very nearly cancel each other out over much of the repulsive (small l) region of the scattering. Much of the inelastic scattering therefore occurs at large l where the OS approximation is not accurate. Furthermore, the scattering at small l depends more strongly on higher-order terms in the perturbation series than in the case of the SR potential. Thus, it is a more stringent test of TDPT. This can be seen from the results. There is a substantial difference between the CC and TDPT-CC and the CS and TDPT-CS results. The accuracy of TDPT for the $0\rightarrow 4$, $0\rightarrow 6$, and $2\rightarrow 4$ transitions is low because much of the transition probability comes from higher-order perturbations in $\Delta\eta$.

Results for Ar + TlF are given in Table IV. The potential is given by[14] Eq. (23) with $\epsilon=0.011\,418$ eV $=92.09$ cm^{-1}, $R_0=5.186$ Å, $a_{12}=0.5$, and $a_6=0.30$. The two available CC cross sections are given.[14] The CS results were calculated using VIVAS. Also shown are the sudden results of Fitz and Kouri.[13] SA (sudden approximation) refers to the energy sudden approximation (using $\omega=0$) but keeping a classical description of the orbital angular momentum so that θ changes during the collision. The IOS (infinite-order sudden) approximation makes the added use of the orbital sudden approximation. Note that for $|\Delta j|>4$ the OS is accurate, but for $|\Delta j|\leq 4$ there is a large error in the OS because mucl of the scattering occurs at large l. The TDPT-CC and SA agree with the CC results, but the TDPT-CS and IOS do not.

DISCUSSION

The exponential time-dependent perturbation theory involves two rather drastic assumptions: the use of a first-order perturbation theory and the use of a time-dependent theory based on a classical trajectory. It is reasonable that this approximation should result in a very large savings in computer time. It is also obvious from the calculations that, in many cases, this is accomplished without much loss in accuracy. The theory has the added virtue of giving a simple picture of the scattering. The orbital motion is treated classically in that one uses the classical deflection angle $\theta(t)$ or $\theta\equiv 0$ for the orbital sudden case. The accuracy of the orbital sudden approximation is seen to be determined by how large $\theta(t)$ gets while the potential is still large.

It might be assumed that, since the first-order Magnus approximation does so well, that the second-order Magnus approximation[6] will greatly improve the accuracy. This is probably not the case, however. The exponential perturbation theory given by Eqs. (1) and (2) can easily be extended to second order.[4] Taking the semiclassical limit of this term gives rise to two terms: the second-order Magnus approximation and a term which corrects the classical trajectory for the inelastic part of the potential. The second-order Magnus approximation[4,6] is a double integral in time of the commutator of $V\exp(i\omega t)$ with itself at another time. In both the sudden and classical limits this term goes to zero because there exists a time-independent transformation which diagonalizes $V\exp(i\omega t)$, and two diagonal matrices always commute. The correction term, however, is present even in the sudden and classical limits and is likely to be the dominant second-order contribution.

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