PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Impulse Approximation for One-Dimensional Atom-Oscillator Collisions. I

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(Received 25 May 1970)

Translational-vibrational energy transfer in collinear collisions of an atom and an harmonic oscillator has been treated in the impulse approximation of Chew. Although transition probabilities for a soft exponential interaction potential compared poorly with exact quantum-mechanical results, for sufficiently small incident masses good results were obtained for a hard impulsive interaction. This is understood in terms of the ratio of the collision time to the oscillator period; the impulse approximation is expected to be valid when this ratio is small. For the smaller incident masses, qualitative agreement with exact results was obtained over a wide energy range for the "hard-sphere" collisions. This represents the first successful approximate treatment of impulsive collisions for this model. In contrast to the familiar perturbative methods, the quality of the approximation does not decrease for multiple-quantum transitions and improves as the energy increases. The one-dimensional impulse-approximation transition probabilities P_{if} are ill behaved at threshold; however, most computed probabilities remained well behaved to within about $\frac{1}{4}\hbar\omega$ of threshold. The approximation fails to conserve probability. It was found that the sums of probabilities $\sum_f P_{if}$ for the various initial states i provided reliable measures of confidence in the approximation. For a given i, if the probability sum was nearly constant with changing energy, the P_{if} curves were qualitatively good; on the contrary, the curves were in less good agreement with exact results if the probability sums were less stable with changing energy. When the curves for a given i were qualitatively good, a simple renormalization yielded quantitative agreement with exact results and minimized the effects of threshold misbehavior.

I. INTRODUCTION

The purpose of this paper is to suggest that the impulse approximation (IA) of Chew[1] may be used to advantage in quantum-mechanical treatments of some inelastic molecular collisions. In particular, we investigate its application to one-dimensional atom-molecule translational-vibrational energy-transfer problems.

In the IA, the collision of an incident particle with a single particle held bound in a complex is assumed to occur so rapidly that during the time of interaction the binding potential can be neglected compared to the potential under which the two particles interact. This will occur when the period τ_i of the internal motion of the bound particle is long compared to the collision time τ_c. The only effect of the binding potential under these conditions is to determine the momentum distribution of the target particle. Thus, the total wave function will be that of a free particle scattering off a target particle represented by a momentum wave packet. If one assigns the coordinate x to the incident particle and y to the target particle, the IA to the wave function may be written

$$\Psi(x, y) \simeq \Psi^{\mathrm{IA}}(x, y) = \int_{-\infty}^{\infty} dk' g_i(k') \psi^F_{k_i, k'}(x, y) , \quad (1)$$

where $g_i(k')$ is the momentum distribution function of the target particle in the ith eigenstate of the binding potential and $\psi^F_{k_i, k'}$ is the wave function for the scattering of two free particles under the same interaction potential as in the bound problem. Equation (1) is often referred to as the quasifree approximation since $\Psi(x, y)$ is taken to be the free wave function but weighted according to the momentum distribution of the bound particle.

Since the IA assumes that τ_c/τ_i is small, it is best suited for high-energy collisions under a short-range potential. In the work reported here, the best results are obtained for an infinite repulsive barrier or "hard-sphere" interaction potential. In the systems where the IA can be validly applied, it offers considerable advantage over Born-type perturbative methods in that the scattered wave need not be small compared to the incident wave. In addition, both nondissociative and dissociative collisions can be treated within a single approximate framework. Although the present calculations deal with a very simplified model, the relative computational ease with which results can be obtained augurs well for possible future application to more complex systems.

The one-dimensional model has been widely used as a prototype for systems where translation-vibration energy transfer occurs.[2] Its admitted inadequacies as a realistic physical model need not concern us here; it has considerable value as a testing ground for approximate methods, especially since some exact quantum-mechanical results are available for comparison.[3,4]

As regards the importance of the size of the ratio τ_c/τ_i in atom-molecule collisions, the viewpoint of Landau and Teller[5] is instructive. They proposed that the transition probability be expressed as

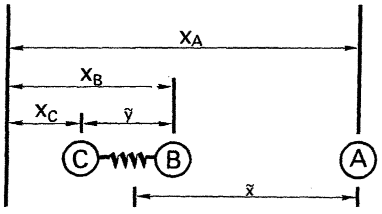

FIG. 1. Coordinates for one-dimensional model.

proportional to $\exp(-\tau_c/\tau_i)$. This was in accordance with the qualitative notion of Ehrenfest that the more rapidly the collision takes place the less chance the molecule has to adjust adiabatically, and therefore the larger the transition probability. But the condition for the validity of the IA is that $\tau_c/\tau_i \sim 0$, which according to this view would correspond to maximum collision efficiency. Thus, the impulse approximation is expected to be most suitable for systems where large transition probabilities occur, and should serve to complement the first Born and first-order distorted-wave approximations, which are valid only when transition probabilities are small.

II. BASIC FORMALISM FOR 1-*D* MODEL

We will consider the collinear collision of an atom of mass m_A and a diatomic molecule consisting of two atoms B and C of masses m_B and m_C. Designating the positions of the three particles as X_A, X_B, X_C (Fig. 1), the time-independent Schrödinger equation takes the form

$$\left\{-\frac{\hbar^2}{2m_A}\frac{\partial^2}{\partial X_A^2}-\frac{\hbar^2}{2m_B}\frac{\partial^2}{\partial X_B^2}-\frac{\hbar^2}{2m_C}\frac{\partial^2}{\partial X_C^2}+U(X_B-X_C)+V(X_A-X_B)+V'(X_A-X_C)\right\}\psi=\mathcal{E}\psi\ . \tag{2}$$

