

Reactive (dissociative) diatom–solid surface collision: A quantum mechanical approach

M. Baer

Citation: *The Journal of Chemical Physics* **81**, 4526 (1984); doi: 10.1063/1.447423

View online: <http://dx.doi.org/10.1063/1.447423>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/81/10?ver=pdfcov>

Published by the **AIP Publishing**

Articles you may be interested in

[Quantum mechanical calculations of collinear reactive collisions at energies above the dissociation threshold: A discretevariablerepresentation approach](#)

J. Chem. Phys. **100**, 1171 (1994); 10.1063/1.466647

[Collision induced dissociation of diatomic molecules on surfaces: A charge transfer mechanism](#)

J. Chem. Phys. **84**, 3502 (1986); 10.1063/1.450236

[Reply to the “Comment on reactive diatom–solid surface collisions: A quantum mechanical approach”](#)

J. Chem. Phys. **83**, 6545 (1985); 10.1063/1.449559

[Comment on reactive diatom–solid surface collision: A quantum mechanical approach](#)

J. Chem. Phys. **83**, 6544 (1985); 10.1063/1.449558

[Rotational rainbows in diatom\(solid\) surface scattering](#)

J. Chem. Phys. **76**, 2352 (1982); 10.1063/1.443263



Reactive (dissociative) diatom–solid surface collision: A quantum mechanical approach

M. Baer

Applied Mathematics, Soreq Nuclear Research Centre, Yavne 70600, Israel

(Received 31 January 1984; accepted 6 June 1984)

In this work a quantum mechanical approach to the study of reactive diatom (stationary) surface collisions is presented. Following the general theory the infinite order sudden approximation (IOSA) is introduced and the corresponding S matrix elements derived. The case of noncorrugated surfaces is treated in detail and a new quasiselection rule is found which governs the reactive process.

I. INTRODUCTION

The theoretical treatment of a reactive collision between an atom and a diatomic molecule constitutes one of the most important subjects in the field of theoretical chemistry. Although in the last few years progress has somewhat slowed down—the transition to three dimensions was found to be more complicated than anticipated—nevertheless significant contributions were made, particularly in employing approximate treatments. One of the approximations for treating quantum mechanical three-dimensional systems is the infinite order sudden approximation (IOSA).^{1–9} It was found to yield (except for the low tunneling region) total cross sections which fit both exact quantum mechanical¹⁰ ($H + H_2$ ^{3,4}) and coupled states (CS)^{7,8,11} ($F + H_2$,⁵ $D + HCl$,⁷ $H(D) + HBr$ ⁸) results, as well as exact classical results^{12–14} ($F + H_2$,⁵ $F + D_2$,⁶ $D + H_2$ ⁹). With more detailed information, such as (vibrational) state-to-state differential and integral cross sections, good agreement is obtained between the IOSA and the CS results for the $D + HCl$ and $H(D) + HBr$ systems^{7,8} as well as for the $F + H_2$ ⁵ system, but rather poor agreement with similar classical results ($F + H_2$,⁵ $F + D_2$,⁶ $D + H_2$ ⁹). These facts lead us to believe that the IOSA is a relevant approximation for treating reactive collisions; it is much more reliable in delivering state-to-state transition probabilities and cross sections than the classical trajectory method^{12–14} and applies to larger energy regions than, for instance, the distorted wave Born approximation (DWBA)¹⁵ or the bend corrected rotating linear model (BCRLM)¹⁶ which seem to be relevant, at most, for the low-energy region.

The treatment of reactive collisions was extended to the molecule–solid surface case in the middle of the seventies by Wolken and co-workers^{17–19} and by Gelb and Cardillo.²⁰ More recent studies of this kind were performed by Tully.²¹ In all these treatments the classical trajectory method was employed and except for the study of Tully the solid surface was assumed to be stationary.

The molecule solid surface interaction was also treated within quantum mechanics, but only for nonreactive collisions.²² The pioneering research on this subject was done by Wolken already in 1973,²³ but intensive studies started to appear in the literature only five to seven years later.^{24–30} It was soon found that exact close coupling calculations can be carried out only for a limited number of interesting cases. In

order to obtain results for realistic systems which are also measurable in the laboratory, approximations have to be incorporated. So far the most favorable approximation is the IOSA which was introduced by Gerber *et al.*²⁵ and Adams²⁷ in 1980 and since then has been used with major success.

In this work a quantum mechanical approach to treating reactive collisions between a molecule and a solid (stationary) surface is presented. However, the main emphasis is on the application of the IOSA for this case. Consequently the paper is arranged in the following way. In the next section the general theory for treating a reactive (or dissociative) collision between a diatomic molecule and a solid (stationary) surface is discussed. In Sec. III the IOSA for this case is presented. The quasicollinear case and the general case for an exchange collision with a noncorrugated surface are analyzed in Sec. IV and in Sec. V the main conclusions are discussed.

II. THE GENERAL CASE

In treating reactive systems one has to consider at least two arrangement channels: the initial one which is the reagents channel and the final one which is the products channel. In the atom–molecule case the initial and the final channels are similar in the sense that in both arrangements we have an atom and a diatomic molecule. Consequently, one would expect that the same kind of coordinates would apply in both cases, namely three polar coordinates (r, θ, ϕ) for the interatomic vibrotational motion and three polar coordinates (R, θ_R, ϕ_R) for the transorbital motion. In the reactive molecule–surface system a different situation is encountered; here the initial channel is a diatomic molecule and a surface and the final arrangement channel is a free atom and an atom bound to an (infinite) surface.

If S stands for “surface,” then the reactions to be treated are of the kind



where A and B are atoms.

The fact that as reagents A and B form a molecule and that as products they are unbound results in two different kinds of coordinates. (i) The reagents channel is best described by the three polar coordinates (r, θ, ϕ) for the interatomic vibrotational motion and the three Cartesian coordinates ($X_\lambda, Y_\lambda, Z_\lambda$) for the translational motion. (Since the

system, due to the existence of the infinite surface, has lost its spherical symmetry, the spherical coordinates for the translational motion are inappropriate.) (ii) The products channel seems to be best described in terms of two sets of Cartesian coordinates: the coordinates (x_v, y_v, z_v) of the bound atom and the coordinates (X_v, Y_v, Z_v) of the unbound atom. The indices λ and v stand for the two arrangement channels, respectively. The various coordinates are shown in Fig. 1.

