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Quantum theory of impulsive collisions

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A quantum theory of atom-molecule collisions is developed for potentials with a hard core. It is assumed that the potential is spherically symmetric in the medium- and the long-range parts. The scattering amplitude is given as a solution of algebraic equations.

I. INTRODUCTION

One of the basic problems in the study of atom-molecule collisions is how the energy transfer is related to the potential between the two species. There have been various attempts to solve this problem, and the simplest is to use the distorted-wave approximation,[1] in which the nonsphericity of the molecule is treated as a perturbation. The number of cases where this approximation is applicable is very limited and therefore it is not generally used.[2] The exact method, solving the close-coupling equations, is also seldom used because in most cases it is nearly impossible to solve multichannel equations numerically, the reason being the large number of channels involved. Furthermore, when molecules are moderately nonspherical the Legendre expansion of potential, which is required as the input to the close-coupling equations, involves a large number of terms from which it is difficult to deduce their contribution[3] in the energy transfer. Multichannel equations can be solved by various approximate techniques, e.g., coupled state or various types of sudden approximations. Among them the method which has been extensively used for analysis of the rotational energy transfer is the infinite-order sudden (IOS) approximation.[4] Despite success in many applications and analysis of rotational energy transfer the IOS approximation has limited use. It can be used in systems with small energy transfer and for nearly spherical molecules. Furthermore in the analysis of rotation-vibrational energy transfer the IOS approximation shows poor performance. Better results are achieved if it is used in conjunction with the exact quantum treatment.[5] The same criticism applies to the other approximate methods, although some are better than the others in different situations.[6]

The breakthrough in understanding of the rotational energy transfer came when it was assumed that the short-range repulsive core of atom-molecule potential determines most of the energy transfer. The concept of molecular shape was introduced which was defined in terms of the repulsive part of the atom-molecule potential. At one of the equipotential lines the repulsive potential was replaced by an infinite wall while the remaining part of the potential was neglected. An order of magnitude estimate showed that indeed this is a reasonable approximation and that deviations from this model are expected for systems with a large attractive and nonspherical part of the potential.[7,8] In fact most of our understanding of the rotational energy transfer stems from this model, but almost all studies of this model were classical.[9,10,8] There have been relatively few quantum formulations of the model that did not solve it in general but were rather specific to a particular system, e.g., the IOS solution of the model is only applicable to systems with little energy transfer into the molecule.[11] The major difficulty in formulating a general quantum theory of the hard-core models is that the appropriate multichannel equations cannot be obtained in the diabatic basis, because the coupling is infinite.[12] Multichannel equations should be formulated in the adiabatic basis[12] but this greatly complicates the theory. Another approach is to use generalized coordinates (e.g., elliptical[13]), but this restricts the theory to only a few shapes of molecules.

The relationship between the shape of the molecule and the energy transfer is therefore crucial for understanding collision processes of atoms and molecules. The link between the two is provided by the general quantum theory of collisions for hard shapes, which also includes molecular vibrations. It is not expected that the model shall give perfect agreement with the real potential but it should be possible to treat deviation from the hard shapes as perturbation. In this work we set out to fulfill this task: to formulate the quantum theory of collisions involving vibrating hard shapes. In fact we go one step further by assuming that outside hard shape the potential is nonzero; however, it is assumed to be spherically symmetric. In this way modification of collision energy at the moment of impact with the hard core is taken into account. Since energy transfer occurs only at the hard core we shall call it the impulsive collision or the impulsive model.

The quantum theory of impulsive collision, as it is formulated, is generalization of the idea developed in the study of molecular-surface transfer,[14] using the hard-core model. The method of solution is relatively simple and the scattering amplitude is obtained as the solution of a set of linear equations rather than solution of the multichannel equations. Within the impulsive model the scattering amplitude is given exactly and has no restrictions, e.g., as the IOS approximation. The solution also includes vibrational energy transfer and therefore the theory can be used in the study of the most general collision problem of atoms and molecules.

