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Criteria for applicability of the impulse approach to collisions

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Using an exact formulation of impulse approach (IA) to atom-diatom collisions, we assess its internal consistency. By comparing the cross sections in the forward and reverse directions for the vibrational-rotational inelastic processes, using the half-on-the-shell (post and prior) models of the two-body t matrix, we show that in both cases the IA leads to a violation of the semidetailed balance (SDB) condition for small scattering angles. An off-shell model for the two-body t matrix, which preserves SDB, is shown to have other serious shortcomings. The cross sections are studied quantitatively as a function of the relative translational energy and the mass of the incident particle, and criteria discussed for the applicability of IA.

I. INTRODUCTION

Since its inception the impulse approach (IA) to collisions has been used in diverse fields of physics.[1-5] The conditions of its validity are often heuristically described, but quantitative measures of its applicability are not available. IA as applied to atom-molecule collisions to date[4-6] consists of three steps: (i) The multiple-collision expansion is truncated, retaining only the single-collision terms. (ii) The three-body T-matrix element is replaced by a two-body t-matrix element. The choice of the energy parameter of the two-body t matrix distinguishes the various models (e.g., post,[4] prior,[4] and full[5]). (iii) A further approximation, the peaking approximation (PA), was invoked in earlier studies[4,5] to evaluate the transition amplitude.

We have recently shown[6,7] how to evaluate the transition amplitude without any approximations, eliminating the errors due to the last step. This now allows us to take a critical look at the choice of the energy parameter in the two-body t matrix. In this paper we show that the two half-on-the-shell models,[4] prior and post, violate the semidetailed balance (SDB) condition for small scattering angles, indicating an internal inconsistency in those approaches. We also show that the (off-shell) full model,[5] which satisfies SDB, has other serious shortcomings. We further suggest alternate models which satisfy SDB (and do not have other formal difficulties) to test the model dependence of the cross sections. Finally, we discuss criteria for the applicability of IA. The detailed results given here are obtained using a two-body interaction with a hard-core potential.[4,5,8] The conclusions reached, however, should be applicable to other potentials as well.

In a multiple-collision expansion[4] of the atom-diatom three-body T matrix,

$$T(z)=T^{(1)}+T^{(2)}+T^{(1)}G_3T^{(2)}+T^{(2)}G_3T^{(1)}+\cdots, \tag{1}$$

where $G_3=(z-H_3)^{-1}\equiv(z-H_0-V_3)^{-1}$ is the propagator corresponding to the atom-diatom Hamiltonian which includes the relative translational energy and potential energy V_3 of the molecule 1-2, but not the interaction energy of the incident atom with atoms 1 (V_2) and 2 (V_1) of the diatom. The first two terms correspond to the collision of the incident atom 3 with atoms 2 and 1, respectively, while atoms 1 and 2 are the spectators, indicated by superscripts. The next two terms represent the double-collision terms.

IA retains only the two single-collision terms.[4-6] The second and crucial step in IA is the reduction of the three-body T matrix to the two-body t matrix by assuming that the time duration of the collision is much shorter than the characteristic times for the molecular motion. The function of the intramolecular potential is then to generate a momentum distribution for the two atoms constituting the diatom. Formally, the two steps are represented by[4,5]

$$\langle\phi_3'|T|\phi_3\rangle\Longrightarrow\langle\phi_3'|T^{(1)}+T^{(2)}|\phi_3\rangle, \tag{2}$$

and

$$\langle\phi_3'|T^{(s)}(E)|\phi_3\rangle\Longrightarrow\int d\mathbf{q}_3\phi'^{*}(\mathbf{q}_3')\langle\mathbf{q}_s'|t^{(s)}(\varepsilon_s)|\mathbf{q}_s\rangle\phi(\mathbf{q}_3), \tag{3}$$

where $|\phi_3\rangle\equiv|v,j,m,\mathbf{p}_3\rangle$ is the initial state, the final state being denoted by primes. E, the eigenvalue of H_3, is the total energy of the initial (and final) state; $\varepsilon_s=E_s=q_s^2/(2m_{tu})$ is the relative kinetic energy of the nonspectator t and u atoms before the collision, $\mathbf{p}_3$ and $\mathbf{p}_3'$ are the momenta of the incident particle before and after the collision in the center-of-mass frame of the atom-molecule system. $T^{(s)}$ and $t^{(s)}$, respectively, generate 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. $\mathbf{q}_s$ and $\mathbf{q}_s'$ are the Jacobi momenta[4,9] be-

fore and after the collision.

