Two-dimensional model of rotationally inelastic collisions

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An analysis of rotationally inelastic collisions is made in a two-dimensional model. It is assumed that the target is a hard-core ellipsoid, and the properties of the deflection functions and the forbidden transitions are investigated. The existence of the rainbow is predicted and the estimate of the rainbow angle is given. The rules for the forbidden transitions, arising from the geometry of the target, are also discussed.

I. INTRODUCTION

There has been a great interest in the calculation of rotationally inelastic cross sections of atom-diatom systems. It is usually assumed that the potential for such systems is given as a sum

$$V(R,\theta)=V_0(R)+V_2(R)P_2(\cos\theta)+\cdots\ , \qquad (1.1)$$

where R is the magnitude of the vector $\vec{R}$ between the atom and the center of mass of diatom molecule. θ is the angle between R and the internuclear vector of the diatom molecule. Since our main interest will be with homonuclear molecules, the odd terms in (1.1) were omitted.

The convergence rate of the series (1.1) is system dependent, e.g., only two terms are needed (i.e., V_0 and V_2) for Ne-N_2 (Ref. 1), He-H_2 (Ref. 2), while for the ion-molecule system such as Li^+-H_2 (Ref. 3) many more must be included. However, such an expansion is not very suitable for the analysis of differential cross sections in terms of the topological structure of the potential surface. Let us examine the reason for this more closely.

For the potential $V(R,\theta)$ the equipotential lines can be calculated, and defined by

$$V(R,\theta)=V_{eq}\ , \qquad (1.2)$$

where V_{eq} is a given value of the potential and θ ranges over $(0,2\pi)$. Equation (1.2) defines the functional relationship

$$R=f(\theta;V_{eq})\,. \qquad (1.3)$$

If we plot the vector $(R\cos\theta,\ R\sin\theta)$ we get a contour, i.e., the equipotential line. By varying V_{eq} a set of equipotential lines is obtained which define the potential surface. There is one characteristic line, defined by

$$V(R,\theta)=E\ , \qquad (1.4)$$

where E is the total c.m. energy. For this line we define two axes:

$$R_{min}=R(\theta=\tfrac{1}{2}\pi) \qquad (1.5)$$

and

$$R_{max}=R(\theta=0)=R(\theta=\pi)\,. \qquad (1.6)$$

If the potential $V(R,\theta)$ does not have a deep well, or if E ismuch larger then the depth of the well, the potential surface can be represented in elliptical coordinates.[4] In the first approximation we can assume that R_{min} and R_{max} define an ellipse with the major axis $A=R_{max}$ and the minor axis $B=R_{min}$. Deviation from the elliptical shape can be treated as a perturbation and an expansion analogous to (1.1) can be formed for the potential surface. Therefore, in such a model R_{min} and R_{max} define the topology of our problem. As will be shown, they determine the essential features of the differential cross section. By assuming expansion (1.1) such an analysis is difficult since both R_{min} and R_{max} are not explicitly given. The difficulty with (1.1) is even more evident if one tries a trial-and-error fitting of the potential to a given differential cross section. However, if our initial guess is an ellipse instead of $V_0(R)$ in (1.1), we already incorporate the most essential features of the differential cross section using only two parameters, namely, A and B.

In our treatment we will assume a model that replaces the true potential surface by a hard-core potential in elliptical coordinates, i.e., the potential surface beyond the line defined by (1.4) is set to zero and it is infinite elsewhere. In other words, the diatomic is treated as a hard-core ellipsoid. Such a model was treated in three dimensions by Beck *et al.*[5] to obtain time-of-flight spectra. In our case we will further simplify the model by assuming that the collision is in a plane and that the out-of-plane scattering does not significantly alter the physics of our problem.

There are several justifications for such a model: (a) It simplifies the mathematics of the problem, in the sense that the problem can be solved almost exactly, and (b) it has been noted,[6] in the phase-space analysis, that for large inelastic transitions most of the scattering occurs in a plane. The physical reason for the latter is obvious: If the initial momentum of the incoming atom is out of the plane defined by the "equator" of the ellipse, there will be a great chance that the atom will either miss the molecule or will only graze the molecule, not causing a large rotational transition.