II. THEORY

In the impulsive model it is assumed that the short-range repulsive atom-molecule potential (for simplicity we shall consider only the atom-diatom potentials) is replaced by infinite potential (hard core) while the remaining part is assumed to be spherically symmetric. The exact point at which the hard core replaces the repulsive potential is to a certain extent arbitrary. Our choice is the following: if the potential is $V(\mathbf{R},\mathbf{r})$ where $\mathbf{R}$ represents the atom-molecule separation and $\mathbf{r}$ the atom-atom separation within the molecule, then the shape of the hard core is determined by the equation

$$V(\mathbf{R},\mathbf{r})=E \tag{1}$$

where E is collision energy. From this equation the relationship

$$R=g(\theta,\phi,\mathbf{r}) \tag{2}$$

is obtained, which we call the boundary of the molecule. θ and ϕ are the polar and azimuthal angles of $\mathbf{R}$, respectively. Energy dependence in Eq. (2) is omitted because it is assumed that in most cases this is negligible.

Beyond the boundary given by (2) the potential is spherically symmetric so that we can write

$$V(\mathbf{R},\mathbf{r})\approx U(R)\eta(\mathbf{R},\mathbf{r}) \tag{3}$$

where η has infinite value if the coordinates are within the boundary (2), but otherwise it is equal to one. The function $U(R)$ is determined by taking a spherically symmetric average of the true potential. It will be assumed that the difference between $U(R)$ and the true potential can be treated as perturbation on the scattering amplitude.

For diatomic molecules the boundary of the molecule g is a function of the relative angle γ between the vectors $\mathbf{R}$ and $\mathbf{r}$, given by

$$\cos(\gamma)=\cos(\theta)\cos(\beta)+\sin(\theta)\sin(\beta)\cos(\phi-\alpha) \tag{4}$$

where α is the azimuthal angle and β is the polar angle of $\mathbf{r}$. This fact will be used in the derivation of the scattering amplitude in the impulsive model.

The Schrödinger equation for an atom-molecule system is

$$[T(\mathbf{R})+T(\mathbf{r})+v(r)+V(\mathbf{R},\mathbf{r})]\Psi=E\Psi \tag{5}$$

where T is the kinetic energy. If we use approximation (3) for the potential V, a particular solution of Eq. (5) anywhere outside the boundary of the molecule is

$$\varphi_{n,j,\mu}(\mathbf{r})\omega_{n,j,l,m}(\mathbf{R}) \tag{6}$$

where n is the vibrational quantum number, (j,μ) are the rotational quantum numbers of the molecule, and (l,m) are the orbital quantum numbers of the relative motion of atom and molecule. Any solution of (5) is therefore a linear combination of the solutions (6), and in particular the one which describes scattering. This linear combination must satisfy the following conditions: (a) all the particular solutions (6) must have the same total energy, (b) at the boundary the solution must be zero, and (c) for large atom-molecule separations the solution must have proper scattering boundary condition. This solution can be written as

$$\Psi=\varphi_{n,j,\mu}(\mathbf{r})\omega^{z}_{n,j}(\mathbf{R})+\sum_{n',j',\mu'}\varphi_{n'j'\mu'}(\mathbf{r})\omega^{s}_{n'j'\mu'}(\mathbf{R}) \tag{7}$$

where the functions ω^z and ω^s are solutions of the Schrödinger equation in the $\mathbf{R}$ coordinates with the following asymptotic forms for large R:

$$\begin{aligned}&\omega^{z}_{nj}\sim e^{iZk_{nj}}\ ,\\&\omega^{s}_{n'j'\mu'}\sim\frac{e^{iRk_{n'j'}}}{R}f_{n'j'\mu';nj\mu}\ .\end{aligned} \tag{8}$$

If the condition (b) is to be applied on (7) the correct form of the functions (8) should be known at the boundary of the molecule. Let us designate by ω^{+}_{njl} and ω^{-}_{njl} the two irregular solutions of the lth partial-wave radial equation for the potential $U(R)$ (for the spherically symmetric potential the solutions are independent of the magnetic quantum number of l), which are defined asymptotically by

$$\omega^{\pm}_{njl}\sim e^{\pm iRk_{nj}}\ . \tag{9}$$

For large R the incident plane wave ω^{z}_{nj} is given as expansion in the Legendre polynomials and the Bessel functions $J_{l+1/2}$.[15] The asymptotic form of the Bessel functions is a linear combination of the incoming and outgoing spherical waves so that for large R

$$\omega^{z}_{nj}\sim\frac{i}{2Rk_{nj}}\sum_{l}(2l+1)P_l(\theta)(-e^{iRk_{nj}}+e^{-iRk_{nj}+i\pi l})\ . \tag{10}$$