The Schrödinger equation for the entrance channel is

$$[T_{R\lambda} + T_{r\lambda} + V(X_\lambda, Y_\lambda, Z_\lambda, r, \theta, \phi)]\psi_\lambda = E\psi_\lambda, \quad (2.2)$$

where

$$T_{R\lambda} = -\frac{\hbar^2}{2\mu_{R\lambda}}\left(\frac{\partial^2}{\partial X_\lambda^2} + \frac{\partial^2}{\partial Y_\lambda^2} + \frac{\partial^2}{\partial Z_\lambda^2}\right), \quad (2.3)$$

$$T_{r\lambda} = -\frac{\hbar^2}{2\mu_{r\lambda}}\left[\frac{1}{r}\frac{\partial}{\partial r}r + \frac{1}{r^2\sin^2\theta}\left(\left(\sin\theta\frac{\partial}{\partial\theta}\right)^2 + \frac{\partial^2}{\partial\phi^2}\right)\right], \quad (2.4)$$

and

$$\psi_\lambda = \psi_\lambda(X_\lambda, Y_\lambda, Z_\lambda, r, \theta, \phi). \quad (2.5)$$

Here $\mu_{R\lambda}$ is the reduced mass of the molecule with respect to the surface, namely:

$$\mu_{R\lambda} = m_A + m_B \quad (2.6)$$

and $\mu_{r\lambda}$ is the reduced mass of the molecule, namely:

$$\mu_{r\lambda} = \frac{m_A m_B}{m_A + m_B}. \quad (2.7)$$

In order to simplify the treatment we introduce the corresponding mass scaled coordinates:

$$\mathbf{R}'_\lambda = a_\lambda^{-1}\mathbf{R}_\lambda; \mathbf{r}'_\lambda = a_\lambda \mathbf{r}_\lambda; \quad a_\lambda = \left(\frac{m_A m_B}{(m_A + m_B)^2}\right)^{1/4}. \quad (2.8)$$

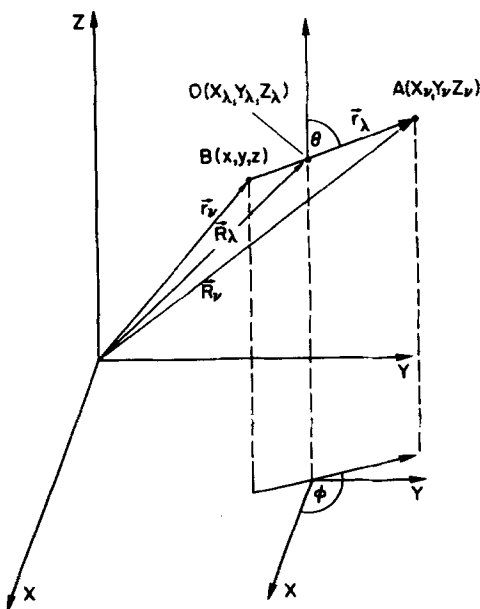


FIG. 1. Coordinates for a diatom-surface system. \mathbf{R}_λ and \mathbf{r}_λ are the appropriate coordinates for the λ arrangement channel and \mathbf{R}_v and \mathbf{r}_v are the appropriate coordinates for the v arrangement channel.

Consequently $T_{R\lambda}$ and $T_{r\lambda}$ become

$$T_{R\lambda} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial X_\lambda^2} + \frac{\partial^2}{\partial Y_\lambda^2} + \frac{\partial^2}{\partial Z_\lambda^2}\right), \quad (2.3')$$

$$T_{r\lambda} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial}{\partial r}r + \frac{1}{r^2\sin^2\theta}\left(\left(\sin\theta\frac{\partial}{\partial\theta}\right)^2 + \frac{\partial^2}{\partial\phi^2}\right)\right], \quad (2.4')$$

where we dropped the primes from $X_\lambda, Y_\lambda, Z_\lambda$ and r , and μ is the mass of the system, i.e.,

$$\mu = (m_A m_B)^{1/2}. \quad (2.9)$$

The Schrödinger equation for the exit channel (in terms of the corresponding mass scaled coordinates) is

$$[T_{Rv} + T_{rv} + V(X_v, Y_v, Z_v, x_v, y_v, z_v)]\psi_v = E\psi_v, \quad (2.10)$$

where

$$T_{Rv} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial X_v^2} + \frac{\partial^2}{\partial Y_v^2} + \frac{\partial^2}{\partial Z_v^2}\right), \quad (2.11)$$

$$T_{rv} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x_v^2} + \frac{\partial^2}{\partial y_v^2} + \frac{\partial^2}{\partial z_v^2}\right). \quad (2.12)$$

The transformation from one system of coordinates to the other is given by

$$\mathbf{R}_v = \mathbf{R}_\lambda \cos\beta + \mathbf{r}_\lambda \sin\beta, \quad (2.13)$$

$$\mathbf{r}_v = \mathbf{R}_\lambda \sin\beta - \mathbf{r}_\lambda \cos\beta,$$

where

$$\cos\beta = \left(\frac{m_A}{m_A + m_B}\right)^{1/2}; \quad \sin\beta = \left(\frac{m_B}{m_A + m_B}\right)^{1/2}. \quad (2.14)$$

Here we assume that the final bound atom is B and the free atom is A.

From Eq. (2.13) the following explicit relations can be obtained:

$$X_v = X_\lambda \cos\beta + r \sin\theta \cos\phi \sin\beta, \quad (2.15a)$$

$$Y_v = X_\lambda \cos\beta + r \sin\theta \sin\phi \sin\beta, \quad (2.15b)$$

$$Z_v = Z_\lambda \cos\beta + r \cos\theta \sin\beta, \quad (2.15c)$$

$$x = X_\lambda \sin\beta - r \sin\theta \cos\phi \cos\beta, \quad (2.15d)$$

$$y = Y_\lambda \sin\beta - r \sin\theta \sin\phi \cos\beta, \quad (2.15e)$$

$$z = Z_\lambda \sin\beta - r \cos\theta \cos\beta. \quad (2.15f)$$

The index v has been dropped from x_v, y_v , and z_v (no confusion results).

For what follows we assume that the surface is a rectangular lattice with dimensions e_x and e_y and an area A . The wave function in the λ arrangement is expanded in terms of the surface diffraction states and molecular rotational states³¹:

$$\psi_\lambda(\mathbf{R}_\lambda, \mathbf{r}_\lambda) = \frac{1}{\sqrt{A}} \sum_{\mathbf{q}, \mathbf{p}_\lambda} \sum_{j, m} \frac{1}{r} \exp[i(\mathbf{G}_{\mathbf{q}, \mathbf{p}_\lambda} + \mathbf{K}_\lambda) \cdot \mathbf{r}_\lambda] \times y_{jm}(\theta, \phi) \chi_{\mathbf{q}, \mathbf{p}_\lambda, j, m}^{(\lambda)}(r, Z_\lambda), \quad (2.16)$$

where $y_{jm}(\theta, \phi)$ are the free rotor states of the diatomic molecule and $\mathbf{G}_{\mathbf{q}, \mathbf{p}_\lambda}, \mathbf{K}_\lambda$, and \mathbf{p}_λ are vectors parallel to the surface

$$\mathbf{p}_\lambda = (X_\lambda, Y_\lambda, 0), \quad (2.17a)$$

$$\mathbf{K}_\lambda = (k_{\lambda x}, k_{\lambda y}, 0), \quad (2.17b)$$

$$\mathbf{G}_{q\lambda p_\lambda} = \left(\frac{2\pi}{e_x} q_\lambda, \frac{2\pi}{e_y} p_\lambda, 0 \right). \quad (2.17c)$$