By replacing the true potential surface by an ellipsoid, we have neglected some features of the cross section. However, by inspecting such a model we will be able to reproduce qualitative characteristics of the collision. We can draw a parallel to the elastic collision case. At high-collision energies the differential cross section for large angles is smooth,[7] almost constant, and resembles to a high degree of accuracy the cross section for two hard-core spheres. In the forward direction the diffraction oscillations are present, the spacing between them being almost that for hard spheres. The rainbow, which arises due to the attractive part of potential, is missing for hard spheres. In other words, we reproduce certain features of the atom-atom cross section by a hard-sphere model, but not all. The same will be true for the hard-core ellipsoid. All the features that arise from the attractive part of the potential will not be present, however, we will be able to observe the essential dynamical properties.

In the two-dimensional model we obtain several results: (a) We obtain the existance of the rainbow, even in the hard-core ellipsoid model; (b) for large inelastic transitions the differential cross section is zero in the forward direction; (c) broad oscillations occur for large-angle scattering; and (d) we find the existence of closed channels, which are primarily due to the topological properties of the target, in addition to the closed channels due to the energy conservation. As will be shown, these effects are entirely determined by two parameters: the difference A-B and the ratio of the reduced mass of the system to the momentum of inertia of the ellipsoid.

In our analysis we will use classical mechanics, but make occasional reference to quantum dynamics, especially in connection with the quantization of the rotational degree of freedom.

II. THEORY

The two-dimensional problem of the rotationally inelastic collision of a particle with an ellipsoid can be solved using the three principles of conservation: total energy, momentum, and angular-momentum conservation. Before the collision it is assumed that the ellipsoid is nonrotating, to simplify discussion, having the c.m. linear momentum p_0. A particle, e.g., an atom, has the same momentum, but in the opposite direction.

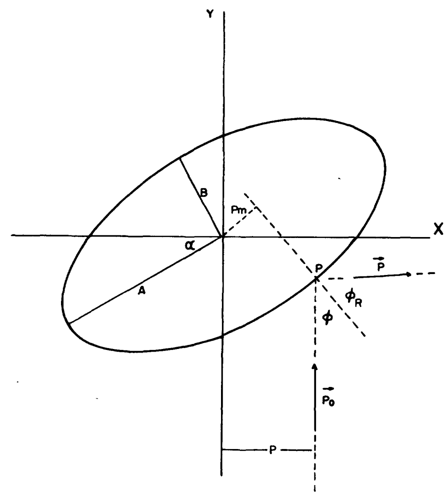

FIG. 1. Definition of the variables in the two-dimensional particle-ellipsoid collision. The ellipsoid is defined with the major axis A and small axis B, and is not rotating before the collision.

The initial state is uniquely defined if we specify two additional parameters: the impact parameter b of the incoming particle and the orientation α of the major axis of the ellipsoid with respect to the line perpendicular to p_0. In Fig. 1. these parameters are shown, where the major axis of the ellipsoid is A and the minor is B.

At the point of impact, in Fig. 1 it is P, the parallel component of p_0 to the surface of ellipsoid which does not change its value. Only the normal component of p_0 to the surface causes the transfer of momentum and energy. Therefore, we have after the collision:

$$p'' = p_0''; \; (p_0^\perp)^2/2\mu = (p^\perp)^2/2\mu + j^2/2I, \qquad (2.1)$$

where μ is the reduced mass of the system and I is the moment of inertia of the ellipsoid.

To determine the rotational angular momentum j of the ellipsoid in the final state we use total angular-momentum conservation. At the moment just before the collision, the total angular momentum for the normal component of p_0 is $b_n p_0^\perp$, where b_n is the "effective impact parameter," i.e., the parameter which in fact is responsible for the transition. It is defined as the shortest distance between the line defined by p_0 and the center of mass of the ellipsoid (see Fig. 1).

After the collision, the total angular momentum is conserved. Therefore we have, in addition to (2.1)

$$b_n p_0^\perp = -b_n p^\perp + j, \qquad (2.2)$$

where the minus sign in front of p means that the particle is flying away from the ellipsoid.

It is now straightforward to obtain j and the recoil angle ϕ_r. It can be shown, from the geometry, that the angle ϕ in Fig. 1 is given by

$$\tan\phi = \frac{-B^2(b\cos\alpha + y_b\sin\alpha)\cos\alpha + A^2(y_b\cos\alpha - b\sin\alpha)\sin\alpha}{B^2(b\cos\alpha + y_b\sin\alpha)\sin\alpha + A^2(y_b\cos\alpha - b\sin\alpha)\cos\alpha}, \quad (2.3)$$

where the y coordinate of P is

$$y_b = \frac{b(A^2 - B^2)\sin\alpha\cos\alpha - AB(B^2\sin^2\alpha + A^2\cos^2\alpha - b^2)^{1/2}}{B^2\sin^2\alpha + A^2\cos^2\alpha}. \quad (2.4)$$