If one neglects $V'(X_A - X_C)$ as being much smaller than the other potentials and transforms to center-of-mass and relative coordinates, one has for the Schrödinger equation

$$\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{2z^2}-\frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial\tilde{y}^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\tilde{x}^2}+U(\tilde{y})+V\left(\tilde{x}-\frac{m_C}{m_B+m_C}\tilde{y}\right)\right\}\psi=\mathcal{E}\psi\ , \tag{3}$$

where

$$\begin{pmatrix} z \\ \tilde{x} \\ \tilde{y} \end{pmatrix} \equiv \begin{pmatrix} \frac{m_A}{M} & \frac{m_B}{M} & \frac{m_C}{M} \\ 1 & -m_B/(m_B+m_C) & -m_C/(m_B+m_C) \\ 0 & 1 & -1 \end{pmatrix} \times \begin{pmatrix} X_A \\ X_B \\ X_C \end{pmatrix}, \tag{4}$$

$$M \equiv m_A + m_B + m_C\ , \qquad \mu_{BC} \equiv \frac{m_B m_C}{m_B + m_C}\ ,$$

and

$$\mu \equiv \frac{m_A(m_B+m_C)}{m_A+m_B+m_C}\ .$$

We now separate out the constant center-of-mass motion and consider the Schrödinger equation for the relative motion only. We further assume that the molecule is bound by harmonic forces, i.e.,

$$U(\tilde{y}) = \tfrac{1}{2}\lambda(\tilde{y}-\tilde{y}_0)^2, \tag{5}$$

with $\tilde{y}_0$ the equilibrium separation of BC and λ the force constant. The following transformation can now be performed[4]:

$$\begin{aligned} y &\equiv (\mu_{BC}\lambda/\hbar^2)^{1/4}(\tilde{y}-\tilde{y}_0), \\ x &\equiv (\mu_{BC}\lambda/\hbar^2)^{1/4}\{[(m_B+m_C)/m_C]\tilde{x}-\tilde{y}_0\}, \end{aligned} \tag{6}$$

to reduce the Schrödinger equation for the relative

TABLE I. Transition probabilities for exponential potential, $\alpha = 0.3$ and $m = \frac{2}{3}$.

E	i	f	P_{if}^{IA}	$P_{if}^{\mathrm{SJ}\,a}$
3	0	1	0.1×10^{-2}	0.2×10^{-1}
3	1	0	0.5×10^{-3}	...
3	1	2	0.1	0.9×10^{-3}
4	0	1	0.7×10^{-4}	0.1
4	0	2	0.1×10^{-2}	0.1×10^{-2}
4	1	0	0.5×10^{-4}	0.1
4	1	2	0.1×10^{-1}	0.4×10^{-1}
4	1	3	0.2×10^{-1}	0.3×10^{-2}
4	2	3	0.7×10^{-1}	0.6×10^{-1}
5	0	1	0.5×10^{-5}	0.3
5	0	2	0.1×10^{-3}	0.1×10^{-1}
5	0	3	0.2×10^{-2}	...
5	1	0	0.3×10^{-5}	0.3
5	1	2	0.2×10^{-2}	0.2
5	1	3	0.2×10^{-1}	0.3×10^{-2}
5	2	3	0.7×10^{-1}	0.6×10^{-1}
6	0	1	0.4×10^{-6}	0.4
6	0	2	0.1×10^{-4}	0.7×10^{-1}
6	0	3	0.2×10^{-3}	...
6	1	0	0.3×10^{-6}	0.4
6	1	2	0.2×10^{-3}	0.3
6	1	3	0.2×10^{-2}	0.4×10^{-1}
6	2	3	0.1×10^{-1}	0.2
6	2	4	0.8×10^{-1}	0.6×10^{-2}
8	0	1	0.3×10^{-8}	0.4
8	0	2	0.1×10^{-6}	0.3
8	1	4	0.7×10^{-3}	0.5×10^{-1}
10	0	1	0.2×10^{-10}	0.2
10	1	4	0.1×10^{-4}	0.2

[a] SJ: Secrest-Johnson, Ref. 4.

TABLE II. Values of 0-*f* transition probabilities for $m = 5.0$.

	0-0		0-1		0-2		0-3	
E	IA	SJ[a]	IA	SJ	IA	SJ	IA	SJ
1.0	0.4×10^{-3}	1.0	b	b	b	b	b	b
1.25	0.3×10^{-3}	1.0	b	b	b	b	b	b
1.5	0.2×10^{-7}	1.0	b	b	b	b	b	b
1.75	c		0.3×10^{-3}	0.1×10^{-1}	b	b	b	b
2.0	c	0.96	0.1×10^{-6}	0.3×10^{-1}	b	b	b	b
2.25	c		c	0.7×10^{-1}	b	b	b	b
2.50	c	0.9	c		b	b	b	b
2.75	c		c		0.4×10^{-5}	d	b	b
3.0	c	0.94	c		0.2×10^{-7}	d	b	b
3.25	c		c		c	d	b	b
3.5	c		c		c	d	b	b
3.75	c		c		c	d	0.1×10^{-6}	d
4.0	c		c		c	d	0.2×10^{-4}	d
4.25	c		c		c		c	d
4.5	c		c		c	0.01	c	d
4.75	c		c		c		c	d
5.0	c		c		c	0.02	c	d

[a] Denotes Secrest and Johnson, Ref. 4.
[b] Energies below threshold.
[c] Values less than 10^{-8}.
[d] Values too small to be read on SJ's graph.

motion to

$$H\Psi \equiv \left\{ -\frac{1}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 + V(x-y) \right\} \Psi = E\Psi, \tag{7}$$

where

$$m \equiv m_A m_C / M m_B, \qquad E \equiv \frac{\mathcal{E}}{\hbar(\lambda/\mu_{BC})^{1/2}} \equiv \frac{\mathcal{E}}{\hbar\omega}, \tag{8}$$

so that the energy E is now measured in units of reduced oscillator quanta.

$V(x-y)$ is typically chosen to be an exponential fit to the repulsive portion of one of the more well-known intermolecular potentials, such as the Lennard-Jones.[2]

With the model so described, one can now proceed to partition the Hamiltonian as

$$H = H_0(x, y) + \mathcal{V}(x, y), \tag{9}$$

with $\mathcal{V}$ chosen such that one can solve exactly for the so-called reference states Φ of H_0, viz.,

$$H_0\Phi = E\Phi. \tag{10}$$

One then writes without loss of generality

$$\Psi(x, y) = \Phi(x, y) + \psi_s(x, y). \tag{11}$$

TABLE III. Values of 2-*f* transition probabilities for $m = 5.0$.