Here \mathbf{K}_λ is the projection of the wave vector $\mathbf{k}_\lambda (= k_{\lambda x}, k_{\lambda y}, k_{\lambda z})$ on the surface and $\mathbf{G}_{q\lambda p_\lambda}$ are the reciprocal space vectors. The appearance of a_λ in the argument of the exponential in Eq. (2.16) is due to the fact that \mathbf{p} is expressed in mass scaled coordinates. Substituting Eq. (2.16) in Eq. (2.2), multiplying through by $\exp[-i(G_{q\lambda p_\lambda} + \mathbf{K}_\lambda) \cdot \mathbf{a}_\lambda \cdot \mathbf{p}_\lambda] y_{jm'}^*(\theta, \phi)$ and integrating over $X_\lambda, Y_\lambda, \theta$, and ϕ , one obtains the following coupled system of differential equations for $\chi_{q\lambda p_\lambda jm}(r, Z_\lambda)$:

$$-\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial Z_\lambda^2} + \frac{\partial^2}{\partial r^2} - \frac{j(j+1)}{r^2} + \overline{k_{q\lambda p_\lambda}^{(\lambda)}} \right] \chi_{q\lambda p_\lambda jm}^{(\lambda)} + \sum_{q'_\lambda p'_\lambda j'm'} \langle q_\lambda p_\lambda jm | V | q'_\lambda p'_\lambda j'm' \rangle \chi_{q'_\lambda p'_\lambda j'm'}^{(\lambda)} = 0, \quad (2.18)$$

where

$$\overline{k_{q\lambda p_\lambda}^{(\lambda)}} = \left\{ \frac{2\mu}{\hbar^2} E - a_\lambda^2 \left[\left(\frac{2\pi}{e_x} q_\lambda + k_{\lambda x} \right)^2 + \left(\frac{2\pi}{e_y} p_\lambda + k_{\lambda y} \right)^2 \right] \right\}^{1/2} \quad (2.19)$$

and

$$\begin{aligned} \langle q_\lambda p_\lambda jm | V | q'_\lambda p'_\lambda j'm' \rangle &= \frac{1}{A} \int_0^{e_x/a_\lambda} \int_0^{e_y/a_\lambda} \int_0^{2\pi} \int_{-1}^{+1} dX_\lambda dY_\lambda d(\cos \theta) d\phi \\ &\times \exp[-ia_\lambda \mathbf{G}_{q\lambda p_\lambda} \cdot \mathbf{p}_\lambda] y_{jm}^*(\theta, \phi) V(X_\lambda, Y_\lambda, Z_\lambda, r, \theta, \phi) \\ &\times y_{j'm'}(\theta, \phi) \exp[ia_\lambda \mathbf{G}_{q'_\lambda p'_\lambda} \cdot \mathbf{p}_\lambda]. \end{aligned} \quad (2.20)$$

$$\begin{aligned} \langle q_\nu p_\nu \alpha \beta | U | q'_\nu p'_\nu \alpha' \beta' \rangle &= \frac{1}{A} \int_0^{e_x/a_\nu} \int_0^{e_y/a_\nu} \int_0^{e_z/a_\nu} \int_0^{e_\nu/a_\nu} dX_\nu dY_\nu dx dy \\ &\times \exp[-ia_\nu \mathbf{G}_{q_\nu p_\nu} \cdot \mathbf{p}_\nu] \xi_{\alpha\beta}^*(x, y) U(X_\nu, Y_\nu, Z_\nu, x, y, z) \xi_{\alpha'\beta'}(x, y) \exp[ia_\nu \mathbf{G}_{q'_\nu p'_\nu} \cdot \mathbf{p}_\nu]. \end{aligned} \quad (2.24)$$

Here $\epsilon_{\alpha\beta}$ is an eigenvalue of the equation

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + v(x, y, \bar{z}) - \epsilon_{\alpha\beta} \right] \xi_{\alpha\beta}(x, y, \bar{z}) = 0. \quad (2.25)$$

The potential $v(x, y, \bar{z})$ is defined as

$$\lim_{Z_\nu \rightarrow \infty} V(X_\nu, Y_\nu, Z_\nu, x, y, \bar{z}) = v(x, y, \bar{z}), \quad (2.26)$$

where $V(X_\nu, Y_\nu, Z_\nu, x, y, z)$ is the potential of the system. The coordinate \bar{z} is a given fixed value of z . [In case it is taken to be equal to z , Eq. (2.22) has to be modified accordingly.]

Finally, the potential $U(X_\nu, Y_\nu, Z_\nu, x, y, z)$ is defined as

$$U(X_\nu, Y_\nu, Z_\nu, x, y, z) = V(X_\nu, Y_\nu, Z_\nu, x, y, z) - v(x, y, \bar{z}). \quad (2.27)$$

In order to find the corresponding S matrix elements the two sets of coupled differential equations, i.e., Eqs. (2.18) and (2.22), each in the corresponding arrangement channel, are integrated to form all the independent solutions. These solutions are then used to construct the total wave function

Here, as was done in other similar cases, the upper limits of the integrals over X_λ and Y_λ were changed due to the scaling.

The wave function in the ν arrangement is expanded in terms of the surface diffraction states and the (x, y) part of the bounded atom eigenstates:

$$\psi(\mathbf{R}_\nu, \mathbf{r}_\nu) = \frac{1}{\sqrt{A}} \sum_{q_\nu p_\nu} \sum_{\alpha\beta} \exp[i(\mathbf{G}_{q_\nu p_\nu} + \mathbf{K}_\nu) \cdot \mathbf{a}_\nu \cdot \mathbf{p}_\nu] \xi_{\alpha\beta}(x, y) \chi_{q_\nu p_\nu \alpha\beta}^{(\nu)}(z, Z_\nu), \quad (2.21)$$

where $\xi_{\alpha\beta}(x, y)$ are the (x, y) part of the bound atom eigenstate, $\mathbf{G}_{q_\nu p_\nu}$, \mathbf{K}_ν and \mathbf{p}_ν are the vectors defined similarly to $\mathbf{G}_{q\lambda p_\lambda}$, \mathbf{K}_λ , and \mathbf{p}_λ [see Eq. (2.17)] and a_ν is a coefficient that enters due to the scaling in the ν arrangement:

$$\mathbf{R}'_\nu = a_\nu^{-1} \mathbf{R}_\nu; \quad \mathbf{r}'_\nu = a_\nu \mathbf{r}_\nu; \quad a_\nu = (m_B/m_A)^{1/4}. \quad (2.8')$$

The corresponding set of coupled differential equations is

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial Z_\nu^2} + \frac{\partial^2}{\partial z^2} + \overline{k_{q_\nu p_\nu \alpha\beta}^{(\nu)}} \right) \chi_{q_\nu p_\nu \alpha\beta}^{(\nu)} + \sum_{q'_\nu p'_\nu \alpha'\beta'} \langle q_\nu p_\nu \alpha\beta | U | q'_\nu p'_\nu \alpha'\beta' \rangle \chi_{q'_\nu p'_\nu \alpha'\beta'}^{(\nu)} = 0, \quad (2.22)$$

where

$$\overline{k_{q_\nu p_\nu \alpha\beta}^{(\nu)}} = \left\{ \frac{2\mu}{\hbar^2} (E - \epsilon_{\alpha\beta}) - a_\nu^2 \left[\left(\frac{2\pi}{e_x} q_\nu + k_{\nu x} \right)^2 + \left(\frac{2\pi}{e_y} p_\nu + k_{\nu y} \right)^2 \right] \right\}^{1/2} \quad (2.23)$$

and

which is continuous and has a continuous derivative over the entire space and also has the correct physical asymptotic form. In order to achieve this the solutions in the two arrangement channels have to be matched on a surface which separates the two channels. It seems that the best (matching) surface is the one described by the equation

$$r = r_0(\text{const}), \quad (2.28)$$

where for a given energy r_0 is large enough so that

$$\lim_{Z_\lambda \rightarrow \infty} \psi(X_\lambda, Y_\lambda, Z_\lambda, r, \theta, \phi)|_{r=r_0} \sim 0. \quad (2.29)$$