In the expression the spherical waves can be replaced by the functions (9) in which case for finite R it goes into

$$\omega^{z}_{nj}=\frac{i}{2Rk_{nj}}\sum_{l}(2l+1)P_l(\theta)[-\omega^{+}_{njl}+(-1)^l\omega^{-}_{njl}]\ . \tag{11}$$

At this point we introduce a complete set of angular functions with the following properties: they are eigenfunctions of the total angular momentum operator and the rotational operator of the molecule. They are also functions of the scattering angles (θ,ϕ), the relative angle γ, defined in (4), and the azimuthal angle Δ defined in the Appendix. These properties of angular functions are essential in finding a solution to our scattering problem. It is shown in the Appendix that the functions

$$\begin{aligned}\Upsilon^{JM}_{jm}&=D^{*J}_{Mm}(\phi,\theta,0)Y_{jm}(\gamma,\Delta)\\&=\frac{\sqrt{4\pi}}{2J+1}\sum_{l,m'}\sqrt{2l+1}\\&\qquad\times C(l,j,J;0,m)C(l,j,J;m',M-m')\\&\qquad\times Y_{jM-m'}(\beta,\alpha)Y_{lm'}(\theta,\phi)\end{aligned} \tag{12}$$

satisfy these requirements. $C(a,b,c;d,e)$ are the Clebsch-Gordan coefficients and $D^{J}_{ab}(\alpha,\beta,\gamma)$ are the rotation matrix elements.[16] Using the functions (12), and relationships developed in the Appendix, it can be shown that the most general particular solution [of the type (6)] of the Schrödinger equation (5), which has the above-mentioned properties, is given by

$$\Phi^{JM}_{njm}(\mathbf{R},\mathbf{r})=\frac{\varphi_{nj}(r)}{2J+1}\sum_{m''}\Upsilon^{JM}_{jm''}\sum_{l}(2l+1)A_{njl}(R)\times C(l,j,J;0,m)\times C(l,j,J;0,m'') \tag{13}$$

where $A_{njl}(R)$ are solutions of the radial equation for the relative motion and $\varphi_{nj}(r)$ are the radial functions for the molecule. The functions (13) are equivalent to those defined in (6). For example the incident wave in (7) is given by

$$\varphi_{nj\mu}\omega^{z}_{nj}=\left[\frac{\pi}{2Rk_{nj}}\right]^{1/2}\sum_{J}(2J+1)\Phi^{J\mu}_{nj\mu} \tag{14}$$

where $A_{njl}(R)=i^{l}J_{l+1/2}(k_{nj}R)$ if $U(R)=0$, i.e., for a plane wave. Likewise the scattered waves in (8) can be written as

$$\varphi_{nj\mu}\omega^{s}_{nj\mu}=\sum_{J,M,m}F^{JMm}_{nj\mu;n_0j_0\mu_0}\Phi^{JM}_{njm} \tag{15}$$

where now $A_{njl}(R)\sim\exp(iRk_{nj})/R$. The set of indices $(n_0j_0\mu_0)$ in (15) designates the state of the incident channel (14). By taking the limit $R\rightarrow\infty$ of (15) it is relatively straightforward to obtain the scattering amplitude, defined in (8). After some manipulation with the Clebsch-Gordan coefficients we obtain

$$f_{nj\mu;n_0J_0\mu_0}=\sum_{J,M,l,m}\frac{\sqrt{4\pi(2l+1)}}{2J+1}F^{JM}_{njm;n_0j_0\mu_0}\times C(l,j,J;0,m)C(l,j,J;M-\mu,\mu)\times Y_{lM-\mu}(\theta,\phi)\ . \tag{16}$$

It will be shown later that for diatomic molecules (i.e., linear) $M=\mu_0$.

