RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 40, NUMBER 3 AUGUST 1, 1989

Rapid Communications

Impulse formalism for atom-molecule collisions: Inadequacy of the peaking approximation

Ramesh D. Sharma
Optical/Infrared Technology Division, Geophysics Laboratory, Hanscom Air Force Base, Massachusetts 01731

Pradip M. Bakshi
Physics Department, Boston College, Chestnut Hill, Massachusetts 02167

Joseph M. Sindoni
Yap Analytics Inc., 594 Marret Road, Lexington, Massachusetts 02173

(Received 11 May 1989)

Expressions for differential and total cross sections for atom-diatom scattering are derived using the impulse formalism without any approximations. Results for the rotational-vibrational scattering are obtained without using the peaking approximation (PA). For the specific case of a hard-core potential, it is shown that, except for elastic scattering, PA results are substantially different from the true impulse results.

The basic idea of impulse approach (IA) to collisions was proposed by Chew.[1] The total scattering amplitude for a projectile incident upon a complex system is taken in IA to be the sum of the various two-body amplitudes (the projectile plus each of the constituent particles of the complex system); the constituents not involved in the two-body scattering remain unaffected during the impact and are termed spectators. The role of the binding potential of the complex system is to generate a momentum distribution of the constituent particles. IA has been applied to atom-diatom collisions by Bogan,[2] Eckelt, Korsch, and Philipp,[3-6] and by Beard and Micha.[7]

In all of these papers an additional simplification, the peaking approximation (PA), is invoked to evaluate the integral over the spectator momentum. In this approximation, the t matrix representing the two-body scattering process is evaluated for a particular value of the spectator momentum. This value of the spectator momentum is taken to be one for which the product of the initial- and final-state molecular wave functions is maximum. Since the two-body t matrix varies much more slowly with internal molecular momentum than does the product of the molecular wave functions, the integral over the spectator momentum factors into two parts: (i) the two-body t matrix evaluated for a specific value of the spectator momentum, and (ii) the molecular form-factor integral which can be evaluated easily for a given value of the momentum transferred. PA not only simplifies the computations but it also gives a very simple physical picture of the impulse formulation. However, its validity and accuracy have not been quantitatively assessed.

We have recently developed a formalism[8] which permits computation of IA cross sections without resorting to PA. This allows us to investigate the validity and assess the accuracy of PA. The purpose of this Rapid Communication is to point out that PA is valid only in the limited range of vibrationally and rotationally elastic scattering. It gives grossly erroneous overestimates for vibrationally inelastic forward scattering. It also does not converge to the true IA results even for high relative translational energies.

The state-to-state differential scattering cross section for a molecule consisting of atoms 1 and 2 to undergo a transition from the initial vibration-rotation state vj upon collision with atom 3 to final state $v'j'$ is given by[3,5,8]

$$\frac{d\sigma}{d\Omega}(vjp_3 \rightarrow v'j'p_3',\theta) = \frac{p_3'}{p_3(2j+1)} \sum_m \sum_{m'} \left| \left(\frac{2\pi}{\hbar} \right)^2 \mu_3 \langle \phi_3' | \sum_{s=1,2} T^{(s)} | \phi_3 \rangle \right|^2 , \tag{1}$$

where

$$\langle \phi_3' | T^{(s)} | \phi_3 \rangle = \int d\mathbf{q}_3 \phi^{*\prime}(\mathbf{q}_3') \langle \mathbf{q}_s' | t^{(s)} | \mathbf{q}_s \rangle \phi(\mathbf{q}_3) , \tag{2}$$

and $|\phi_3\rangle \equiv |v,j,m,\mathbf{p}_3\rangle$ is the initial state, the final state being denoted by primes. $\mathbf{p}_3$ and $\mathbf{p}_3'$ are the momenta of the incident particle before and after the collision in the center-of-mass (c.m.) frame of the atom-molecule system. $\mathbf{p}_3$ is also the momentum of the incident particle 3 with respect to the c.m. of the molecule consisting of atoms 1 and 2. $\mathbf{p}_a$ denotes the momentum of particle a with respect to the c.m. of bc and $\mathbf{q}_a$ is the relative momentum of b and c. This set of momenta are called Jacobi momenta.[3,5] μ_a denotes the reduced mass of the system (a,bc). θ is the scattering angle, i.e., the angle between $\mathbf{p}_3$ and $\mathbf{p}_3'$. Summation over m and m' has removed the dependence of the differential cross section on the azimuthal angle. $T^{(s)}$ and $t^{(s)}$ are, respectively, the three-body and two-body transition matrix elements, s being the spectator atom. $\phi(\mathbf{q}_3)$ and $\phi'(\mathbf{q}_3)$ are the initial- and final-state molecular wave functions in the momentum representation.