III. THE INFINITE ORDER SUDDEN APPROXIMATION (IOSA) FOR THE REACTIVE MOLECULE-SURFACE SYSTEM

In collision processes between molecular species the number of degrees of freedom is usually large. The minimal number is six (for an atom-diatom case) and each additional atom adds three more degrees of freedom thus making the

treatment of any realistic system a formidable task. However, with many degrees of freedom, one is usually able to distinguish between fast varying and slow varying degrees of freedom. In case such a distinction can be made, a variety of approximations become apparent. The first to employ this idea successfully in atomic physics were Born and Oppenheimer³² who separated the treatment of the fast moving electrons from the slow moving nuclei, thus opening the field of atomic and molecular physics to theoretical investigations. Since then this idea was used under different names in various cases. In molecular scattering processes it goes under the name infinite order sudden approximation (IOSA).³³ The IOSA was developed and then mainly applied for atom molecule collisions, but was recently also extended to molecule–surface collisions.^{22,25–30}

According to this approximation the translational coordinate R and eventually the vibrational coordinate r are the “fast” coordinates, whereas the “slow” ones are the angular coordinates. In nonreactive collisions one encounters, in the simple atom–diatom case, only one angular coordinate $\gamma = \cos^{-1}(\hat{R} \cdot \hat{r})$ because the other three can be eliminated by symmetry. In exchange collisions two angles are encountered, namely, again γ and an angle $\Delta = \cos^{-1}(\hat{R}_\lambda \cdot \hat{R}_\nu)$ which is associated with transformation from the λ arrangement to the ν arrangement (\hat{R}_λ and \hat{R}_ν are the two corresponding translational unit vectors).

The study of the molecule surface interaction is much more complicated because, in general, no symmetry relations hold. Therefore none of the four coordinates (besides R and r , or to be more exact Z and r) can be eliminated, like in the previous case. Thus the IOSA has to be applied with respect to each of the four degrees of freedom in order to be able to reduce the problem to a tractable numerical one. The treatment of such a system becomes much more involved when the molecule is allowed to react with the surface. In such a case, as we have seen in the previous chapter, one encounters at least two arrangements, each characterized by six coordinates. The difficulty is not only in handling two arrangement channels instead of one, but also in guaranteeing that in the transformation from one arrangement to the other, the slow coordinates of the first arrangement will transform, independent of the fast coordinates, to the slow coordinates of the second arrangement.

In order to show how such a transformation can be constructed we consider first the atom–diatom case. In each arrangement one encounters four coordinates ($R_\alpha, r_\alpha, \gamma_\alpha, \theta_\alpha$) where $\alpha = \lambda, \nu$, of which the two fast coordinates are R_α and r_α and the slow ones are γ_α and θ_α . [It has to be emphasized that in contrast to R_α, r_α , and γ_α , the angles θ_λ and θ_ν are relevant only for the transformation from one arrangement to the other. In fact only the difference between the two, namely $\Delta = \theta_\nu - \theta_\lambda$, is of importance and it can be shown that $\Delta = \Delta(R_\lambda, r_\lambda, \gamma_\lambda)$.]

In the general case the transformation from one arrangement to the other is performed on a surface which separates the two arrangements. Such a surface is obtained, for instance, from the relation

$$r_\nu = Br_\lambda \quad (3.1)$$

which yields the equation of the surface^{1–3,34}

$$R_\lambda^2 \sin^2 \beta + r_\lambda^2 (\cos^2 \beta - B^2) - r_\lambda R_\lambda \cos \gamma_\lambda \sin 2\beta = 0, \quad (3.2)$$

where B is a given constant and

$$\cos \beta = \sqrt{\frac{m_A m_C}{(m_A + m_B)(m_C + m_B)}},$$

$$\sin \beta = \sqrt{1 - \cos^2 \beta}. \quad (3.3)$$

Here m_A , m_B , and m_C are the masses of the three interacting atoms. It can be shown that on the surface the relation between the two sets of the slow coordinates is

$$\cos \gamma_\nu = -\frac{\cos \gamma_\lambda - (1 - B^2) \tan \eta \cot \beta}{B [1 + (1 - B^2) \tan^2 \eta]^{1/2}} \quad (3.4)$$

and

$$\cos(\theta_\nu - \theta_\lambda) = \cos \Delta = -\frac{\cos \beta + \cos \gamma_\lambda \sin \beta \tan \eta}{[1 + (1 - B^2) \tan^2 \eta]^{1/2}}, \quad (3.5)$$

where

$$\tan \eta = \frac{\sin \beta}{B^2 - \cos^2 \beta} [-\cos \beta \cos \gamma_\lambda + (B^2 - \sin^2 \gamma_\lambda \cos^2 \beta)^{1/2}]. \quad (3.6)$$

In the framework of the IOSA the surface given by Eq. (3.2) reduces to a straight line which goes through the origin and the relations (3.4)–(3.6) are all still valid.

In order to look for a separating surface like that in the molecule–solid surface case, we have to consider Eq. (2.13) as evaluated in Eqs. (2.15). The fast coordinates in the λ channel will be like in the atom–molecule case (but with the obvious changes), i.e., the translational coordinate Z_λ and the vibrational coordinate r . Consequently the slow coordinates are $X_\lambda, Y_\lambda, \theta$, and ϕ . For the ν channel one obvious fast coordinate will be, like in all previous cases, the translational coordinate Z_ν . The best choice for the other fast coordinate is probably z which is the obvious choice for the collinear case (when $\theta = \phi = 0$). If Z_ν and z are the fast coordinates, then X_ν, Y_ν, x , and y are the corresponding slow coordinates. Therefore we have to guarantee that in transforming from the λ arrangement to the ν arrangement the four slow λ coordinates ($X_\lambda, Y_\lambda, \theta, \phi$) will transform to the slow ν coordinates, i.e., (X_ν, Y_ν, x, y) independent of the fast coordinates in the two arrangements. It should be mentioned that making slow the horizontal coordinates $X_\lambda, Y_\lambda, X_\nu$, and Y_ν in comparison with the normal coordinates Z_λ and Z_ν implies that the approaching and receding particles are moving in the vicinity of the normal to the surface.

At this stage we have to distinguish between two cases:

(i) $\theta = 0$.