	2-0		2-1		2-2		2-3	
E	IA	SJ[a]	IA	SJ	IA	SJ	IA	SJ
2.5		b	b	b		1.0	b	b
2.75	0.4×10^{-5}	d	0.2×10^{-1}		0.4		b	b
3.0	0.7×10^{-7}	d	0.2×10^{-3}	0.2×10^{-1}	0.2×10^{-1}	0.98	b	b
3.25	c	d	0.2×10^{-5}		0.3×10^{-3}		b	b
3.5	c	d	0.2×10^{-7}	0.12	0.1×10^{-5}	0.88	b	b
3.75	c	d	c		0.1×10^{-7}		0.1×10^{-7}	d
4.0	c	d	c	0.3	b	0.70	0.7×10^{-2}	d
4.25	c		c		b		0.1×10^{-3}	d
4.5	c	0.01	c	0.4	b	0.55	0.2×10^{-5}	d
4.75	c		c		b			d
5.0	c	0.02	c	0.3	b	0.48		d

[a] Denotes Secrest and Johnson, Ref. 4.
[b] Energies below threshold.
[c] Values less than 10^{-8}.
[d] Values too small to be read on SJ's graph.

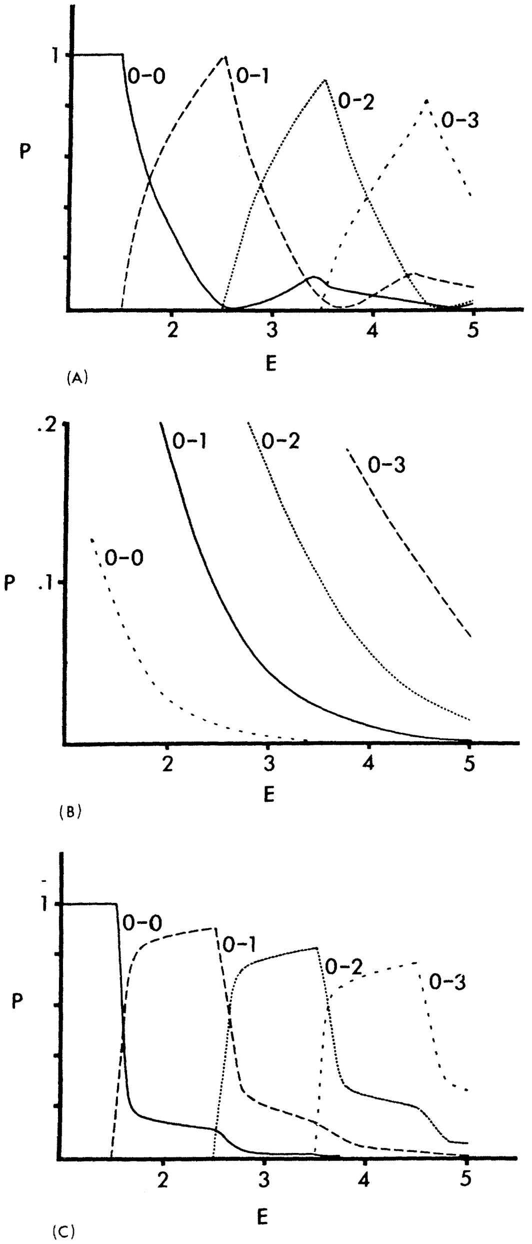

FIG. 2. (A) Exact 0-f transition probabilities for $m = 0.5$, Ref. 3. E is in units of $\frac{1}{2}h\nu$. (B) IA 0-f transition probabilities for $m = 0.5$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 0-f transition probabilities for $m = 0.5$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

An integral equation can now be developed for ψ_s in terms of the Green's function G_0 for the operator $(H_0 - E)$. There are at least two fruitful choices for $\mathcal{V}$ in the present problem. The first is $\mathcal{V}(x, y) = V(x, y)$, which will give rise to expansion of the Green's function in "plane-wave" reference states. The second is $\mathcal{V}(x, y) = V(x - y) - V(x)$, which will lead to a Green's-function expansion in terms of "distorted-wave" reference states.[6] Corresponding to these two partitions, there result two forms of the IA, the *plane-wave impulse approximation* (PWIA) and the *distorted-wave impulse approximation* (DWIA). The present paper reports the first

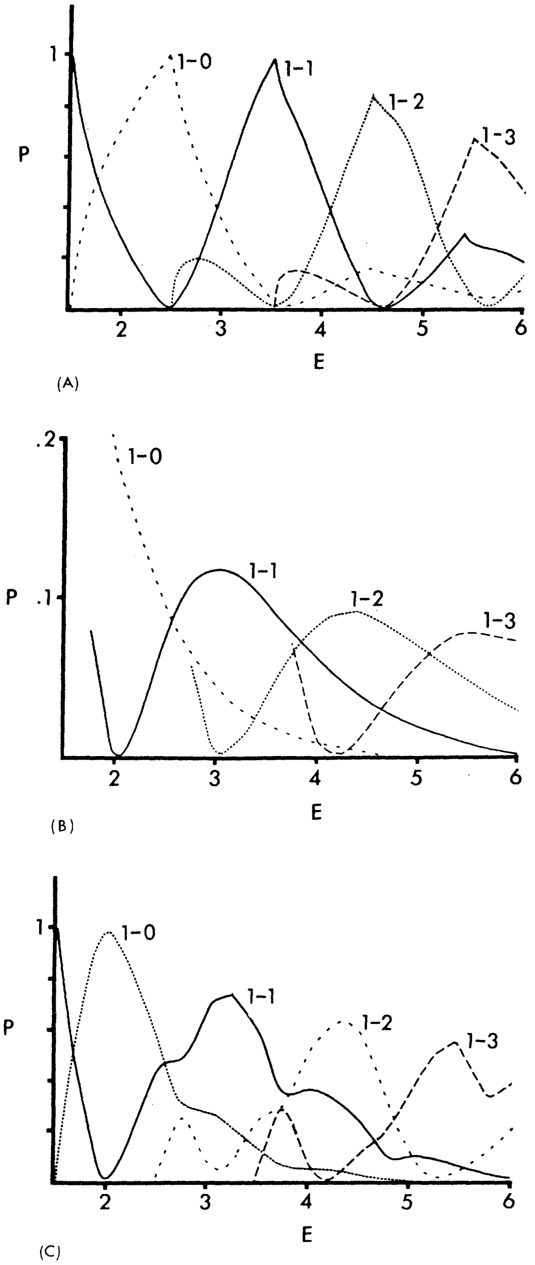

FIG. 3. (A) Exact 1-f transition probabilities for $m = 0.5$, Ref. 3. E is in units of $\frac{1}{2}h\nu$. (B) IA 1-f transition probabilities for $m = 0.5$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 1-f transition probabilities for $m = 0.5$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