The coefficients F determine the scattering amplitude. They can be obtained from the requirement that the wave function (7) is zero at the boundary of the molecule. Using the basis functions (13) the wave function is given by

$$\Psi=\Psi_{\rm inc}+\Psi_{\rm sc} \tag{17}$$

where

$$\Psi_{\rm inc}=\frac{i\varphi_{n_0j_0}(r)}{2Rk_{n_0j_0}}\sum_{J,m}D^{*J}_{\mu_0m}(\phi,\theta,0)Y_{j_0m}(\gamma,\Delta)\sum_{l}(2l+1)\omega_{n_0j_0l}(R)C(l,j_0,J;0,\mu_0)C(l,j_0,J;0,m) \tag{18}$$

where $\omega=-\omega^{+}+(-1)^{l}\omega^{-}$. The scattered part of the wave function is

$$\Psi_{\rm sc}=\frac{1}{R}\sum_{J,M,j,m,n}\frac{\varphi_{nj}(r)}{2J+1}F^{JM}_{N,N_0}\sum_{m'}D^{*J}_{Mm'}(\phi,\theta,0)Y_{jm'}(\gamma,\Delta)\sum_{l}(2l+1)\omega^{+}_{njl}(R)C(l,j,J;0,m)C(l,j,J;0,m') \tag{19}$$

where the simplicity the index N of F designates the triad $N\equiv(n,j,m)$. If R now takes values on the boundary of the molecule, i.e., R is given by (2), then $\Psi=0$, which determines the coefficients F. They are obtained by multiplying (17) with $D^{J'}_{M'm'}(\phi,\theta,0)$ and integrating over the solid angle spanned by the angles θ and ϕ. It should be recalled that R is not a function of these angles. As the result of this integration it is obtained that $M=\mu_0$. In the next step the set is multiplied with $Y^{*}_{j'm'}(\gamma\Delta)$ and integrated over the solid angle spanned by the angles γ and Δ. Finally the set is multiplied by $\varphi_{n'j'}$ and integrated over the coordinate r. The set of equations thus obtained can be given in a compact form if we define new matrices W and W^{+}, having the matrix elements

$$W^{J}_{n'j'm';njm}=\sum_{l}(2l+1)C(l,j,J;0,m)C(l,j,J;0,m')\times\int_{0}^{\infty}dr\,r^{2}\varphi_{nj}\varphi_{n'j'}\int d\Omega\,Y_{jm'}\omega_{njl}Y^{*}_{j'm'} \tag{20}$$

where the solid angle integration is over the variables (γ,Δ). The matrix elements of W^{+} are the same as in (20) except that ω is replaced by ω^{+}. The set of equations is now

$$\frac{i(2J'+1)}{2k_{n_0j_0}}W^{J'}_{N';N_0}+\sum_{N}W^{+J'}_{N';N}F^{J'\mu_0}_{N,N_0}=0 \tag{21}$$

which is easily solved for the unknown coefficients F. The set (21) is solved for each J' and then the scattering amplitude is obtained from (16).

The scattering problem in the impulsive model is solved. The only problem is calculating matrices W and W^{+} and subsequently solving the set of equations (21).

III. ROTATIONAL ENERGY TRANSFER

As an example the theory will be applied to the atom-molecule rotational energy transfer. The formulas (21) and (16) are used in this case without referencing to the vibrational quantum n. For simplicity it will be assumed that initially the molecule is not rotating.

Calculation of the scattering amplitude can be much simplified by a suitable modification of the previously mentioned formulas. If the partial scattering amplitude is written as

$$F^{Jm_0}_{jm;j_0m_0}=\sum_{l'}C(l',j,J;0,m)f^{J}_{jl';j_0m_0}\ , \tag{22}$$

then the product of W and F matrices in (21) is given by

$$\sum_{j,m}W^{+}_{j'm';jm}F^{Jm_0}_{jm;j_0m_0}=\sum_{l,j}(2J+1)C(l,j,J;0,m')\times\langle j'm'|jl|jm'\rangle f^{Jm_0}_{jlj_0m_0} \tag{23}$$

where ⟨ | | ⟩ designates the integral over the solid angle in (20) with, however, ω^+ replacing ω. In this form one saves time by not having to evaluate the sum in the expression for W^+ in (20). If the parametrization of the partial-wave scattering amplitudes (22) is introduced into (16) the scattering amplitude becomes

$$f_{j\mu;j_0\mu_0}(\theta,\phi)=\sqrt{4\pi}\sum_{J,l}\frac{C(l,j,J;\mu_0-\mu,\mu)}{\sqrt{2l+1}} \times Y_{l\mu_0-\mu} f^{J}_{jl;j_0\mu_0}\,, \qquad (24)$$

which is also a simplification since only one summation index involves the angular-dependent functions, the spherical harmonics.