We have [see Eq. (2.15)]

$$X_\nu = X_\lambda \cos \beta; \quad Y_\nu = Y_\lambda \cos \beta, \quad (3.7)$$

$$x = X_\lambda \sin \beta; \quad y = Y_\lambda \sin \beta.$$

It can be seen that the slow coordinates will always transform to slow coordinates. The case $\theta = 0$ is an extended “collinear” case for the atom–surface case. Note that the collinear arrangement is encountered without making any addi-

tional requirements concerning X_λ and Y_λ .

(ii) $\theta \neq 0$.

In the general case the slow \rightarrow slow transformation can be obtained only along the surface

$$r = \text{const} = r_0 \quad (3.8)$$

which becomes a straight line in the IOSA reduced space. Thus, the slow \rightarrow slow transformation is

$$\begin{aligned} X_\nu &= X_\lambda \cos \beta + r_0 \sin \theta \cos \phi \sin \beta, \\ Y_\nu &= Y_\lambda \cos \beta + r_0 \sin \theta \sin \phi \sin \beta, \\ x &= Y_\lambda \sin \beta - r_0 \sin \theta \cos \phi \cos \beta, \\ y &= Y_\lambda \sin \beta - r_0 \sin \theta \sin \phi \cos \beta. \end{aligned} \quad (3.9)$$

The IOSA Schrödinger equation for the λ channel is [see Eq. (2.18)]:

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial Z_\lambda^2} + \frac{\partial^2}{\partial r^2} \right) + V(Z_\lambda, r; X_\lambda, Y_\lambda, \theta, \phi) - \frac{\hbar^2}{2\mu} \bar{k}_{\lambda z}^2 \right] \chi^\lambda(Z_\lambda, r; X_\lambda, Y_\lambda, \theta, \phi) = 0. \quad (3.10)$$

Here it is assumed that $\bar{k}_{\lambda z}$ introduced in Eq. (2.19) fulfills the condition

$$\bar{k}_{\lambda z}^2 \gg G_{q_\lambda p_\lambda}^2 a_\lambda^2 \quad (3.11)$$

so that [see Eq. (2.19)]

$$\bar{k}_{\lambda z}^2 = k_{q_\lambda p_\lambda}^2 = \frac{2\mu}{\hbar^2} E - (k_{\lambda x}^2 + k_{\lambda y}^2) a_\lambda^2. \quad (3.12)$$

The rotational energy term $j(j+1)\hbar^2/(2\mu r^2)$ is discarded by the same reasoning (or we may assume that the initial j is equal to zero). The corresponding IOSA Schrödinger equation for the ν channel is [see Eq. (2.22)]

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial Z_\nu^2} + \frac{\partial^2}{\partial z^2} \right) + V(Z_\nu, z; X_\nu, Y_\nu, x, y) - \frac{\hbar^2}{2\mu} \bar{k}_{\nu z}^2 \right] \chi^\nu(Z_\nu, z; X_\nu, Y_\nu, x, y) = 0, \quad (3.13)$$

where [see Eq. (2.23)]

$$\bar{k}_{\nu z}^2 = k_{q_\nu p_\nu}^2 = \frac{2\mu}{\hbar^2} E - (k_{\nu x}^2 + k_{\nu y}^2) a_\nu^2. \quad (3.14)$$

Here, like in the λ channel, it is assumed that

$$\bar{k}_{\nu z}^2 \gg G_{q_\nu p_\nu}^2 a_\nu^2; \quad \bar{k}_{\nu z}^2 \gg \frac{2\mu}{\hbar^2} \epsilon_{\alpha\beta}. \quad (3.15)$$

Integration of Eqs. (3.10) and (3.13) and matching the solutions along a straight line in the interaction region as discussed earlier, leads to a reactive S matrix element of the type

$$\begin{aligned} \langle q_\nu p_\nu \alpha \beta n_\nu | S | q_\lambda p_\lambda j m n_\lambda \rangle &= \frac{1}{A} \int_0^{e_x/a_\lambda} \int_0^{e_y/a_\lambda} \int_{-1}^{+1} \int_0^{2\pi} dX_\lambda dY_\lambda d(\cos \theta) d\phi \\ &\times \xi_{\alpha\beta}^*(x, y) \exp[-ia_\nu(\mathbf{G}_{q_\nu p_\nu} + \mathbf{K}_\nu) \cdot \mathbf{p}_\nu] S_{\lambda n_\lambda}^{\nu n_\nu}(X_\lambda, Y_\lambda, \theta, \phi) \exp[ia_\lambda(\mathbf{G}_{q_\lambda p_\lambda} + \mathbf{K}_\lambda) \cdot \mathbf{p}_\lambda] y_{jm}(\theta, \phi), \end{aligned} \quad (3.16)$$

where X_ν , Y_ν , x , and y are all dependent on X_λ , Y_λ , θ , and ϕ as given by Eq. (3.9). The term $S_{\lambda n_\lambda}^{\nu n_\nu}(X_\lambda, Y_\lambda, \theta, \phi)$ is the reactive IOSA S -matrix element as calculated for fixed X_λ , Y_λ , θ , and ϕ . Here n_λ is the (initial) vibrational state of the diatomic molecule and n_ν is the (final) vibrational state (in the z direction) of the bound atom.

Equation (3.16) can be simplified by using Eq. (3.9), i.e.,

$$\mathbf{p}_\nu = \cos \beta \mathbf{p}_\lambda + r_0 \sin \theta \sin \beta \hat{\mathbf{u}}, \quad (3.17)$$

where $\hat{\mathbf{u}}$ is unit vector along the projected axis of the molecule:

$$\hat{\mathbf{u}} = \cos \hat{u}_x + \sin \hat{u}_y, \quad (3.18)$$

where \hat{u}_x and \hat{u}_y are unit vectors along the x and y axes. From Eqs. (2.8), (2.14), and (2.8') we also have

$$a_\lambda = a_\nu \cos \beta. \quad (3.19)$$

Substituting Eqs. (3.17) and (3.19) in Eq. (3.16), one obtains

$$\begin{aligned} \langle q_\nu p_\nu \alpha \beta n_\nu | S | q_\lambda p_\lambda j m n_\lambda \rangle &= \frac{1}{A} \int_0^{e_x/a_\lambda} \int_0^{e_y/a_\lambda} \int_{-1}^{+1} \int_0^{2\pi} dX_\lambda dY_\lambda d(\cos \theta) d\phi \\ &\times \xi_{\alpha\beta}^*(x, y) \exp[ia_\lambda \Gamma] S_{\lambda n_\lambda}^{\nu n_\nu}(X_\lambda, Y_\lambda, \theta, \phi) y_{jm}(\theta, \phi), \end{aligned} \quad (3.20)$$

where Γ is given in the form

$$\begin{aligned} \Gamma &= (\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_\nu p_\nu} + \mathbf{K}_\nu - \mathbf{K}_\lambda) \cdot \mathbf{p}_\lambda \\ &- r_0 \sin \theta \tan \beta (\mathbf{G}_{q_\nu p_\nu} + \mathbf{K}_\nu) \cdot \hat{\mathbf{u}}. \end{aligned} \quad (3.21)$$

So far the value of \mathbf{K}_ν is undetermined. However, in order to obtain a Hermitian S matrix for the quasicollinear systems, the two k 's appearing in Eqs. (3.10) and (3.13), namely $\bar{k}_{\lambda z}$ and $\bar{k}_{\nu z}$, have to be identical. Thus, employing Eqs. (3.12) and (3.14), we have that this requirement is fulfilled if

$$\mathbf{K}_\nu = \mathbf{K}_\lambda \cos \beta. \quad (3.22)$$

Equation (3.21) simplifies significantly for the case $\beta \sim 0$, namely when the reacting atom (i.e., atom B) is much lighter than the dissociative atom. For this case Eq. (3.21) becomes

$$\Gamma = (\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_\nu p_\nu}) \cdot \mathbf{p}_\lambda, \quad (3.23)$$

which is very similar to the inelastic result.