We have shown[8] how the integral in Eq. (2) can be evaluated without any approximations. We start by expanding the two-body t-matrix element in a spherical harmonics expansion in the unit vector $\hat{\mathbf{q}}_3$,

$$\langle \mathbf{q}_s' | t^{(s)} | \mathbf{q}_s \rangle = \sum_{L,M} t^{(s)}_{L,M}(q_3,\mathbf{p}_3,\mathbf{q}) Y_{LM}(\hat{\mathbf{q}}_3) \,, \tag{3}$$

with $t^{(s)}_{L,M}$ given by

$$t^{(s)}_{L,M}(q_3,\ldots) = \int d\hat{\mathbf{q}}_3 Y^*_{LM}(\hat{\mathbf{q}}_3) \langle \mathbf{q}_s' | t^{(s)} | \mathbf{q}_s \rangle \,. \tag{4}$$

Substituting Eq. (3) in Eq. (2), after some algebra, we get

$$\langle \phi_3' | T^{(s)} | \phi_3 \rangle = \sum_{\beta,\lambda,\gamma,\mu,L,M} (\pm i)^{\beta} i^{(j-\lambda)} \left(\frac{\hat{j}\hat{L}\hat{\beta}}{\hat{j}'} \right)^{1/2} Y^*_{\beta\gamma}(\hat{\mathbf{q}}) N^{(s)}_{LM\lambda\beta}(\mathbf{q}) C(jL\lambda;00) C(jL\lambda;mM\mu) C(\lambda\beta j';00) C(\lambda\beta j';\mu\gamma m') \,, \tag{5}$$

where ± means a plus sign for $s=1$ and a minus sign for $s=2$, $\mathbf{q}$ is the momentum transferred during the collision, $\hat{j} \equiv (2j+1)$, etc., C's are the Clebsch-Gordan coefficients,[9] and

$$N^{(s)}_{LM\lambda\beta}(\mathbf{q}) = \int_0^\infty dr\, r^2 j_\beta(|\alpha_s| rq) K^{(s)}_{LM\lambda}(r) \chi_{v'j'}(r) \,, \tag{6}$$

with $\alpha_s \equiv (-1)^s [m_s/(m_1+m_2)]$, and

$$K^{(s)}_{LM\lambda}(r) = \frac{2}{\pi} \int_0^\infty dq_3\, q_3^2 j_\lambda(q_3 r) t^{(s)}_{L,M}(q_3) I_{vj}(q_3) \,, \tag{7}$$

$$I_{vj}(q_3) = \int_0^\infty dr\, r^2 \chi_{vj}(r) j_j(q_3 r) \,, \tag{8}$$

$\chi_{vj}(r)$ being the radial part of the vibration-rotation wave function and j_j is the spherical Bessel function of order j.

To simplify the remaining algebra it is convenient to choose the z axis of the coordinate system along $\mathbf{q}$, the direction of momentum transfer. Then

$$Y^*_{\beta\gamma}(\hat{\mathbf{q}}) = (\hat{\beta}/4\pi)^{1/2} \delta_{\gamma 0} \,. \tag{9}$$

Using the properties of Clebsch-Gordan coefficients[9] C's, and Racah coefficients W's, Eq. (5) can be rewritten as

$$\langle \phi_3' | T^{(s)} | \phi_3 \rangle = \sum_{\beta,\lambda,L,J} (\pm i)^{\beta} i^{(j-\lambda)} \left(\frac{\hat{j}\hat{L}\hat{\lambda}\hat{J}}{4\pi \hat{j}'} \right)^{1/2} \hat{\beta} N^{(s)}_{LM\lambda\beta}(q) C(jL\lambda;00) C(\lambda\beta j';00) C(jJj';mM) C(L\beta J;M0) W(jLj'\beta;\lambda J) \,. \tag{10}$$

The C and W coefficients express the relation between the total angular momentum change J during the collision, and the initial and final rotational quantum numbers, j and j'. We also note the total angular momentum change J is composed of two parts, L coming from the two-body t matrix and β, the usual component, derived from the momentum transferred during the collision.