The systems on which we wanted to test the impulsive model are D_2-Ne and HD-Ne, well studied both experimentally and theoretically.[17,18] Although the system appears to be quite simple, because at the considered collision energies only a few open channels are involved, it is, in fact, quite a difficult test case for many approximate schemes, e.g., for various types of the sudden approximations. The quantum effects are also quite pronounced (e.g., diffraction in the forward direction) and therefore the tail of the potential may play a significant role in the rotational energy transfer, while in the impulsive model it is ignored. However, we have chosen these systems in order to show how successful the model is for interpreting the rotational energy transfer in what we believe is the worst test case.

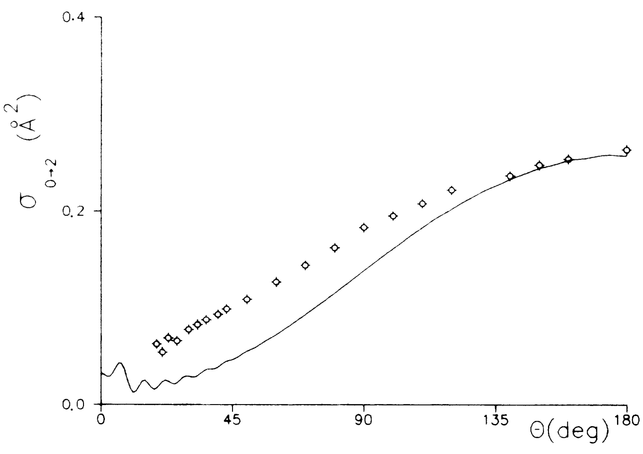

FIG. 2. Comparison between the cross sections calculated from the impulsive model (solid line) and the full potential (circles) from Ref. 18, for the system D_2-Ne.

Rotational energy transfer in the D_2-Ne system was studied for collision energy $E=84.9$ meV. At this energy the channels $j=0$, 2, and 4 are open. The shape of the molecule D_2 was assumed to be an ellipsoid, the axes of which were determined from the potential which was used in the analysis of the experiments on the same system.[18] The choice of these axes is to a certain extent arbitrary. We have decided on the values of the atom-molecule separation in the collinear (the major axis A) and the perpendicular configurations (the minor axis B) at which the kinetic energy of the relative translational motion equals the potential energy. The values of A and B thus obtained are $A=2.364$ Å and $B=2.255$ Å, from which it is inferred[10] that the maximal accessible final rotational state is $j=2$. This implies that a relatively large fraction of the total collision energy could be transferred into the rotation of the molecule. As a result the basis which was needed to converge the scattering amplitude included also a $j=6$ channel, which is closed at this collision energy.

The solid line in Fig. 1 shows inelastic 0→2 differential cross for the given values of A and B. The interesting feature of this system is that the differential cross section is very sensitive to the variations in A and B. The same figure shows differential cross section for two other values for A. The long-dashed line is the cross section for $A=2.464$ Å, which is an increase of 0.1 Å compared to the previous choice for the major axis. A dramatic change in the cross section is noticed, which is an indication that fitting of the potential to the experimental data

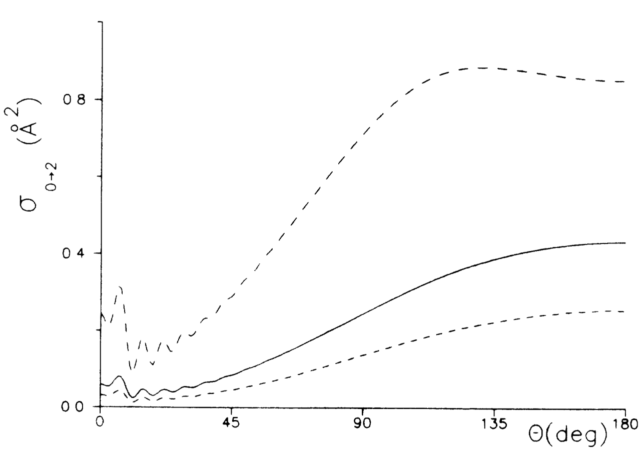

FIG. 1. Inelastic differential cross section for the system D_2-Ne in the impulsive model. Different curves correspond to the various values of the large axis of the ellipsoid representing the molecule. The values for the axes are given in the text.