Furthermore, the effective impact parameter is obtained from simple geometrical considerations and is given by

$$b_n = b\cos\phi + y_b\sin\phi. \quad (2.5)$$

So far only the geometric properties of the system were considered. The dynamic properties of the system must be included when calculating the angle ϕ_r since it measures the reflection angle from the surface of ellipsoid. The angle ϕ_r is obtained from (2.2):

$$\tan\phi_r = b_n\sin\phi/(j/p_0 - b_n\cos\phi). \quad (2.6)$$

The final rotational angular momentum j is then given from (2.1)

$$j/p_0 = 2b_n\cos\phi/(1 + b_n^2\mu/I). \quad (2.7)$$

The set of equations (2.3)–(2.7) define the geometry and the dynamical properties of the system. The initial conditions are the impact parameter b and the orientation angle α, and the quantities that we obtain are ϕ_r and j/p_0. However, in the experiment ϕ_r cannot be measured, only the deflection (scattering) angle θ (see Fig. 1), which is related to ϕ and ϕ_r by

$$\theta = \pi - (\phi + \phi_r). \quad (2.8)$$

Therefore, from the previous equations the functional relationships $j = j(b, \alpha)$ and $\theta = \theta(b, \alpha)$.

III. ANALYSIS OF THE DEFLECTION FUNCTION

In our analysis let us first consider the deflection function, defined in an analogy to the elastic collision case. For a given transition $\Delta j = j/p_0$ (from now on we will use the symbol Δj replacing j/p_0), we look at the properties of the scattering angle as a function of the impact parameter b. For a fixed transition Δj, Eq. (2.7) is solved for α and with these roots, for a given b, to obtain the appropriate deflection angle θ. Such an analysis gives information about the characteristic features of the differential cross section, especially concerning the singularities and classically inaccessible regions.

It turns out that Eq. (2.7) has two roots, therefore there are two trajectories for a given b which produce a given transition Δj. In other words, there are two impact parameters which for a given Δj deflect the trajectory into the same angle θ. In Fig. 2 we show these two possibilities calculated for a fictitious system: $A=2$, $B=1$, $\mu/I=1$. The scattering angle in both cases is $\theta=140°$ and the transition $\Delta j=0.8$.

For the same system we have calculated the deflection functions for three different transitions: (a) elastic, (b) $\Delta j=0.4$, (c) $\Delta j=0.8$, and they are shown in Fig. 3. As it was already noted, since there are two trajectories leading to the same final state, we have two deflection functions. In Fig. 3 one is shown by a solid line and the other is represented by a broken line.

It should be recognized that in two dimensions the scattering angle is defined for 360°. By definition, in the forward direction there is no deflection, i.e., $\theta=0°$, so that in fact θ is defined in the interval $-180° \leq \theta \leq 180°$. The deflection function, as shown in Fig. 3 is not symmetric

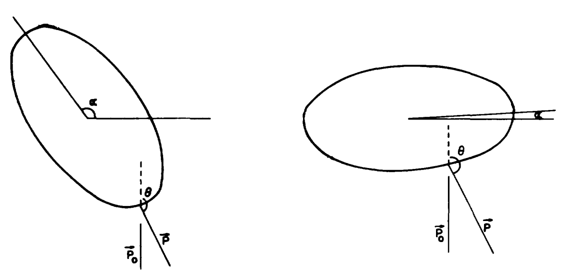

FIG. 2. Two orientations of ellipsoid which deflect the incoming particle in a given angle θ. In our case $\theta=140°$ and $\Delta j=0.8$.

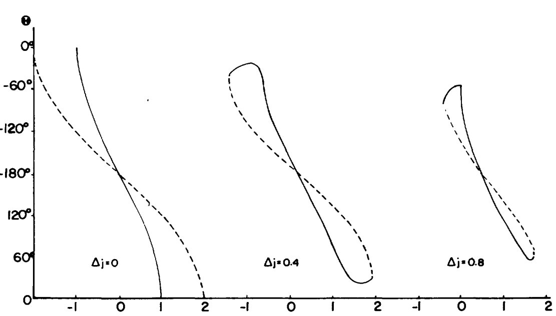

FIG. 3. Deflection functions for three different Δj transitions. The parameters for ellipsoid are $A=2$, $B=1$, $\mu/I=1$.

with respect to $\theta = 180°$ except for the elastic transition. It is also evident from the same figure that the zero impact parameter does not necessarily produce deflection of 180°, but that for $\Delta j > 0$ this is the case for $b > 0$.