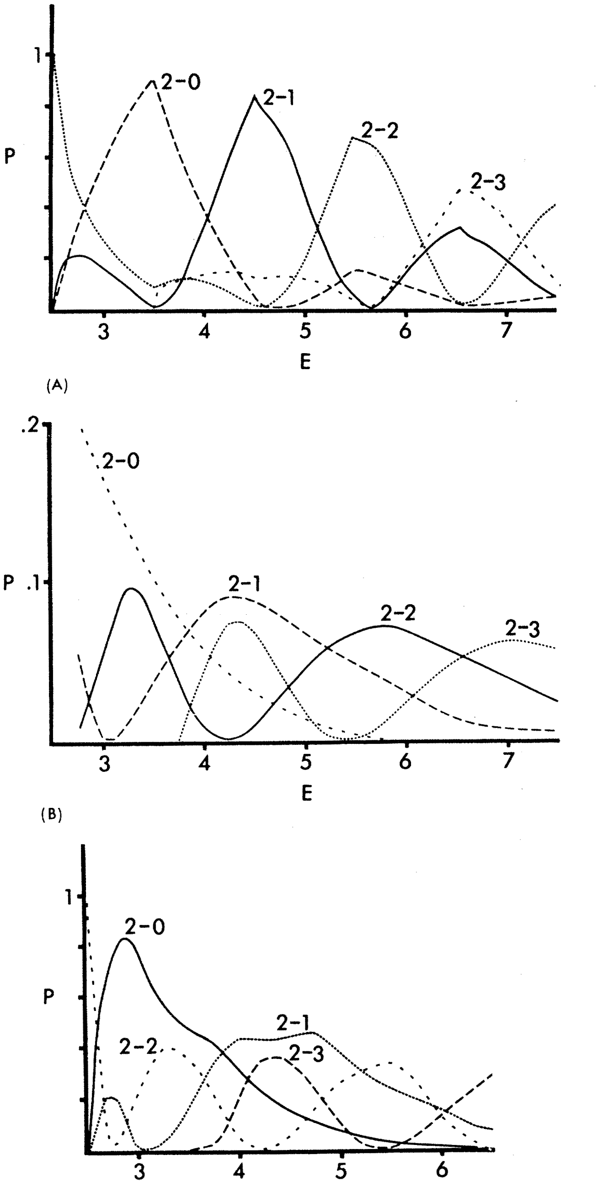

FIG. 4. (A) Exact 2-*f* transition probabilities for $m = 0.5$, Ref. 3. E is in units of $\frac{1}{2}h\nu$. (B) IA 2-*f* transition probabilities for $m = 0.5$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 2-*f* transition probabilities for $m = 0.5$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

application of the PWIA to atom-molecule translation-vibration energy transfer. Application of the DWIA is currently under investigation.

III. PLANE-WAVE IMPULSE APPROXIMATION

When one chooses $\mathcal{V}$ in Eq. (6) to be the interaction potential $V(x,y)$, the reference-state Schrödinger equation for the one-dimensional atom-oscillator problem becomes

$$H_0\Phi \equiv \left\{ -\frac{1}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 \right\} \Phi(x,y) = E\Phi(x,y). \tag{12}$$

The functions Φ are products of plane waves and harmonic-oscillator eigenfunctions. The solution to the scattering problem can be written

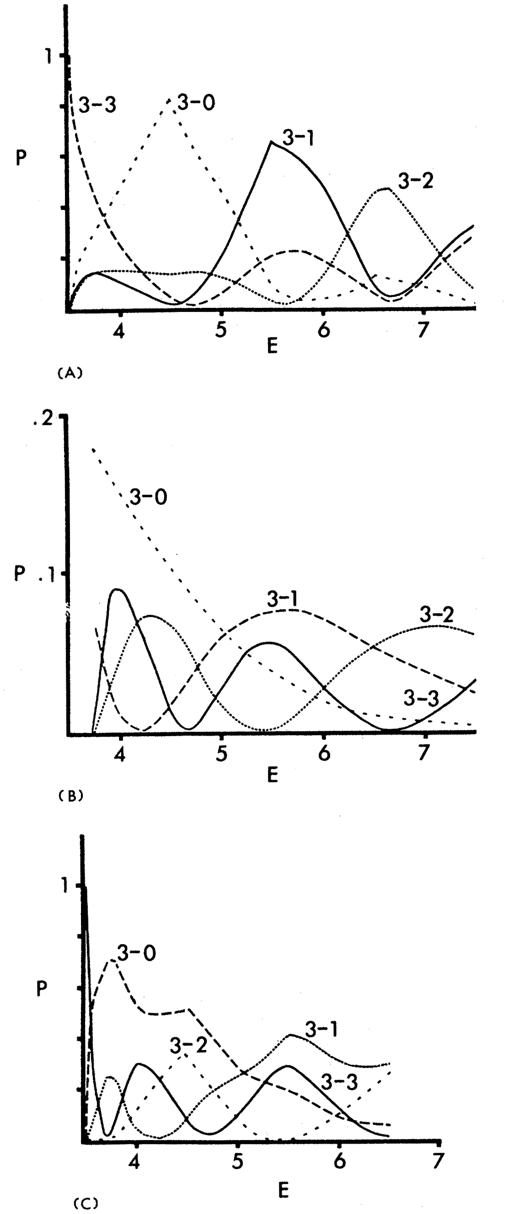

FIG. 5. (A) Exact 3-*f* transition probabilities for $m = 0.5$, Ref. 3. E is in units of $\frac{1}{2}h\nu$. (B) IA 3-*f* transition probabilities for $m = 0.5$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 3-*f* transition probabilities for $m = 0.5$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

$$\Psi(x, y) = (2\pi)^{-1/2} e^{-ik_i x} \varphi_i(y) + \psi_s(x, y), \tag{13}$$

where φ_i is a normalized harmonic-oscillator function corresponding to the state of the molecule before scattering and the x part is a travelling wave incident from the right with momentum

$$k_i \equiv + (2mE - i - \tfrac{1}{2})^{1/2}.$$

For $x \to \infty$, we impose the boundary condition

$$\lim_{x \to \infty} \Psi(x, y) = (2\pi)^{-1/2} e^{-ik_i x} \varphi_i(y) + (2\pi)^{-1/2} \textstyle\sum_f a_{if} e^{ik_f x} \varphi_f(y), \tag{14}$$