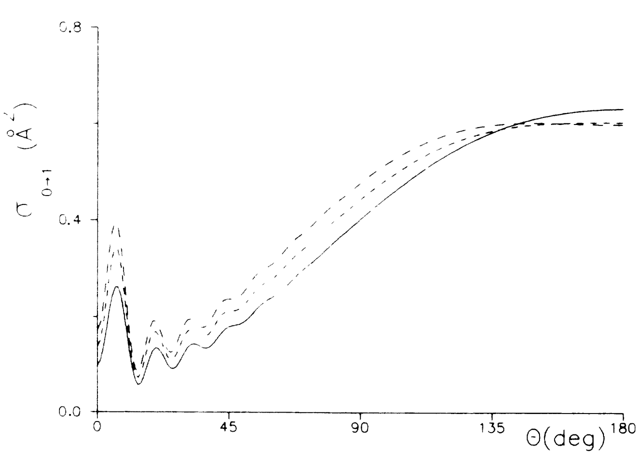

FIG. 3. Inelastic differential cross section for the system HD-Ne in the impulsive model. Different curves correspond to the various values of the large axis of the ellipsoid representing the molecule. The values for the axes are given in the text.

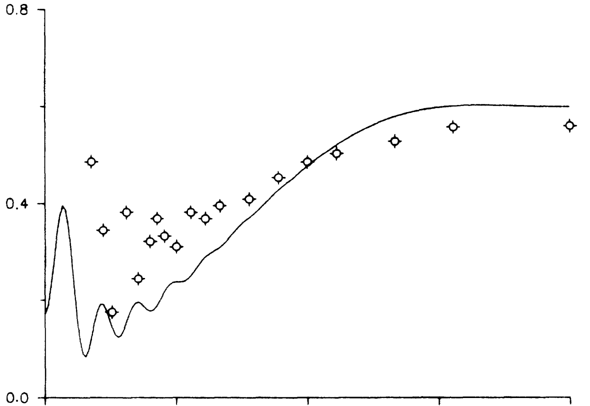

FIG. 4. Comparison between the cross sections calculated from the impulsive model (solid line) and the full potential (circles) from Ref. 17, for the system HD-Ne.

will be quite sensitive to the choice of parameters. The short-dashed line is the cross section with the choice $A=2.334$ Å. Again by lowering the value of the major axis by only 0.03 Å the differential cross section decreases considerably for large scattering angles, bringing it to a relatively good agreement with the cross section which was obtained from the full potential.[18] This comparison is shown in Fig. 2 where the circles designate the points which were calculated from the full potential. Considering that the whole potential was parametrized using only two variables (A and B axes), which is a great simplification of the system, the comparison is relatively good. In fact this shows that energy transfer is mainly determined by the shape of the repulsive core of the potential. Furthermore we have concluded that differential cross section is a very sensitive probe of this shape.

Another system which was studied is HD-Ne at collision energy $E=31.5$ meV. At this energy only the channels $j=0$ and 1 are open. The shape of the HD molecule was assumed to be a shifted ellipsoid, the shift being determined by the isotope difference of the two hydrogen atoms. The axes of the ellipsoid were determined as in the previous example, from the potential for H_2-Ne.[19] Their values were $A=2.56$ Å and $B=2.46$ Å. For this shape the maximal value of the effective impact parameter[2,20] is $b_n \approx 0.2$ Å thus giving the estimate that energy transfer is well over the $\Delta j=1$ transition. This implies that closed channels were needed in calculation of the scattering amplitude. Indeed it was found that channels up to $j=4$ had to be included in order to achieve accurate cross sections. Figure 3 shows calculation of the differential cross section for transition $0\to1$ for three values of A. The solid line represents the cross section for the initial choice of the axes A and B. The long-dashed line represents cross section for $A=2.65$ Å and the short-dashed line for $A=2.70$ Å. Unlike the system D_2-Ne here the cross section is not particularly sensitive to the variations of the shape of the molecule. However, this may be due to the fact that only one inelastic channel is open which is very efficiently populated through the energy transfer. Making the energy transfer more efficient, by increasing A, does not contribute much in terms of drastic change in the cross section.