The interesting result, however, is that in the forward direction there is an interval of angles that is not accessible to a classical trajectory. In other words, the differential cross section for $\Delta j > 0$ is zero in the forward direction and remains zero till reaching an angle which is accessible to a classical trajectory. For example, we read from Fig. 3 that for $\Delta j = 0.4$ the differential cross section is zero between $0° \leq \theta \leq 20°$. This is not an artifact of our two-dimensional model, since quantum-mechanical calculations exist where such behavior of the cross section is found for three-dimensional realistic potentials.[8,9] For large Δj the differential cross section goes rapidly to zero in the forward direction.

In addition to the above-mentioned feature of the deflection function, we also find that one of them (in Fig. 3 solid line) has a minimum, similar to the rainbow minimum in an elastic collision with a potential that has an attractive well. In our case, however, such a minimum is not a consequence of the attraction, since it is assumed that the potential in our case is either zero or infinite. We can understand why the rainbow minimum occurs by giving simple arguments. More exact treatments would require looking for the minima of Eq. (2.8); however, this is not analytically possible.

Let us simplify the discussion by assuming $\mu/I \ll 1$. The deflection function is not very sensitive to large variations of this quantity and for our discussion it is reasonable to assume such a limiting case.

For $\mu/I \ll 1$ we obtain by combining (2.7) and (2.6)

$$\tan\phi_r = \frac{1 + (\mu/I)b_n^2}{1 - (\mu/I)b_n^2} \tan\phi \sim \tan\phi \,, \tag{3.1}$$

and (2.7) becomes

$$\Delta j = 2b_n \cos\phi \,. \tag{3.2}$$

By taking into account (2.8) we get

$$\Delta j = 2b_n \sin\tfrac{1}{2}\theta \,, \tag{3.3}$$

where Δj has a fixed value. It should be noted that b_n is a bounded function of b. In the simplest case for $\alpha = 0$ we have

$$b_n = b\,\frac{A^2 - B^2}{A}\left(\frac{A^2 - b^2}{A^4 - b^2(A^2 - B^2)}\right)^{1/2} . \tag{3.4}$$

For $b = 0$ and $b = A$, the effective parameter b_n is zero. It reaches its maximum for $b = A[A/(A+B)]^{1/2}$, in which case

$$b_n = A - B \,. \tag{3.5}$$

Therefore, by increasing b from $b = 0$ the parameter b_n also increases. The deflection angle is a decreasing function of b_n, which is deduced from (3.3) since Δj is constant. However, when b_n reaches its maximum value $b_n = A - B$ Eq. (3.3) does not permit further decrease of θ. The deflection angle reaches its minimum value

$$\sin\tfrac{1}{2}\theta_R = \Delta j / 2(A - B) \tag{3.6}$$

and for even larger b, the b_n is decreasing. The deflection function then increases, thus forming the rainbow minimum. In our discussion we did not take into account variations of α with b. Therefore the position of the rainbow angle, given by (3.6), is only approximate. However, comparing (3.6) with the values from Fig. 3, we obtain good agreement, e.g., the exact rainbow angle for $\Delta j = 0.4$ is $\theta_R \sim 20°$ but from (3.6) we obtain $\theta_R \sim 23°$. Likewise for $\Delta j = 0.8$ the exact $\theta_R = 54°$, but the approximate is $\theta_R = 47°$.

Since we have established the existence of the rainbow, we can describe in a qualitative way the shape of the differential cross section. In the forward direction the cross section is zero, but for θ_R, approximately given by (3.6), it rises to the rainbow peak. Beyond that there will be broad oscillations of the cross section, since there are two trajectories resulting in the same scattering angle θ.

Another interesting case to analyze is an almost spherically symmetric ellipse, i.e., when $A \sim B$. We have taken an example with $A = 2.2$ and $B = 2$, for which the corresponding deflection functions are shown in Fig. 4.