The choice $\varepsilon_s = E_s$ (the kinetic energy of the colliding pair *before* collision) in the two-body t-matrix element

$$\langle \mathbf{q}_s' | t^{(s)}(\varepsilon_s) | \mathbf{q}_s \rangle \equiv t^{(s)}(\mathbf{q}_s', \mathbf{q}_s; \varepsilon_s) \quad (4)$$

seems to be the natural one in the spirit of IA and is called the *post* form[4] of IA. Other choices have been considered; $\varepsilon_s = E_s' = q_s'^2/(2m_{tu})$ is called the *prior* form,[4] m_{tu} being the reduced mass of the t and u atoms. The choice[5] $\varepsilon_s = E - p_s^2/2\mu_s$, μ_s being the reduced mass of the s and $(t+u)$ system, may be called the *full* form in that it subtracts the spectator atom energy from E, the total physical energy of the process. The post and prior forms are half-on-the-shell, since one of the momenta, $\mathbf{q}_s$ or $\mathbf{q}_s'$, lies on the energy shell. The full form is off shell. The basic assumption of IA, that the spectator momentum p_s has not changed during the collision, is incorporated in each case. Calculation of cross sections using different ε_s will generally give different results. We return to this point later.

To compare the relative merits of different models, we apply symmetry considerations. Since the Hamiltonian is independent of time and quadratic in momenta, it is invariant under time reversal. Combined with the space-inversion symmetry, this leads to the SDB relation[10,11] between the differential cross sections for the forward and reverse processes,

$$p[d\sigma(i \rightarrow f)/d\Omega]/\rho(f) = p'[d\sigma(f \rightarrow i)/d\Omega]/\rho(i) , \quad (5)$$

where $\rho(i)$ and $\rho(f)$ are the densities of state in the initial and final states, and p and p' represent the incident flux densities. A valid theory must lead to cross sections which satisfy Eq. (5).

II. RESULTS

We have computed the differential cross sections for the much studied process[4-6]

$$Li^+ + N_2(v,j) \leftrightarrow Li^+ + N_2(v',j') \quad (6)$$

in the forward and reverse directions using IA, Eq. (3), with the previously employed[4,5] hard-core two-body (atom-atom) potential[12] for various values of the relative translational energies E_{rel}. In Fig. 1 the differential cross section using the post model for the process $v=0$, $j=12 \rightarrow v=1$, $j=6$ in the forward direction at $E_{rel}=1$ eV is given by the solid line. The cross section for the reverse process multiplied by $p_3\rho(f)/p_3\rho(i)$, the ratio of the densities of state times the incident flux $\{\rho(f) \propto [(2j'+1)p_3']$ and $\rho(i) \propto [(2j+1)p_3]\}$, and termed "normalized" reverse differential cross section, is given by the dotted line. The two curves should be identical if the theory obeys SDB. Up to a scattering angle of about 50° the two curves do not appear to be related. From 50° to 70° the two curves have a similar structure. For larger scattering angles they are indistinguishable.

The dotted line in Fig. 2 gives a plot of the ratio of the two differential cross sections of Fig. 1 as a function of the scattering angle for E_{rel} of 1 eV, its departure from unity

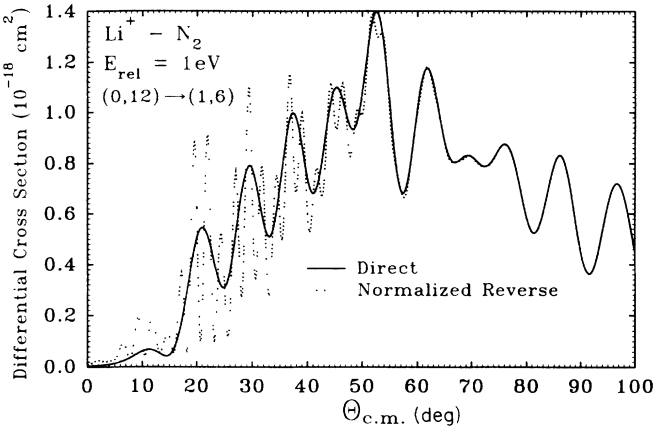

FIG. 1. Direct (solid line) and normalized reverse (dotted line) differential cross sections for $Li^+ + N_2(v=0, j=12) \rightarrow Li^+ + N_2(v'=1, j'=6)$ at relative translational energy $E_{rel}=1$ eV as a function of center-of-mass scattering angle θ°.

providing a quantitative measure of the violation of SDB. The solid line represents a similar ratio for $E_{rel}=4$ eV. It is clearly seen that the two curves which appear unrelated in Fig. 1 show a definite periodicity in their ratio, and the whole structure gets squeezed towards smaller angles at higher relative translational energy.