where a_{if} is the scattering amplitude for transition from state i to state f. We will consider the case where the interaction potential allows no transmission, so for $x \to -\infty$, our boundary condition is

$$\lim_{x \to -\infty} \Psi(x, y) = 0. \tag{15}$$

The probability that the oscillator has undergone a transition from state i to state f is given by

$$P_{if} = (k_f / k_i) |a_{if}|^2, \tag{16}$$

the ratio of outgoing flux arising from transitions to state f to the incident flux. Substituting expression (11) for Ψ into the Schrödinger equation (7) and making use of Eq. (10), we obtain

$$(H_0 - E)\psi_s = - V(x - y)\Psi(x, y). \tag{17}$$

Then, given that the Green's function for $(H_0 - E)$ satisfies

$$(H_0 - E) G_0(x, y; x', y') = \delta(x - x')\delta(y - y'), \tag{18}$$

we have the integral equation

$$\psi_s(x, y) = - \int dx' dy' G_0(x, y; x', y') V(x' - y') \Psi(x', y'). \tag{19}$$

The eigenfunction expansion for G_0 is[7]

$$G_0(x, y; x', y') = \frac{m}{i} \sum_{f=0}^{\infty} \frac{1}{k_f} \varphi_f(y) \varphi_f^*(y') e^{ik_f |x-x'|}. \tag{20}$$

Using this expression in Eq. (19) and taking the $x \to \infty$ limit, we identify [cf. Eq. (14)]

$$a_{if} = [(2\pi)^{1/2} m / ik_f] \int dx' dy' e^{-ik_f x'} \times \varphi_f^*(y') V(x' - y') \Psi(x', y'). \tag{21}$$

The IA to a_{if} is obtained by substituting $\Psi^{\mathrm{IA}}(x', y')$ into Eq. (21), giving

$$a_{if}^{\mathrm{IA}} = [(2\pi)^{-1/2} m / ik_f] \int dx' dy' dk' e^{-ik_f x'} \varphi_f^*(y') \times V(x' - y') g_i(k') \psi_{k_i, k'}^F(x', y'), \tag{22}$$

where $\psi_{k_i, k'}^F(x, y)$ satisfies

$$\left\{ -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V(x - y) \right\} \psi_{k_i, k'}^F(x, y) = \left\{ \frac{k_i^2}{2m} + \frac{k'^2}{2} \right\} \psi_{k_i, k'}^F(x, y). \tag{23}$$

The scattering amplitude expression can be simpli-

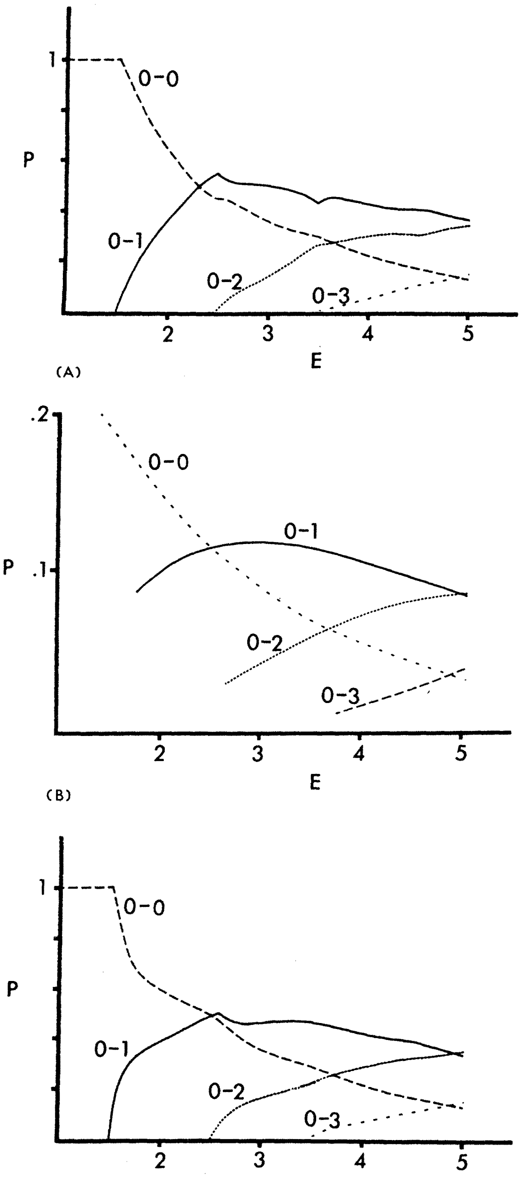

FIG. 6. (A) Exact 0-f transition probabilities for $m = 0.125$, Rev. 4. E is in units of $\frac{1}{2}h\nu$. (B) IA 0-f transition probabilities for $m = 0.125$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 0-f transition probabilities for $m = 0.125$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

fied by transforming the integration variables to center-of-mass and relative coordinates, since $\psi^F_{k_i,k'}(x,y)$ can be factored in these coordinates. The transformations are

$$\begin{pmatrix} R \\ r \end{pmatrix} = \begin{pmatrix} m/(m+1) & 1/(m+1) \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$\begin{pmatrix} k_R \\ k_r \end{pmatrix} = -\begin{pmatrix} 1 & 1 \\ 1/(m+1) & -m/(m+1) \end{pmatrix}\begin{pmatrix} -k_i \\ k' \end{pmatrix}, \tag{24}$$

where R is the center-of-mass coordinate, k_R the momentum of the center of mass, r the relative coordinate, and k_r the relative momentum. [The somewhat unconventional signs appearing in the second of Eqs. (24) is dictated by the fact that k_i is taken to be the positive number $(2mE-i-\frac{1}{2})^{1/2}$.] In these coordinates

$$\psi^F_{k_i,k'}(R,r)=(2\pi)^{-1/2}e^{-ik_RR}\chi_{k_r}(r), \tag{25}$$

where $\chi_{k_r}(r)$ satisfies the free relative Schrödinger equation

$$\left\{\frac{d^2}{dr^2}+k_r^2-\frac{2m}{m+1}V(r)\right\}\chi_{k_r}(r)=0. \tag{26}$$

Putting Eq. (25) for $\psi^F_{k_i,k'}$ into Eq. (22), replacing $\varphi_f^*(y')$ by its Fourier transform and using the δ function from the R integration to perform one momentum integration, one obtains finally the IA expression for the scattering amplitude

$$a_{if}^{\text{IA}}=(2\pi)^{1/2}m/ik_f\int_{-\infty}^{\infty}dk'g_i(k')g_f^*(k'-k_f-k_i)$$
$$\times\int_{-\infty}^{\infty}dr\exp\left[-i\left(k_f+\frac{m}{m+1}(k_i-k')\right)r\right]$$
$$\times V(r)\chi_{(k_i+mk')/(m+1)}(r). \tag{27}$$

Note that the second integral is proportional to the (non-energy-conserving) amplitude for scattering from relative momentum state $(k_i+mk')/(m+1)$ to a final relative momentum state $k_f+m\times(k_i-k')/(m+1)$ under the potential $V(r)$. Thus, for application of the IA, one needs to concentrate one's attention on the evaluation of the free relative scattering amplitude for arbitrary momenta. The free amplitudes are evaluated in Sec. V for the examples considered here.