Comparison with the cross section which was obtained from the full potential[17] is shown in Fig. 4, where the circles designate points of that calculation. The solid line is the cross section of the ellipsoid with $A=2.70$ Å. Again the two curves are not far apart and deviation may be due to the details of potential.

IV. DISCUSSION

Within the proposed model the expression for the scattering amplitude (16), together with solution of (21), is exact. From that expression one can derive various approximations for the scattering amplitude. For example, one could search for approximate ways of evaluating the integrals (20). However, more important is to find approximations of the inverse $(W^+)^{-1}$ since these usually give relatively simple expression for the scattering amplitude (from now on we drop the reference to J). If the matrices W and W^+ can be partitioned in the form

$$W=W_0+W'; \quad W^+=W_0^+ + W^{+\prime} \tag{25}$$

where W' and $W^{+\prime}$ are small, it is then approximately

$$(W^+)^{-1}W \approx (W_0^+)^{-1}W_0 + (W_0^+)^{-1}[W'W_0^{-1} - W^{+\prime}(W_0^+)^{-1}]W_0 \, . \tag{26}$$

The product of this form is the solution of (21) for the coefficients F. The approximation of the product (26) is useful if the inverse $(W_0^+)^{-1}$ is simple. The diagonal matrix for W_0^+ is the simplest choice, which is only possible if it is assumed that the function g in (2) is constant. This corresponds to the choice of the spherically symmetric and nonvibrating molecule for the unperturbed system. In other words, it is assumed that the function g in (2) can be written as

$$R=R_0+\epsilon(\theta,\phi,r) \tag{27}$$

where ϵ is small. The radial wave function is then approximately

$$\omega_{njl}^+ \approx \omega_{njl}^+(R_0)+\epsilon(\theta,\phi,r)\frac{d}{dR}\omega_{njl}^+(R_0) \tag{28}$$

which simplifies for the WKB solution of ω_{njl}^+

$$\omega_{njl}^+ \approx \omega_{njl}^+(R_0)[1+i\epsilon(\theta,\phi,r)k_{njl}(R_0)] \tag{29}$$

where k_{njl} is the wave number which corresponds to the relative momentum of atom and molecule at the moment of impact.

The matrix elements of $W^{+\prime}$ are related to the integrals over the function ϵ. These elements are small compared to the matrix elements of W_0^+ provided that

$$k_{njl}(R_0)\overline{|\epsilon(\theta,\phi,r)|} \ll 1 \tag{30}$$

where the average of the absolute value of ϵ was taken. The inequality (30) determines the quality of the approximation (26). The expansion of the scattering amplitude based on (27) is very similar to the distorted-wave Born series. The difference is that the former is based on distortion of the boundary of the molecule, while the latter is based on the off-diagonal elements of the potential matrix in the multichannel equations.

Another very useful approximation for the inverse of W^+ is obtained in the limit of large number of open channels, small overall energy transfer into the molecule, and nearly spherical molecule. The conjecture is

$$(W^+)^{-1}_{n'j'm';njm}=\frac{2\pi}{(2J+1)^2}\sum_l (2l+1)C(l,j',J;0,m')C(l,j',J;0,m)\int_0^\infty dr\, r^2\varphi_{nj}\varphi_{j'j'}\int d\Omega\, Y^*_{j'm}(\omega^+_{j'l})^{-1}Y_{jm} \tag{31}$$

which can be shown by multiplying (20) from the left with (31). The completeness of the spherical harmonics is invoked, of the form

$$\sum_j Y_{jm}(\theta,\phi)Y^*_{jm}(\theta',\phi')=\frac{\delta(\cos\theta-\cos\theta')}{2\pi}e^{im(\phi-\phi')} . \tag{32}$$

Furthermore, it is assumed that k_{nj} is independent of the value of the channel indices n and j (the assumption of small energy transfer) and that change in the orbital angular momentum l is not large (the assumption of nearly spherical molecule). The last assumption is required for the approximate equality $\omega^+_{njl}/\omega^+_{njl'}\approx 1$. All these implicitly assume a large number of channels since, for example, the completeness (32) would not have been fulfilled even approximately. This approximation produces the same result for the scattering amplitude as the IOS method.