The expression for the differential cross section is now obtained by summing the absolute square of the collision amplitude over m and $M = m' - m$ leading to

$$\frac{d\sigma}{d\Omega}(vjp_3 \rightarrow v'j'p_3',\theta) = \left(\frac{2\pi}{\hbar} \right)^4 \mu_3^2 \frac{p_3'}{p_3} \sum_{J=|j-j'|}^{J=(j+j')} \sum_M |F_{JM}|^2 \,, \tag{11}$$

where

$$F_{JM} = \sum_{L\beta\lambda} (i)^{(j-\lambda+\beta)} \hat{\beta} \left(\frac{\hat{L}\hat{\lambda}}{4\pi} \right)^{1/2} C(jL\lambda;00) C(\lambda\beta j';00) C(L\beta J;M0) W(jLj'\beta;\lambda J) [N^{(1)}_{LM\lambda\beta} + (-1)^{\beta} N^{(2)}_{LM\lambda\beta}] \,. \tag{12}$$

In contrast, the differential cross section in the peaking approximation is given by[3]

$$\left(\frac{d\sigma}{d\Omega}(vjp_3 \rightarrow v'j'p_3',\theta) \right)_{\text{PA}} = \left(\frac{2\pi}{\hbar} \right)^4 \mu_3^2 \frac{p_3'}{p_3} \sum_{\lambda=|j-j'|}^{\lambda=(j+j')} \hat{\lambda} C^2(j\lambda j';00) | f^{(1)}_{v'j',vj;\lambda} t^{(1)}_{\text{PA}} + (-1)^{\Delta j} f^{(2)}_{v'j',vj;\lambda} t^{(2)}_{\text{PA}} |^2 \,, \tag{13}$$

where

$$f^{(s)}_{v'j',vj;\lambda} \equiv \int_0^\infty dr\, r^2 \chi_{v'j'}(r) j_\lambda(|\alpha_s| rq) \chi_{vj}(r) \,. \qquad (14)$$

Our Eq. (11) can be shown to reduce to the PA result Eq. (13) as follows: In PA the two-body t-matrix element, on the right-hand side of Eq. (2), is evaluated at a fixed value of the internal momentum $\mathbf{q}_3$, where the product of the initial- and final-state wave functions is at its maximum. The resulting matrix element, denoted by $t^{(s)}_{\mathrm{PA}}$, is pulled out of the integral which now becomes the familiar form-factor integral. Mathematically, this amounts to retaining only the isotropic component ($L=0$ and $M=0$) in the expansion of the two-body t matrix of Eq. (3) and assigning it the value $t^{(s)}_{\mathrm{PA}}$. Substituting $L=0$ in Eq. (12) gives $\lambda=j$ and $\beta=J$, and when $t^{(s)}_{00}(q_3) \equiv \sqrt{4\pi} t^{(s)}_{\mathrm{PA}}$ is taken outside the integral in Eq. (7), we get $K^{(s)}_{00j} = \sqrt{4\pi} t^{(s)}_{\mathrm{PA}} \chi_{vj}(r)$. Equation (6) now becomes $N^{(s)}_{00jJ} = \sqrt{4\pi} f^{(s)}_{v'j',vj;J} t^{(s)}_{\mathrm{PA}}$, which upon substitution into Eq. (11) gives Eq. (13). This reduction makes it clear that PA is obtained by (i) assuming that t matrix varies slowly over the range of q_3 over which the product of the initial and final states is significant and (ii) by ignoring the angular structure of the t matrix and the rotational transitions it may cause.