IV. SPECIAL CASES

A. The collinear case

The collinear case is of particular importance because it is the only case where the matching line does not have to be defined by $r = r_0$, but can also be chosen as

$$z = Br, \quad (4.1)$$

where B is a given constant. This choice is used extensively in IOSA treatments for atom-molecule collisions and was found to yield reliable results.^{1-3,34}

In this case Eq. (3.10) reduces to

$$\begin{aligned} \langle q_v p_v \alpha \beta n_v | S | q_\lambda p_\lambda n_\lambda \rangle \\ = \frac{1}{A} \int_0^{e_x/a_\lambda} \int_0^{e_y/a_\lambda} dX_\lambda dY_\lambda \xi_{\alpha\beta}^*(x, y) e^{ia_\lambda \Gamma} S_{\lambda n_\lambda}^{v n_v}(X_\lambda, Y_\lambda), \end{aligned} \quad (4.2)$$

where Γ is given as

$$\Gamma = (\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_v p_v} + \mathbf{K}_\lambda - \mathbf{K}_v) \cdot \mathbf{p}_\lambda \quad (4.3)$$

or if the relation in Eq. (3.22) is assumed:

$$\Gamma = [\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_v p_v} + \mathbf{K}_\lambda (1 - \cos \beta)] \cdot \mathbf{p}_\lambda. \quad (4.4)$$

For the case $\beta \sim 0$, Eq. (4.4) reduces to Eq. (3.23).

B. The treatment for an uncorrugated surface

To treat the uncorrugated case one may assume that the quasicollinear S matrix elements $S_{\lambda n_\lambda}^{v n_v}$ are independent of X_λ , Y_λ , and the angle ϕ and can therefore be shifted in front of the corresponding integrals.

In this particular case we also have to refer to the horizontal basis set functions $\xi_{\alpha\beta}(x, y)$ in greater detail. Since the surface is flat the potential is not dependent on x and y (or on X_λ and Y_λ) and therefore $\xi_{\alpha\beta}(x, y)$ are no longer a discrete set of functions, but rather a continuous one. Consequently $\xi(x, y)$ satisfies the equation

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + a_v^{-2} Q_v^2 \right) \xi(x, y) = 0, \quad (4.5)$$

where \mathbf{Q}_v is the horizontal momentum associated with the bound particle. The solution of this equation is

$$\xi(x, y) = (1/2\pi) \exp[i a_v^{-1} (\mathbf{Q}_v \cdot \mathbf{r}_v)], \quad (4.6)$$

where

$$\mathbf{r}_v = (x, y). \quad (4.7)$$

Due to this modification Eq. (3.16) becomes

$$\langle q_v p_v n_v | S | q_\lambda p_\lambda j m n_\lambda \rangle = \int_{-1}^{+1} d(\cos \theta) S_{\lambda n_\lambda}^{v n_v}(\theta) W(\theta), \quad (4.8)$$

where

$$W(\theta) = \frac{1}{2\pi A} \int_0^{e_x/a_\lambda} \int_0^{e_y/a_\lambda} \int_0^{2\pi} dX_\lambda dY_\lambda d\phi y_{jm}(\theta, \phi) e^{-i\Gamma}. \quad (4.9)$$

$$\begin{aligned} \Gamma = a_\lambda (\mathbf{G}_{q_\lambda p_\lambda} + \mathbf{K}_\lambda) \cdot \mathbf{p}_\lambda - a_\lambda \cos^{-1} \beta (\mathbf{G}_{q_v p_v} + \mathbf{K}_\lambda \cos^2 \beta + P_u \hat{\mathbf{u}} + P_\tau \hat{\boldsymbol{\tau}}) \\ \cdot (\mathbf{p}_v \cos \beta + r_0 \sin \beta \sin \theta \hat{\mathbf{u}}) + a_\lambda \sin^{-1} \beta \\ \times (\mathbf{K}_\lambda \sin^2 \beta - P_u \hat{\boldsymbol{\tau}} - P_\tau \hat{\mathbf{u}}) (\mathbf{p}_\lambda \sin \beta - r_0 \cos \beta \sin \theta \hat{\mathbf{u}}). \end{aligned} \quad (4.18)$$

Thus,

$$\begin{aligned} \Gamma = a_\lambda \left\{ (\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_v p_v}) \cdot \mathbf{p}_\lambda \right. \\ \left. - r_0 \tan \beta \sin \theta (\mathbf{G}_{q_v p_v} \cdot \hat{\mathbf{u}}) - \frac{4\pi r_0 \sin \theta P_u}{\sin 2\beta} \right\}. \end{aligned} \quad (4.19)$$

Substituting Eq. (4.16a) for P_u and recalling that by definition:

Here

$$\Gamma = a_\lambda (\mathbf{G}_{q_\lambda p_\lambda} + \mathbf{K}_\lambda) \cdot \mathbf{p}_\lambda - a_v (\mathbf{G}_{q_v p_v} + \mathbf{K}_v) \cdot \mathbf{p}_v - a_v^{-1} \mathbf{Q}_v \cdot \mathbf{r}_v. \quad (4.10)$$

Before continuing we have to elaborate on \mathbf{K}_v and \mathbf{Q}_v , the horizontal linear moments of the free particle and of the bound particle, respectively. In order to derive them explicitly we have to differentiate Eqs. (3.9) with respect to time. Thus

$$\dot{\mathbf{p}}_v = \dot{\mathbf{p}}_\lambda \cos \beta + r_0 \sin \beta (\cos \theta \dot{\theta} \hat{\mathbf{u}} - \sin \theta \dot{\phi} \hat{\boldsymbol{\tau}}), \quad (4.11a)$$

$$\dot{\mathbf{r}}_v = \dot{\mathbf{p}}_\lambda \sin \beta - r_0 \cos \beta (\cos \theta \dot{\theta} \hat{\mathbf{u}} - \sin \theta \dot{\phi} \hat{\boldsymbol{\tau}}). \quad (4.11b)$$

Here $\hat{\mathbf{u}}$ is a unit vector along the projected axis of the molecule and $\hat{\boldsymbol{\tau}}$ is a unit vector perpendicular to it:

$$\hat{\mathbf{u}} = \cos \phi \hat{\mathbf{u}}_x + \sin \phi \hat{\mathbf{u}}_y, \quad (4.12a)$$

$$\hat{\boldsymbol{\tau}} = -\sin \phi \hat{\mathbf{u}}_x + \cos \phi \hat{\mathbf{u}}_y. \quad (4.12b)$$