The general pattern is the same as for the previous case, except for a few differences: (a) The deflection functions are almost symmetric with respect to 180°; (b) there are fewer accessible rotational states (e.g., the $j = 0.8$ transition is forbidden); and (c) the rainbow angle θ_R, for the same transition, is larger. The agreement be-

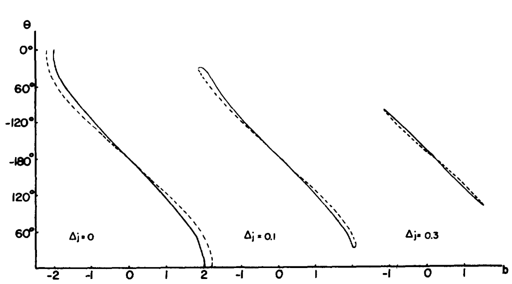

FIG. 4. Deflection functions for the parameters: $A = 2.2$, $B = 2$, $\mu/I = 1$.

tween the exact θ_R and (3.6) is better than in the previous case.

For small impact parameters and for an almost spherically symmetric ellipse we can calculate the deflection function exactly. If we put $A = B + \epsilon$, where ϵ is small, we get for (2.4)

$$y_b \sim -A + \epsilon \cos^2\alpha \tag{3.7}$$

and

$$\tan\phi \sim \mu A^{-1}[b + \epsilon \sin\alpha \cos\alpha(2 + \cos^3\alpha - \cos^2\alpha)], \tag{3.8}$$

where we have neglected the second-order terms in b and ϵ. From (3.7) and (3.8) we obtain b_n:

$$b_n \sim -\epsilon \sin\alpha \cos\alpha(2 + \cos^3\alpha - \cos^2\alpha) \tag{3.9}$$

and it follows from (3.1) that $\phi_R \sim \phi$. Equation (2.7) gives for α

$$\sin 2\alpha \sim -\Delta j/2\epsilon, \tag{3.10}$$

which has two solutions in the interval $-\frac{1}{2}\pi \leq \alpha \leq \frac{1}{2}\pi$. However, in our approximation both solutions give the same deflection function

$$\theta \sim -2A^{-1}(b - \Delta j/2) + \pi \tag{3.11}$$

this being the average of the exact. The result (3.11) is in good agreement with the exact calculation in Fig. 4.

Equation (3.10) does not have solution if Δj is so large that the right-hand side of the equation is greater than one, i.e.,

$$|\Delta j|/2\epsilon > 1. \tag{3.12}$$

Therefore, this estimate gives also μ the maximum classically allowed transition. In the case of $\epsilon = 0.2$, treated in Fig. 4, this is $\Delta j = 0.4$.

IV. FORBIDDEN TRANSITIONS

Several laws of conservation operate in inelastic collisions, thus preventing access to all possible states. For example, all states that do not conserve energy are ruled out as unphysical asymptotic states and cannot be included as possible observable final states of scattering. It can easily be shown that for rotationally inelastic collisions, if the target is initially nontrotating, the maximum allowed final state is given by

$$\Delta j_{\max} = (I/\mu)^{1/2}. \tag{4.1}$$

In addition to the forbidden transition governed by the laws of conservation, we also have forbidden transitions which are inaccessible owing to the geometry or topology of the target. Such transitions are discussed briefly in this section.

In Fig. 5 we plot Δj versus the angle α for a given scattering angle θ. Therefore, we observe all possible transitions that are allowed in a specified direction θ. For example, for $\theta = 10°$ all the transitions $\Delta j < 0.18$ are allowed. Likewise, for $\theta = 50°$ all Δj below $\Delta j = 0.77$ are allowed. Beyond $\theta = 100°$ there is no further increase in transitions but this is to be expected since (4.1) does not allow it. In this particular case, the geometry of the target allows all the transitions which are also allowed by energy conservation.

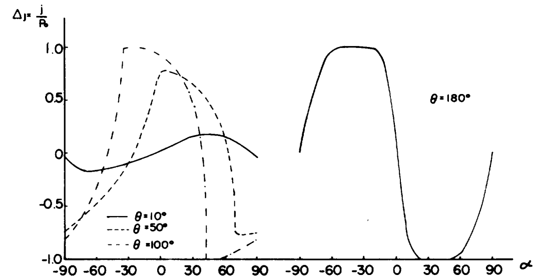

FIG. 5. The figure shows the relationship between the canonical variables $(\Delta j, \alpha)$ for several fixed scattering angles θ. The parameters for the ellipsoid are $A = 2$, $B = 1$, $\mu/I = 1$.