IV. REGIONS OF VALIDITY FOR IMPULSE APPROXIMATION

Necessary conditions for the validity of the IA are elusive. It seems clear, however, that a sufficient condition for IA validity is the physically intuitive one given by Chew[1]: that the ratio of the collision time to the period of the internal motion of the bound particle be small. For typical atom-molecule systems where vibration-translation energy transfer occurs, this ratio is of order unity

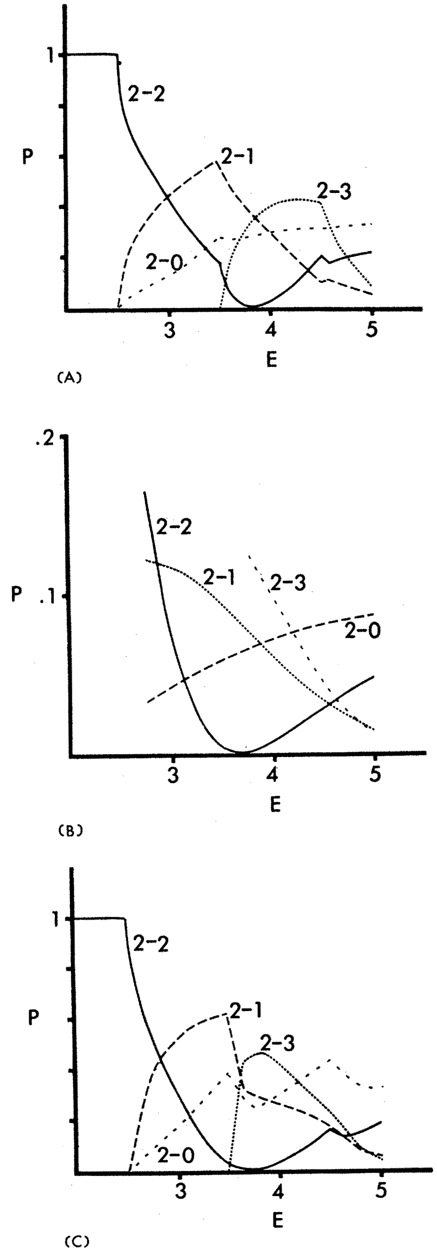

FIG. 7. (A) Exact 2-f transition probabilities for $m=0.125$, Ref. 4. E is in units of $\frac{1}{2}h\nu$. (B) IA 2-f transition probabilities for $m=0.125$. Graphs constructed from values computed every $\frac{1}{4}$ energy unit. (C) Renormalized IA 2-f transition probabilities for $m=0.125$. Graphs extrapolated to threshold from $\frac{1}{4}$ energy unit above.

for thermal energies. Thus, one would expect the use of the IA would have to be restricted to certain energy regions and then used in conjunction with other approximations to obtain a meaningful thermal average.

Expressing τ_c/τ_i in terms of the range r_0 of the potential, we have for our atom-oscillator system

$$\frac{\tau_c}{\tau_i} \sim \frac{r_0}{v_i}\,\frac{\omega}{2\pi} = \frac{r_0}{2\pi}\left(\frac{m}{2(E-i-\frac{1}{2})}\right)^{1/2} . \tag{28}$$

Thus, the IA would be expected to improve with (i) decreasing range, (ii) decreasing mass ratio, (iii) increasing energy, and (iv) decreasing initial quantum number. In particular the IA should be best suited for short-range interactions and low incident-particle mass.

There are at least two limits in which the IA becomes exact. When U, the binding potential, vanishes, Ψ^{IA} becomes the correct wave function for the scattering of two free particles under the interaction potential V. Similarly in the Born (no-scattering) limit, Ψ^{IA} becomes exact, so that the IA is always at least as good as the first Born approximation. However, it is most significant that validity of the IA, unlike the first Born, in no way requires that the scattering be small, so one may expect to apply the IA successfully in cases where the Born approximation breaks down because the transition probability is too large.

Although the first Born approximation is not appropriate for potentials which prohibit transmission, it is also true that the distorted-wave Born approximation (which is appropriate) breaks down when the inelastic scattering becomes important. Thus, the IA might be the best approximate method to employ for impulsive efficient molecular collisions as a complement to the distorted-wave Born method which is best for slow, near adiabatic, or inefficient collisions.

There are two shortcomings to the IA as formulated for this problem. First, in common with most approximate methods, the probability conservation condition

$$\textstyle\sum_f P_{if}(E) = 1, \quad \text{all } E \tag{29}$$

is not observed. Second, the IA expression [Eq. (27)] for the scattering amplitude becomes infinite at threshold. The lack of probability conservation is due to the fact that the IA corresponds to an approximate scattering or $\underline{S}$ matrix which is not unitary. Additional steps would be required to ensure a unitary $\underline{S}$ matrix. This would be a simple matter if there were an obvious IA to the Hermitian reactance, or $\underline{K}$, matrix (as indeed there is for the distorted-wave Born approximation).[8] One would merely compute a unitary $\underline{S}$ from the defining relation

$$\underline{S} = (\underline{1} - \tfrac{1}{2} i\underline{K})/(\underline{1} + \tfrac{1}{2} i\underline{K}) , \tag{30}$$

which involves only energy-conserving states. Unfortunately, there seems to be no obvious first approximation to $\underline{K}$ corresponding to the IA.

In the best of the calculations reported below it is found that although Eq. (29) is not satisfied, the individual probabilities are in the correct ratio so that a simple probability renormalization brings the results into quantitative agreement with the exact probabilities.