Since

$$\frac{1}{2\pi} \mathbf{K}_\lambda = (m_A + m_B) a_\lambda \dot{\mathbf{p}}_\lambda, \quad (4.13a)$$

$$\frac{1}{2\pi} \mathbf{K}_v = m_A a_v \dot{\mathbf{p}}_v, \quad (4.13b)$$

$$\frac{1}{2\pi} \mathbf{Q}_v = m_B a_v^{-1} \dot{\mathbf{r}}_v, \quad (4.13c)$$

we obtain

$$\mathbf{K}_v = \mathbf{K}_\lambda \cos^2 \beta + \mathbf{P}, \quad (4.14a)$$

$$\mathbf{Q}_v = \mathbf{K}_\lambda \sin^2 \beta - \mathbf{P}, \quad (4.14b)$$

where

$$\mathbf{P} = P_u \hat{\mathbf{u}} + P_\tau \hat{\boldsymbol{\tau}}. \quad (4.15)$$

Here \mathbf{P}_u and \mathbf{P}_τ are

$$\frac{1}{2\pi} P_u = \mu a_\lambda r_0 \cos \theta \dot{\theta}, \quad (4.16a)$$

$$\frac{1}{2\pi} P_\tau = -\mu a_\lambda r_0 \sin \theta \dot{\phi}. \quad (4.16b)$$

From Eqs. (4.14), it also follows that

$$\mathbf{K}_\lambda = \mathbf{K}_v + \mathbf{Q}_v. \quad (4.13d)$$

This equation represents the conservation of the horizontal linear momentum. As a final expression to be considered, Eqs. (3.9) are rewritten as

$$\mathbf{p}_v = \mathbf{p}_\lambda \cos \beta + r_0 \sin \beta \sin \theta \hat{\mathbf{u}}, \quad (4.17a)$$

$$\mathbf{r}_v = \mathbf{p}_\lambda \sin \beta - r_0 \cos \beta \sin \theta \hat{\mathbf{u}}. \quad (4.17b)$$

Substituting Eqs. (4.14)–(4.17) in Eq. (4.10) and using Eq. (4.4), one obtains

$$j = \mu r_0^2 \dot{\theta}, \quad (4.20)$$

we obtain

$$\begin{aligned} \Gamma = a_\lambda \left\{ (\mathbf{G}_{q_\lambda p_\lambda} - \mathbf{G}_{q_v p_v}) \cdot \mathbf{p}_\lambda \right. \\ \left. - r_0 \tan \beta \sin \theta (\mathbf{G}_{q_v p_v} \cdot \hat{\mathbf{u}}) \right\} - \pi j \sin 2\theta. \end{aligned} \quad (4.21)$$

The integration in Eq. (4.9) with respect to X_λ and Y_λ can be performed without any difficulties. Thus if

$$f(q_v, p_v, j, m | \theta) = \int_0^{2\pi} d\phi y_{jm}(\theta, \phi) \exp[-ia_\lambda r_0 \tan \beta \sin \theta \times (\mathbf{G}_{q_v p_v} \cdot \hat{\mathbf{u}}) + \pi j \sin 2\theta], \quad (4.22)$$

the function $W(\theta)$ becomes

$$W(\theta) = \frac{e^{2\pi i(q_\lambda - q_v)} - 1}{2\pi(q_\lambda - q_v)} \cdot \frac{e^{2\pi i(p_\lambda - p_v)} - 1}{2\pi(p_\lambda - p_v)} f(q_v, p_v, j, m | \theta) \quad (4.23)$$

or

$$W(\theta) = \delta_{q_\lambda q_v} \delta_{p_\lambda p_v} f(q_\lambda, p_\lambda, j, m | \theta), \quad (4.24)$$

where q_v and p_v were replaced by q_λ and p_λ , respectively. To evaluate $f(q_\lambda, p_\lambda, j, m | \theta)$ we have to fix $\mathbf{G}_{q_\lambda p_\lambda}$. In fact, in the noncorrugated case $\mathbf{G}_{q_\lambda p_\lambda}$ is not well defined because the unit cell dimensions e_x and e_y are not known. Therefore, one assumes either e_x and e_y become infinity or q_λ and p_λ become zero. In either case the result is the same, namely:

$$W(\theta) = \delta_{q_\lambda p_\lambda} \delta_{q_v p_v} \bar{f}(j, m | \theta), \quad (4.25)$$

where

$$\bar{f}(j, m | \theta) = \int_0^{2\pi} d\phi y_{jm}(\theta, \phi) \exp[-ij\pi \sin 2\theta]. \quad (4.26)$$

Since the spherical harmonics $y_{jm}(\theta, \phi)$ for any j and m , including $j = m = 0$, are an orthonormal set, the integration over ϕ leads to

$$\bar{f}(j, m | \theta) = 2\pi \delta_{m0} y_{j0}(\theta, 0) e^{-ij\pi \sin 2\theta}. \quad (4.27)$$

Further simplifications are obtained from the relation

$$y_{jm}(\theta, 0) = \sqrt{\frac{2j+1}{4\pi}} P_j(\cos \theta), \quad (4.28)$$

so that

$$\bar{f}(j, m | \theta) = \delta_{m0} \sqrt{\pi(2j+1)} P_j(\cos \theta) e^{-ij\pi \sin 2\theta}. \quad (4.29)$$

Finally the function $W(\theta)$ becomes

$$W(\theta) = \delta_{q_\lambda q_v} \delta_{p_\lambda p_v} \delta_{m0} \sqrt{\pi(2j+1)} P_j(\cos \theta) e^{-ij\pi \sin 2\theta} \quad (4.30)$$

and the physical S matrix

$$\langle q_v p_v n_v | S | q_\lambda p_\lambda j m n_\lambda \rangle = \delta_{q_\lambda p_\lambda} \delta_{q_v p_v} \delta_{m0} \sqrt{\pi(2j+1)} \int_{-1}^{+1} d(\cos \theta) P_j(\cos \theta) \times e^{-ij\pi \sin 2\theta} S_{\lambda n_\lambda}^{v n_v}(\theta). \quad (4.31)$$

The corresponding cross section is given in the form

$$\sigma(n_v | j m n_\lambda) = \frac{\pi(2j+1)}{k_{n_j}^2} \delta_{m0} \left| \int_{-1}^{+1} d(\cos \theta) P_j(\cos \theta) e^{-ij\pi \sin 2\theta} S_{\lambda n_\lambda}^{v n_v}(\theta) \right|^2, \quad (4.32)$$

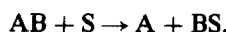
where the diffraction quantum numbers were ignored (due to redundancy). Summing over m and dividing by $(2j+1)$ one obtains

$$\sigma(n_v | j n_\lambda) = \frac{\pi}{k_{n_j}^2} \left| \int_{-1}^{+1} d(\cos \theta) P_j(\cos \theta) e^{-ij\pi \sin 2\theta} S_{\lambda n_\lambda}^{v n_v}(\theta) \right|^2 \quad (4.33)$$

which is the corresponding reactive molecule surface version for the degeneracy averaged cross section.