However, this is not always the case as we shall now show. For the scattering angle $\theta = 180°$ we have the largest phase space for the final rotational states. Therefore, if in the backward scattering some rotational states are missing, we will also not find them for small angles; hence such transitions are forbidden. However, $\theta = 180°$ implys $\phi = \phi_R = 0$, which can be proved from (2.8) and (3.1); hence, from (2.3) we have

$$-B^2(b\cos\alpha + y_b \sin\alpha)\cos\alpha + A^2(y_b\cos\alpha - b\sin\alpha)\sin\alpha = 0. \tag{4.2}$$

By replacing y_b with (2.4) and after some algebra, we obtain

$$b_n = b = \frac{A^2 - B^2}{\sqrt{2}} \frac{\sin 2\alpha}{[A^2 + B^2 - (A^2 - B^2)\cos 2\alpha]^{1/2}}. \tag{4.3}$$

Let us now look for the maximum of Δj with respect to α, i.e.,

$$d\Delta j/d\alpha = 0. \tag{4.4}$$

The solution is

$$\cos 2\alpha = (A - B)/(A + B) \tag{4.5}$$

and the maximum of Δj is

$$\Delta j_{\max} = 2(A - B)/[1 + (\mu/I)(A - B)^2]. \tag{4.6}$$

From the last result it is now easy to deduce the conditions that there be closed channels because of the geometry of the target. This is obtained from

$$\sqrt{I/\mu} > 2(A - B)/[(\mu/I)(A - B)^2 + 1], \tag{4.7}$$

which is always true except when

$$\sqrt{\mu/I}(A-B)=1\,. \tag{4.8}$$

In such a case there are equal number of open channels due to (4.1) and the geometry of the target. In all other cases there will always be fewer accessible states than the number allowed by the energy conservation.

Let us discuss a few examples. For an almost spherical target, i.e., $A\sim B$ (4.6) is

$$\Delta j_{\max}\sim 2(A-B); \tag{4.9}$$

hence, the maximum rotational transfer is independent of the dynamical properties of the system, such as the ratio μ/I, and it only depends on the difference in the major and minor axes of the target. The final c.m. momentum p is

$$\begin{aligned} p &= p_0[1-(\mu/I)\Delta^2 j]^{1/2} \\ &\sim p_0[1-(\mu/I)4(A-B)^2]^{1/2}\sim p_0\,, \end{aligned} \tag{4.10}$$

therefore, there is practically no momentum transfer during the collision. It should, however, be remembered that $\Delta j_{\max}$ is related to the final rotational state by $j_{\max}=p_0\Delta j_{\max}$, and we may have large rotational states if p_0 is large, but the total amount of energy transfer is small. For example in He-H_2 collisions[9] the difference $A-B$ at energy $E=1.2$ eV is $A-B=0.063A$ and $\Delta j_{\max}=0.126$. The largest classically accessible state, in this model, is $j_{\max}\sim 3$. However, by the energy conservation these are up to $j\sim 12$ states. The maximum momentum transfer is only 4%.

The relationship (4.9) also allows for direct measurement of the quantity $A-B$. However, $j_{\max}$ is only determined to the quantum $2\hbar$; hence the error is

$$2\hbar/p_0=2\Delta(A-B)\,, \tag{4.11}$$

or

$$p_0\Delta(A-B)\sim\hbar\;, \tag{4.12}$$

which is the uncertainty relationship for the quantity $A-B$.

We can also look at another extreme case when the ratio μ/I is small. In that case the relationship (4.9) also holds, but $\Delta j_{\max}$ is constant for large changes of μ/I. However, to observe transitions in such cases the experimental apparatus should have resolution power in the final momentum of the atoms corresponding to the transtions $j\hbar$ and $(j+2)\hbar$. From (4.10) we obtain that this resolution power in p should be better then

$$\Delta p\sim 2(\mu/I)(A-B)\hbar\;. \tag{4.13}$$

In the limit $\mu/I\rightarrow 0$, the momentum selector should be infinitely accurate. In other words, the total number of rotational states is constant in the limit $\mu/I\rightarrow 0$, but we cannot observe them.

V. CONCLUSION

We have shown some properties of atom-diatom collisions using a simple model of two-dimensional scattering of a particle by an ellipsoid, which can be deduced from classical mechanics. Some results are suggestive even for quantum mechanics and deal with (a) the effects one should expect in fully quantum-mechanical calculations and (b) approximations that can be used to obtain such results, especially for the systems where there is no large momentum transfer. In particular, we refer to the distorted-wave approximation (case $A\sim B$) and the energy sudden or infinite-order sudden approximation (case $\mu/I\ll 1$). Generalization to three dimensions of this model raises additional difficulties (there is one more degree of freedom), but some estimates given here are believed to be applicable even in such a case.

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