The threshold singularity seems to be an artifact of the one dimensionality of the problem. One easily sees, from Eqs. (16) and (27) that

$$\begin{aligned} &\lim_{k_f \to 0^+} P_{if}^{\mathrm{IA}} \sim 1/k_f , \\ &\lim_{k_i \to 0^+} P_{if}^{\mathrm{IA}} \sim 1/k_i , \end{aligned} \tag{31}$$

the first resulting in a singularity at threshold for upward transitions and the second for downward. This difficulty was circumvented in our calculations by the practical expedient of avoiding the evaluation of probabilities very near threshold. Generally, it was possible to approach to within about $\frac{1}{4}\hbar\omega$ of threshold without encountering strongly singular behavior.

V. FREE SCATTERING PROBLEM FOR EXPONENTIAL POTENTIAL

As noted in Sec. III, the use of the IA demands that one have an expression for the free relative scattering amplitude for arbitrary initial and final momenta.

In the present paper we consider only the exponential interaction potential, $V(r) = Ae^{-\alpha r}$. This has been widely used to represent the atom-mole-

TABLE IV. Sum of IA transition probabilities for $m = 0.5$.

E	$\sum_f P_{0f}$	$\sum_f P_{1f}$	$\sum_f P_{2f}$	$\sum_f P_{3f}$
1.0	0.21	...	...	...
1.25	0.13	...	...	...
1.50	0.08	...	...	...
1.75	0.29	...	...	...
2.0	0.21	0.17	...	...
2.25	0.15	0.16	...	...
2.5	0.10	0.17	...	...
2.75	0.28	0.22	...	...
3.0	0.21	0.16	0.22	...
3.25	0.16	0.15	0.24	...
3.5	0.12	0.15	0.22	...
3.75	0.27	0.22	0.17	0.25
4.0	0.22	0.16	0.19	0.30
4.25	0.15	0.14	0.21	0.27
4.5	0.14	0.13	0.19	0.21
4.75	0.27	0.23	0.17	0.21
5.0	0.27	0.17	0.16	0.25

cule interaction and in the limit $\alpha \to \infty$ encompasses the infinite repulsive barrier, where the IA should be most likely to give good results.

We seek first the solution to

$$\left\{ \frac{d^2}{dr^2} + k^2 - 2\mu A e^{-\alpha r} \right\} \chi_k(r) = 0 , \tag{32}$$

where $\mu \equiv m/(m+1)$. The solution has been given by Jackson and Mott,[9]

$$\chi_k(r) = 2e^{-i\eta} (2\pi)^{-1/2} [(q \sinh \pi q)/\pi]^{1/2} K_{iq}(y), \tag{33}$$

where

$$\begin{aligned} y &\equiv [2(2\mu A)^{1/2}/\alpha] e^{-\alpha r/2}, \\ q &\equiv 2k/\alpha, \\ \eta &\equiv (2k/\alpha) \ln[\alpha(2\mu A)^{-1/2}] - \arg\Gamma(2ik/\alpha), \end{aligned} \tag{34}$$

and $K_{iq}(y)$ is a modified Bessel function of the second kind. This solution satisfies the boundary conditions

$$\begin{aligned} &\lim_{r \to \infty} \chi_k(r) = 2e^{-i\eta} (2\pi)^{-1/2} \cos(kr + \eta) , \\ &\lim_{r \to \infty} \chi_k(r) = 0. \end{aligned} \tag{35}$$

The free amplitude can now be evaluated giving

$$\begin{aligned} a^F_{k,k'} &\equiv \int_{-\infty}^{\infty} dr\, e^{-ik'r} A e^{-\alpha r} \chi_k(r) \\ &= \frac{\alpha}{2\sqrt{2}\,\pi\mu} \left(\frac{\alpha^2}{2\mu A}\right)^{i(k'-k)/\alpha} e^{i \arg\Gamma(iq)} (q \sinh \pi q)^{1/2} \\ &\quad \times \Gamma\left(1 + i\frac{k'+k}{\alpha}\right) \Gamma\left(1 + i\frac{k'-k}{\alpha}\right) , \end{aligned} \tag{36}$$

by use of the integral[10]

$$\int_0^{\infty} dt\, t^{\rho} K_{\nu}(t) = 2^{\rho - 1} \Gamma\left(\frac{\rho + \nu + 1}{2}\right) \Gamma\left(\frac{\rho - \nu + 1}{2}\right) . \tag{37}$$

The limit for $\alpha \to \infty$ gives the infinite-barrier free amplitude

$$a^F_{k,k'} = ik/(2\pi)^{1/2} \mu . \tag{38}$$

The same result is obtained by evaluating the free amplitude for a finite step potential and then letting the step height go to infinity.

The IA expression for the scattering amplitude can now be expressed as

$$\begin{aligned} a^{\mathrm{IA}}_{if} &= [(2\pi)^{1/2} m/ik_f] \int_{-\infty}^{\infty} dk' g_i(k') g_f^*(k' - k_f - k_i) \\ &\quad \times a^f_{(k_i + mk')/(m+1),\, k_f + [m/(m+1)](k_i - k')}, \end{aligned} \tag{39}$$

with the expressions Eq. (36) or (38) substituted in for the exponential or hard-sphere interactions, respectively.

VI. RESULTS FOR EXPONENTIAL POTENTIAL

IA transition probabilities for the exponential potential were computed at a number of values of α, m, and E. Comparison with the exact results of Secrest and Johnson[4] showed that the IA is unsuitable at the values of α, m, and E considered. The results for $\alpha = 0.3$, $m = \frac{2}{3}$ are given in Table I as typical. IA transition probabilities for the (α, m) parameter sets $(0.114, \frac{1}{2})$, $(0.1287, \frac{5}{11})$ and $(0.1287, \frac{13}{37})$ are in similarly poor agreement with the exact probabilities. This is in accord with our expectation that the IA would be marginal in typical soft thermal atom-molecule collisions. However, as the results of Sec. VII show, as the collisions become more impulsive, that margin can be crossed.