We conclude that the post form does not satisfy the SDB condition for small angles. If we use the prior form for ε_s, the forward process is represented by the dotted line in Fig. 1 and the normalized reverse process is represented by the solid line. Thus the prior form also fails to satisfy SDB where the post form fails. It can be shown from the structure of the post and prior t-matrix elements that the post↔prior interchange is equivalent to the forward↔(normalized) reverse interchange. The full form obeys SDB, a result predictable from the structure of its t matrix.

Now we examine the mass dependence of the SDB

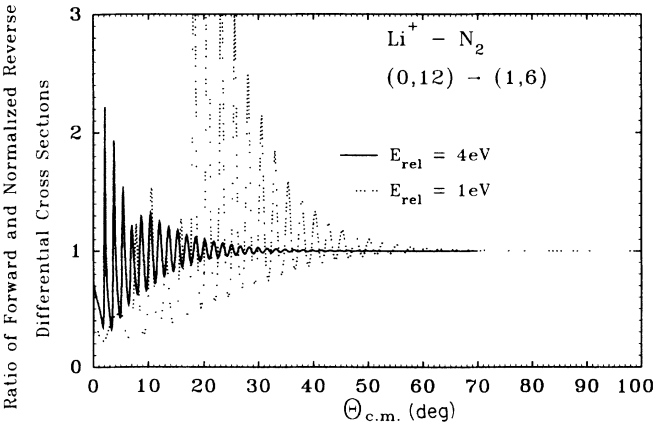

FIG. 2. Ratio of the forward and normalized reverse differential cross sections of Fig. 1 as function of center-of-mass scattering angle θ° at $E_{rel}=1$ eV (dotted line) and $E_{rel}=4$ eV (solid line).

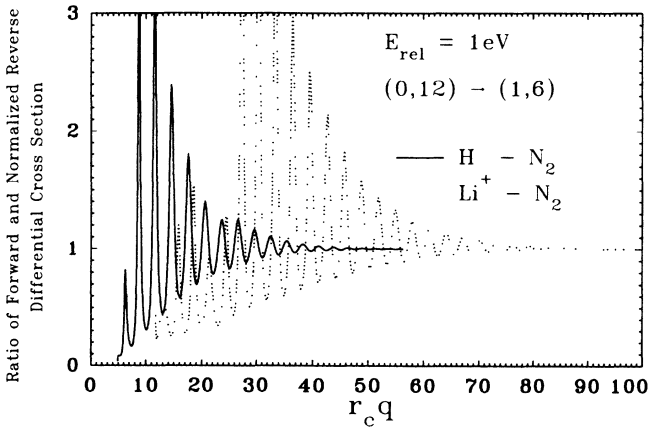

FIG. 3. Ratios of the forward and normalized reverse differential cross sections for the $(0,12)\rightleftarrows(1,6)$ transitions of N_2 at relative translational energy of 1 eV for collision with Li^+ (dotted line) and H (solid line).

violation. Figure 3 shows the ratio of the forward and normalized reverse differential cross sections for the same N_2 transition caused by a collision with the H atom (solid curve) or Li^+ (dotted curve), both at E_{rel} of 1 eV, as functions of $r_c q$, $q = |\mathbf{p}_3' - \mathbf{p}_3|$ being the momentum transfer. This is a more convenient parameter to compare processes with different projectile masses. For $r_c q \geq 20$ the two curves show a period of π with the H-atom curve having a smaller amplitude. The effect of a lighter incident particle appears similar to that of increasing the energy of relative motion as seen in Fig. 2. Figure 4 displays $(r_c q)_1$, the smallest value of $r_c q$ at which SDB is satisfied to 1% as a function of relative energy[12] for the two incident particles studied.

III. DISCUSSION

We have shown above that *both* the post and prior forms violate the SDB criterion for small angles. The other model used in the literature,[5] the full form, does not violate SDB but poses other problems. The first is a conceptual difficulty; the choice $\varepsilon_s = E - p_s^2/2\mu_s$ always leads to a negative energy ε_s for a part of the range of integration over $\mathbf{q}_3$ in Eq. (3). Thus the amplitude integral in Eq. (3) remains ill-defined without introducing a cutoff (in the range of integration) or attempting analytical continuation into negative energies. Second, even if a cutoff is introduced as a practical measure, the full form leads to very high cross sections for the smaller angles, yielding an unreasonably large total cross section in significant excess of the quantum-mechanical shadow. On the other hand, the total cross sections based on the post and prior forms understate the shadow limit.