V. CONCLUSIONS

In this paper a theory is presented which permits calculating transition probabilities and cross sections for reactions taking place between a diatomic molecule AB and a solid surface S, i.e.,



The theory is derived within the framework of the IOSA. Besides presentation of the general expression for a corrugated surface, a more detailed study is performed with respect to a flat noncorrugated surface. For this case the expressions simplify significantly. Here we also find some interesting features.

(i) The final physical S matrix is independent of the direction of approach of the molecule. Thus the calculations can be done for one given fixed direction of approach, say the perpendicular one, and then easily extended to any other direction. This outcome is probably also related to the fact that the motion of the particles as treated within the IOSA is close to the normal to the surface.

(ii) For a given initially rotating molecule the reactive process is not possible unless the z component of j , namely m , is zero. In other words, a rotating molecule will react if and only if the axis of rotation is parallel to the surface. This is a very interesting result which should be tested using quasi-classical trajectory calculations. It is expected to hold for a realistic system as well and therefore can be considered as a quasiselection rule that governs the reactive process between a molecule and a flat surface. It is expected that it will have important implications for an interaction with a noncorrugated surface as well.

From the expressions derived in this work it is seen that a general quantum IOSA calculation seems to be complicated and time consuming for today's computing facilities. However, there is no doubt that a calculation within the IOSA can be carried out for a flat surface and the results compared with exact classical results. In this way one may be able to estimate the relevance of the IOSA results, as well as study quantum effects such as tunneling, interference effects and resonances.

ACKNOWLEDGMENTS

I would like to thank Professor D. J. Kouri for many conversations on this subject and for his outstanding hospitality during my visit at the University of Houston where most of this research was carried out. I would also like to thank Professor J. Bear for arranging my stay at the University.

¹M. Baer, Adv. Chem. Phys. **49**, 191 (1982).

²J. Jellinek and D. J. Kouri, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (Chemical Rubber, Boca Raton, FL, 1984).

³V. Khare, D. J. Kouri, and M. Baer, J. Chem. Phys. **71**, 1188 (1979); **75**, 1179 (1981).

⁴J. M. Bowman and K. T. Lee, J. Chem. Phys. **72**, 507 (1980).

⁵M. Baer, J. Jellinek, and D. J. Kouri, J. Chem. Phys. **78**, 2962 (1983); J. Jellinek, D. J. Kouri, and M. Baer, Phys. Rev. Lett. **47**, 1588 (1981).

⁶C. L. Shoemaker, D. J. Kouri, J. Jellinek, and M. Baer, Chem. Phys. Lett.

- ⁹4, 359 (1983); N. Abu Salbi, C. L. Shoemaker, D. J. Kouri, J. Jellinek, and M. Baer, *J. Chem. Phys.* **80**, 3210 (1984).
- ⁷D. C. Clary and G. Drolshagen, *J. Chem. Phys.* **76**, 5027 (1982).
- ⁸D. C. Clary, *Chem. Phys.* **81**, 379 (1983).
- ⁹N. Abu Salbi, D. J. Kouri, Y. Shima, and M. Baer, *Chem. Phys. Lett.* **105**, 472 (1984).
- ¹⁰G. C. Schatz and A. Kuppermann, *J. Chem. Phys.* **65**, 4668 (1976).
- ¹¹M. J. Redmon and R. E. Wyatt, *Chem. Phys. Lett.* **63**, 209 (1979); R. E. Wyatt, J. E. McNutt, and M. J. Redmon, *Ber. Bunsenges. Phys. Chem.* **86**, 437 (1982).
- ¹²S. Ron, M. Baer and E. Pollak, *J. Chem. Phys.* **78**, 4414 (1983).
- ¹³S. Ron, E. Pollak and M. Baer, *J. Chem. Phys.* **79**, 5204 (1983).
- ¹⁴H. R. Mayne and J. P. Toennies, *J. Chem. Phys.* **75**, 1194 (1981).
- ¹⁵K. T. Tang, in *The Theory of Chemical Reaction Dynamics*, edited by M. Baer (Chemical Rubber, Boca Raton, FL, 1984).
- ¹⁶R. B. Walker and E. E. Hayes, *J. Phys. Chem.* **87**, 1255 (1983).
- ¹⁷J. H. McCreery and G. Wolken, *J. Chem. Phys.* **63**, 4072 (1975); **64**, 2845 (1976); **65**, 1310 (1976); **67**, 2551 (1977); **66**, 2316 (1977).
- ¹⁸A. B. Elkovitz, J. H. McCreery, and G. Wolken, *Chem. Phys.* **17**, 423 (1976).
- ¹⁹G. D. Purvis and G. Wolken, *Chem. Phys. Lett.* **62**, 42 (1979).
- ²⁰A. Gelb and J. M. Cardillo, *Surf. Sci.* **59**, 128 (1976); **64**, 197 (1977); **75**, 199 (1978).
- ²¹J. C. Tully, *J. Chem. Phys.* **73**, 6333 (1980).
- ²²D. J. Kouri and R. B. Gerber, *Isr. J. Chem.* **22**, 321 (1982).
- ²³G. Wolken, *J. Chem. Phys.* **59**, 1159 (1973); *Chem. Phys. Lett.* **21**, 373 (1973).
- ²⁴R. B. Gerber, A. T. Yinnon and, J. N. Murrell, *Chem. Phys.* **31**, 1 (1978).
- ²⁵R. B. Gerber, A. T. Yinnon, Y. Shimoni, and D. J. Kouri, *J. Chem. Phys.* **73**, 4397 (1980).
- ²⁶D. E. Fitz, L. H. Beard, and D. J. Kouri, *Chem. Phys.* **59**, 257 (1981).
- ²⁷J. E. Adams, *Surf. Sci.* **97**, 43 (1980).
- ²⁸R. Schinke, *J. Chem. Phys.* (in press).
- ²⁹R. B. Gerber, L. H. Beard and D. J. Kouri, *J. Chem. Phys.* **74**, 4709 (1981).
- ³⁰T. R. Proctor, D. J. Kouri and R. B. Gerber, *J. Chem. Phys.* **(80)**, 3845 (1984).
- ³¹F. O. Goodman and H. Y. Wachman, *Dynamics of Gas Surface Scattering* (Academic, New York, 1976).
- ³²M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)* **84**, 457 (1927).
- ³³K. Takayanagi, *Prog. Theor. Phys. Suppl.* **25**, 1 (1963); T. P. Tsien and R. T. Pack, *Chem. Phys. Lett.* **6**, 54 (1970); T. P. Tsien, G. A. Parker and R. T. Pack, *J. Chem. Phys.* **59**, 5373 (1973); D. Secrest, *ibid.* **62**, 710 (1975); R. Goldflam, S. Green, and D. J. Kouri, *ibid.* **67**, 4149 (1977); R. Schinke and D. McGuire, *Chem. Phys.* **28**, 129 (1978); D. J. Kouri, in *Atom Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979).
- ³⁴J. Jellinek and M. Baer, *J. Chem. Phys.* **76**, 4883 (1982).