The total cross section is obtained from the differential cross section by the relation

$$\sigma(vjp_3 \rightarrow v'j'p'_3) = \frac{2\pi}{p_3 p'_3} \int_{|p_3-p'_3|}^{p_3+p'_3} \left[\frac{d\sigma}{d\Omega} \right] q\, dq \,. \qquad (15)$$

Equation (11) is our result for an impulse calculation without further approximations, whereas Eq. (13) is the standard PA result. To compare the two sets of calculations we pick a hard-core potential to represent the two-body interaction. The two-body t matrix for this potential is available in a closed form[10] and is, in fact, the only potential used in the previous atom-diatom studies. We compare the results for a system that was extensively studied previously,[3,6]

$$\mathrm{Li}^+ + \mathrm{N}_2(v,j) \rightarrow \mathrm{Li}^+ + \mathrm{N}_2(v',j') \,. \qquad (16)$$

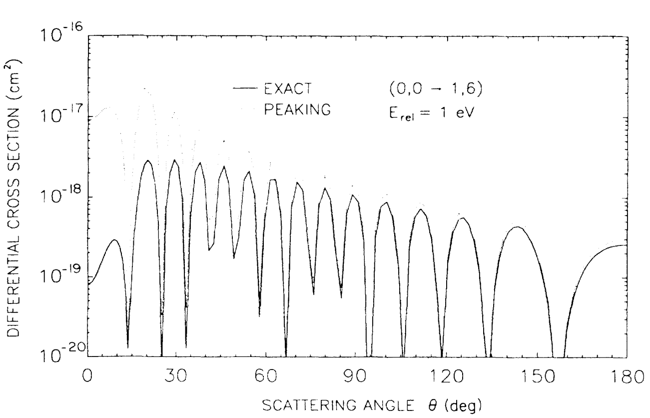

FIG. 1. Plot of differential cross section of the $\mathrm{Li}^+ + \mathrm{N}_2(0,0) \rightarrow \mathrm{Li}^+ + \mathrm{N}_2(1,6)$ at relative energy of 1 eV as a function of scattering θ. The exact calculation is shown as a solid line while the PA result is shown as a dotted line.

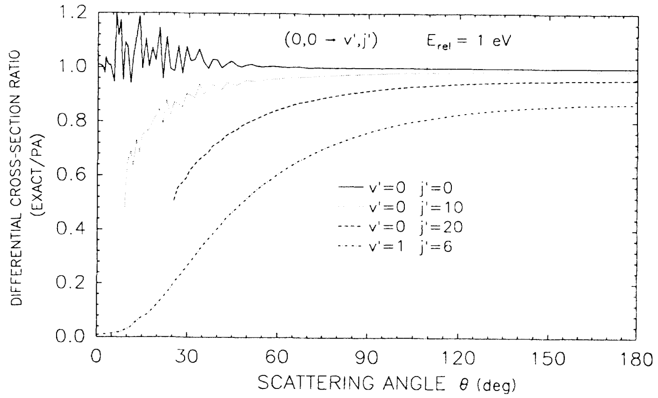

FIG. 2. Plot of the ratio of the exact and PA differential cross sections as a function of the scattering angle for various final states of N_2 resulting from a collision with Li^+ at a relative translational energy of 1 eV.

The computations have been performed for the initial vibrational level $v=0$ and final levels $v'=0$, 1, and 2. For relative kinetic energy of 1 eV, the hard-core radius is taken to be[3] 1.62 Å. In PA, for homonuclear diatomic molecules, the product of the initial and final wave functions is assumed to peak at the midpoint of their two centers, $q_3=0$ and $q'_3=0$, and the two-body t matrix is evaluated at fixed internal momentum $\mathbf{q}_3 = \frac{1}{4}\mathbf{q}$, where $\mathbf{q} = \mathbf{p}'_3 - \mathbf{p}_3$ is the momentum transferred during the collision.[3,7]

Molecular wave functions used in this calculation were obtained by numerical integration of the radial Schrödinger equation[11] using the Rydberg-Klein-Rees theory of constructing the diatom potential from spectroscopic constants.[12] Previous work used the harmonic-oscillator potential to obtain the diatom wave functions. We find that there are substantial differences between peaking calculations using the harmonic oscillator and the more accurate wave functions for situations involving large vibrational-rotational inelasticity. To highlight the differences be-