In view of these intrinsic difficulties with the models used in the literature, one can consider other *ad hoc* choices for ε_s which avoid some of these problems. An obvious choice is $\varepsilon_s = \frac{1}{2}(E_s + E_s')$, which may be termed the *mean* model. This introduces a symmetry in the structure of the t matrix and the SDB criterion is automatically satisfied. It is also free from any definition problems. Figure 5 provides a comparison of these four models for the same process as in Figs. 1 and 2 with $E_{rel} = 4$ eV. The full model is evaluated by cutting off the range of $\mathbf{q}_3$ where ε_s would become negative. For this energy, the wave functions' product in Eq. (3) in the excluded domain is quite insignificant, making this a practical calculation. (For an energy such as $E_{rel} = 1$ eV, the cutoff for the full model would take away a significant part of the form-factor integral, making it a meaningless calculation.) It is clear from Fig. 5 that for larger angles these results are *model independent*. For intermediate angles the post, prior, and mean models trace similar patterns. For small angles the models vary significantly.

In conclusion, we suggest (i) the SDB condition and (ii) model independence as two criteria to be employed in assessing the applicability of IA. In domain I where both the criteria are met, one may use IA with confidence. Figure 4 provides the boundary of this domain for 1% accura-

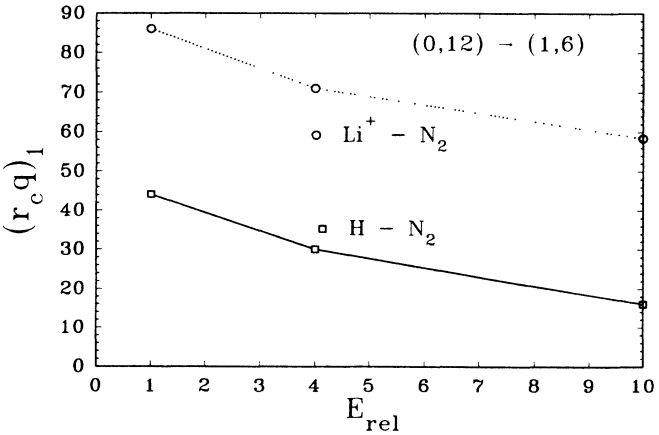

FIG. 4. Threshold value of $r_c q$ for 1% deviation from the SDB condition as a function of relative translational energy in eV for the $(0,12)\rightleftarrows(1,6)$ transitions of N_2. Dotted line is for collision with Li^+ and solid line is for collision with H.

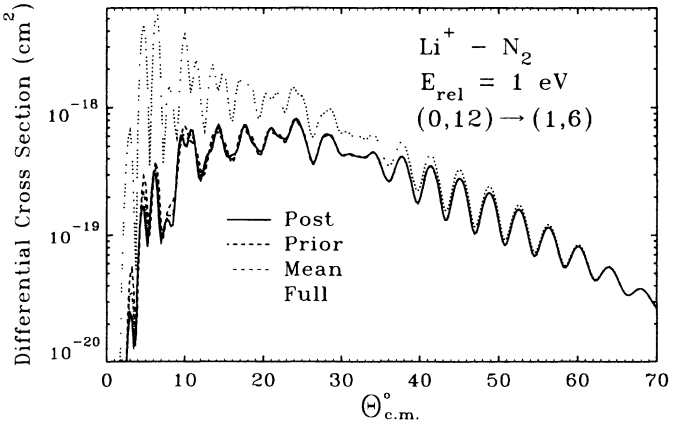

FIG. 5. Comparison of the differential cross sections for the process $Li^+ + N_2(v=0, j=12) \rightarrow Li^+ + N_2(v'=1, j'=6)$ at relative translational energy of 4 eV for four models of ε_s: post (solid line), prior (dashed line), mean (dash-dotted line), and full (dotted line).

cy for both the post and prior models. In domain II, where the post, prior, and mean models retain the same patterns with slight quantitative differences, IA may be expected to be a good approximation with any of these models, with possible errors of the same magnitude as their differences. The full model seems to overstate the cross sections and seems much less reliable in this domain. For the small angles, domain III, all the models give rather different results. This is also the domain where higher-collision terms may make significant contributions. Thus IA at the level of Eq. (3) may not be applicable with any of the models in this domain. One should return to step (i) in this domain, and recognize that the multiple collision terms in Eq. (1) can make significant contributions at small angles. One can use the impulse ansatz to evaluate the matrix elements of the higher-collision terms by replacing the three-body elements by appropriate two-body elements as in step (ii). These detailed calculations are beyond the scope of this paper, but we note that the same two criteria (viz., satisfying SDB for a given model and insensitivity to the choice of ε_s in final results) can still be applied to judge the validity of IA at this level. Finally, we would like to point out that even for large angles, using PA leads to violation of SDB for post as well as prior models, and the two-body energy model independence of the cross section is lost as well.

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[12]r_c is taken to be 1.62, 1.10, and 1.05 Å for $Li^+ - N$ at 1-, 4-, and 10-eV relative translational energies. The same values are used for $H - N$ so that the role of the mass of the incident particle can be brought out more clearly.