VII. RESULTS FOR INFINITE-BARRIER POTENTIAL

For the "hard-sphere" interaction, using Eq. (38) in Eq. (39), one has in the IA

$$a^{\mathrm{IA}}_{if} = (1/k_f) \int_{-\infty}^{\infty} dk' (k_i + mk') g_i(k') g_f(k' - k_f - k_i). \tag{40}$$

Thus, the IA hard-sphere scattering amplitude can be expressed simply in terms of oscillator function convolutions. IA transition probabilities for m values of 5.0, 0.5, and 0.125 were computed using Eq. (40) and compared to the exact results of Shuler and Zwanzig,[3] and Secrest and Johnson.[4]

A comparison of the Secrest-Johnson hard-sphere transition probabilities with those of the IA for $m = 5.0$ is given in Tables II and III. The IA probabilities are poor for this case, disagreeing with the exact results by orders of magnitude at most points.

The IA results for $m = 0.5$ shown in Figs. 2–5 are considerably better, as would be expected for the

TABLE V. Sum of IA transition probabilities for $m = 0.125$.

E	$\sum_f P_{0f}$	$\sum_f P_{1f}$	$\sum_f P_{2f}$	$\sum_f P_{3f}$
1.0	0.24	···	···	···
1.25	0.22	···	···	···
1.5	0.19	···	···	···
1.75	0.18	0.30	···	···
2.0	0.24	0.24	···	···
2.25	0.24	0.19	···	···
2.5	0.24	0.16	···	···
2.75	0.22	0.14	0.32	···
3.0	0.25	0.24	0.22	···
3.25	0.25	0.22	0.18	···
3.5	0.24	0.21	0.16	···
3.75	0.29	0.25	0.27	0.32
4.0	0.25	0.24	0.24	0.22
4.25	0.25	0.24	0.21	0.18
4.5	0.25	0.24	0.19	0.16
4.75	0.25	0.25	0.27	0.29
5.0	0.22	0.25	0.24	0.22

smaller m. Although the IA transition probabilities are too low throughout, the qualitative behavior with changing E is good, in an average sense. The presence of the threshold singularity is plainly evident, especially in the steep upward slopes of the P_{0f} curves and the upward turns of the P_{1f} probabilities as their respective thresholds are approached from above. Note that the IA transition probabilities observe microscopic reversibility, even though this is not in general guaranteed by the approximation.

The IA is expected to be better for $m = 0.125$ than for the other two values, based on the considerations of Sec. IV. This expectation is amply borne out by the results presented in Figs. 6 and 7. Again, the probabilities are usually on the small side, at least away from threshold, but they are closer to the exact results. Also, the threshold singularities make their presence felt but not nearly so strongly as for $m = 0.5$. Over-all, the qualitative behavior of the IA transition probabilities relative to one another is very good for $m = 0.5$ and $m = 0.125$. For the lower value of m, this good behavior extends closer to threshold.

In order to assess the lack of probability conservation in the calculations, the sums of probabilities $\sum_f P_{if}$ for the various initial states i were computed as functions of energy. These are presented in Tables IV and V for values of $m = 0.5$ and 0.125, respectively. Note that the probability curves are best where this sum is more stable. Thus, there is a definite correlation between the stability of the sum $\sum_f P_{if}$ with changing energy and the over-all qualitative goodness of the $i-f$ transition probabilities themselves. This suggests that in future calculations this sum might serve as an *a priori* indication of the quality of the IA transition probabilities from a given level.

Although the IA probabilities do not sum to unity, if they are in the correct ratio to one another, as appears often to be the case, a simple renormalization should give results approaching quantitative agreement with the exact probabilities. The IA probabilities were renormalized so that

$$P_{if}^R = P_{if}/\textstyle\sum_{f'} P_{if'} . \qquad (41)$$

Renormalized transition probabilities for $m = 0.5$ and $m = 0.125$ are plotted in Figs. 2(C)–5(C) and 6(C)–7(C), respectively.

It should be noted that unless $\sum_f P_{if}(E) = \sum_f P_{i'f}(E)$ for all E, microscopic reversibility will be destroyed by renormalization. These conditions are much more nearly satisfied for the $m = 0.125$ probabilities than for $m = 0.5$ as Tables IV and V show. The renormalized results are best in the 0-f transitions for both mass ratios. In the $m = 0.125$ case the results are quantitatively excellent.

In summary, it appears that wherever $\sum_f P_{if}$ is relatively constant with energy and i, one may expect renormalization of the transition probabilities to convert qualitatively good results to quantitatively good ones, while minimizing any effects of threshold misbehavior.

VIII. CONCLUSION

The calculations reported here represent the first successful attempt at an approximate treatment of impulsive collinear atom-diatom collisions. Qualitative and order-of-magnitude agreement with exact results as to correct energy dependence of inelastic transition probabilities has been obtained for mass ratio values of 0.5 and 0.125, with the lower m yielding the better results. This is true for all transitions among the oscillator states of quantum number 0, 1, 2, and 3. Unlike the familiar perturbative methods, the quality of the approximation does not decrease for multiple-quantum transitions and improves as the energy increases.

It should be noted that the customary low-order perturbative methods could not reasonably be expected to give good results over such a range of energy and initial and final states as that over which the IA was examined here, even for the softer exponential-type collisions for which they are best. On the other hand, the IA is not good for those soft collisions, and the two methods serve to complement one another.

Although the typical incident energies and vibrational periods occurring in atom-vibrating-molecule collisions suggest that the IA must be used with caution, the results reported here show that reasonably good results can be expected for sufficiently small mass ratios in hard collisions. Inherently poor threshold behavior of the IA one-dimensional transition probabilities requires that points very near threshold be avoided. In the present results, probabilities were computed to within $\frac{1}{4}\hbar\omega$ of threshold and then extrapolated to zero.

The approximation used here does not conserve probability. It was found that the sums of probabilities $\sum_f P_{if}$ for various initial states i computed as a function of energy provided a good measure of confidence for the approximation. For a given i, if the probability sum was very nearly constant, the P_{if} curves were qualitatively good, and conversely. When the curves for a given initial state were qualitatively good, a simple renormalization yielded quantitative agreement and minimized the effects of threshold misbehavior. The very good qualitative results obtained before renormalization lead to the conclusion that an early effort to formulate an impulse (or impulselike) approximation which conserves $\underset{\sim}{S}$-matrix unitarity would be well worthwhile.

Finally, the IA may serve as a useful adjunct to exact calculations which use the method of Shuler and Zwanzig for impulsive interactions. It has been noted by several workers[4,11,12] that the Shuler-Zwanzig method encounters severe truncation errors at high energies.[13] Fortunately, for sufficiently small mass ratios, the IA could be used with relatively high confidence in this energy region.

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