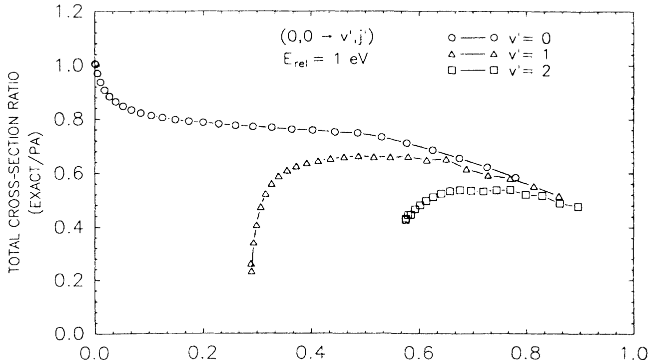

FIG. 3. Total cross section for the $\mathrm{Li}^+ + \mathrm{N}_2(0,0) \rightarrow \mathrm{Li}^+ + \mathrm{N}_2(v',j')$ process as a function of energy loss for $v'=1$ (circles), $v'=2$ (triangles), and $v'=3$ (squares). Each point represents a j' starting with zero on the left-hand side and increasing in steps of two. The relative translational energy is again 1 eV.

tween the peaking and exact IA calculations we used the more accurate wave functions throughout this work.

Figure 1 gives a plot of the differential cross section for the process $(0, 0 \rightarrow 1, 6)$ as a function of scattering angle θ. For forward scattering the exact IA result is about *two orders of magnitude smaller* than the PA result. Even though the peaks and valleys for the two calculations track each other closely, the discrepancy between the two sets of calculations is visible even on the log scale. The quantitative difference between the two calculations is best described by the ratio ρ of the exact and the PA results, displayed in Fig. 2. It is clear from Fig. 2, which also displays this ratio for $(00 \rightarrow 0j')$, $j'=0$, 10, and 20, that, except for elastic $(00 \rightarrow 00)$ scattering, there are noticeable differences between the two calculations. These differences appear to increase with energy loss, independent of whether the energy ends up in vibration or rotation. Further, even for large angles PA continues to overestimate the exact results.

It was pointed out earlier that PA is obtained by keeping only the $L=0$ and $M=0$ term in the expansion of the t matrix [Eq. (3)] and assigning it the value $t_{\rm PA}^{(s)}$. The exact calculation outlined here permits interference between terms with different L but with the same M. This interference is responsible for the drastic change of the differential cross section, especially in the forward direction, for the vibrationally inelastic processes.

Figure 3 displays the total cross section $\sigma_T(00 \rightarrow n'j')$ for $n'=0$, 1, and 2 as a function of energy loss. PA grossly overestimates the true result for small j' for $n'=1$ and 2. This is because small Δj scattering is essentially forward scattering for which the two calculations give very different results. The total cross section mirrors this disparity, weight factor $\sin\theta$ notwithstanding. For large j', when almost all the energy loss goes into molecular rotation and the energy loss is almost independent of n', the three curves approach the same asymptote—showing that in this range the ratio of the total cross sections is a function of energy loss alone.

In summary, we have developed IA formalism without PA. It is shown that for most situations of interest PA overestimates the true IA results. All of these features continue to persist for higher relative translational kinetic energies. Further details and an extension of this work are to be given elsewhere.[8]

This investigation was, in part, funded by the U.S. Air Force Office of Scientific Research.

---

[1] G. F. Chew, Phys. Rev. **80**, 196 (1950).

[2] A. Bogan, Jr., Phys. Rev. A **9**, 1230 (1974).

[3] P. Eckelt, H. J. Korsch, and V. Philipp, J. Phys. B **7**, 1649 (1974).

[4] H. J. Korsch and V. Philipp, Phys. Rev. A **13**, 497 (1976).

[5] V. Philipp, H. J. Korsch, and P. Eckelt, J. Phys. B **9**, 345 (1976).

[6] V. Philipp, H. J. Korsch, and P. Eckelt, J. Phys. B **10**, 117 (1977).

[7] L. H. Beard and D. A. Micha, J. Chem. Phys. **74**, 6700 (1981).

[8] R. D. Sharma, P. M. Bakshi, and J. M. Sindoni (unpublished).

[9] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[10] J. M. J. Van Leeuwen and A. S. Reiner, Physica **27**, 99 (1961).

[11] R. Tipping (private communication); the authors are grateful to Dr. Tipping for a computer code which generates the wave functions.

[12] K. P. Huber and G. Hertzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).