In conclusion we can say that there are at least two merits of the theory which was developed here. Firstly within the impulsive model it is possible to relate directly the shape of the molecule to the cross sections, the deviations being small and treatable as perturbation. For this model the quantum theory of collisions was developed. Secondly, the scattering amplitude is given as solution of a set of linear equations and it is not necessary to solve multichannel equations. This is not a minor point knowing that any moderately large scattering problem of atom and molecule is nearly impossible to solve from the close-coupling equations. The only alternative is the IOS method which works under rather restrictive assumptions. Our result is exact and relatively simple, but it is based on the assumption of the impulsive model, which is not far detached from the reality.

APPENDIX

We show how to obtain angular functions (12). First it is necessary to transform

$$Y_{j\mu}(\beta,\alpha)Y_{lm}(\theta,\phi) \tag{A1}$$

into a linear combination of the product of two functions, one of which is a function of the relative angle γ, defined in (4), and another which is a function of the angles (θ,ϕ). This is achieved by applying rotation to $Y_{j\mu}$

$$\begin{aligned}Y_{j\mu}(\beta,\alpha)&=\sum_{\mu'}\delta_{\mu\mu'}Y_{j\mu'}(\beta,\alpha)\\&=\sum_{\mu',\mu''}D^{*j}_{\mu\mu''}(\phi,\theta,0)D^{j}_{\mu'\mu''}(\phi,\theta,0)Y_{j\mu'}\end{aligned} \tag{A2}$$

where D^l_{ab} is the rotation matrix.[16] In the derivation of (34) we have used the orthogonality properties of the rotation matrices with respect to the summation index μ''. The sum over the index μ' is recognized as rotation of the spherical harmonic so that

$$Y_{j\mu}(\beta,\alpha)=\sum_{\mu''}D^{*j}_{\mu\mu''}(\phi,\theta,0)Y_{j\mu''}(\gamma,\Delta) \tag{A3}$$

where γ is the polar angle of the molecular axis with respect to the new coordinate system and it is given by (4). The angle Δ is the azimuthal angle of the molecular axis with respect to the same coordinate system and it is given by

$$\tan(\Delta)=\frac{\sin\beta\sin(\alpha-\phi)}{\cos\theta\sin\beta\cos(\phi-\alpha)-\sin\theta\cos\beta} . \tag{A4}$$

If the spherical harmonic Y_{lm} is written in terms of the rotation matrix

$$Y_{lm}(\theta,\phi)=\left[\frac{2l+1}{4\pi}\right]^{1/2}D^{*l}_{m0}(\phi,\theta,0) , \tag{A5}$$

then the product (A1) is

$$\begin{aligned}&Y_{j\mu}(\beta,\alpha)Y_{lm}(\theta,\phi)\\&\quad=\left[\frac{2l+1}{4\pi}\right]^{1/2}\sum_{J,\mu''}C(l,j,J;m,\mu)C(l,j,J;0,\mu'')\\&\qquad\times D^{*J}_{m+\mu\mu''}(\phi,\theta,0)Y_{j\mu''}(\gamma,\Delta)\end{aligned} \tag{A6}$$

where we have used the coupling rule for the rotation matrices. From the product of the two eigenfunctions (A6) we can produce eigenfunction $Y_{JM}(j,l)$ of the total angular momentum operator using the coupling rule of angular momenta. If we designate $M=m+\mu$ then

$$\begin{aligned}Y_{JM}(j,l)&=\sum_m C(l,j,J;m,M-m)Y_{jM-m}(\beta,\alpha)Y_{lm}(\theta,\phi)\\&=\left[\frac{2l+1}{4\pi}\right]^{1/2}\sum_{\mu''}C(l,j,J;0,\mu'')\\&\qquad\times D^{*J}_{M\mu''}(\phi,\theta,0)Y_{j\mu''}(\gamma,\Delta) .\end{aligned} \tag{A7}$$

Any linear combination with respect to l of these functions is again eigenfunction of the total angular momentum and the rotational angular momentum operator of the molecule. In particular we can make linear combination with the coefficients $C(J,j,l;-\mu',\mu')$, in which case we obtain the functions (12).

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