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QUANTUM DISTORTED WAVE BORN CALCULATIONS FOR ATOM — DIATOMIC COLLISIONS

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A distorted wave Born (*DWB*) approximation is used to examine rearrangement scattering in the exchange reaction $H + H_2 \rightarrow H_2 + H$. The interaction of the three particles is described by the Porter-Karplus potential surface in order to permit comparison with quasiclassical and close — coupling calculations. The *T*-matrix elements are calculated by the method of Miller. Our calculations are carried for a complete and a linear *DWBA*. Total reaction cross section and differential cross section are estimated for the $0 \rightarrow 0$ rotational transition. The results are compared with the available measurements, especially with the *DWB* calculations of Karplus and Tang. The *DWB* quantum calculations for the total reaction cross section yield a significantly higher effective threshold energy than does the quasiclassical treatment.

1. Introduction

The first application of a distorted wave Born approximation (*DWBA*) of the first-order on the atom-diatomic molecule exchange reaction (A + BC reaction) and its isotopic analogues was given in a series of papers by Micha$^{1)}$. In order to reduce the numerical procedure to a minimum, a series of additional approximations have been introduced there, which enabled for an analytical calculation of the *T*-matrix elements. The work of Micha is considered as the basis of a consequent application of the *DWBA* to a chemical elementary process.

The first calculations with a complete *DWBA* for the static approximation of distorsion potentials and for adiabatic perturbed molecule-functions was given by Karplus and Tang[2,3] on the $H + H_2$ system. Two limiting approximations were used. In one, the molecule is unperturbed by the incoming atom, and in the other, the molecule adiabatically follows the incoming atom. They considered in their work a modified two-body potential including long-range attractive terms. Elastic differential and total cross sections were calculated for energies between 0.025 and 1.0 eV.

Recently[4], the *DWBA* has been used as an approach to describe the threshold region of chemical reactions. The description of the tunneling behaviour of the threshold region requires sufficient and accurate description of the nonreactive scattering. There have been many applications of *DWBA*'s to reactive scattering[5-9], and the results often seem to describe relative cross sections quite well.

The purpose of this paper is to use the *DWBA* to examine the total and differential cross sections of the exchange reaction $H + H_2 \rightarrow H_2 + H$. We used the method worked out by Miller[10] to calculate the *T*-matrix elements. The calculations were carried out for the complete and linear *DWBA* for a wide range of relative energies.

2. *Sumary of general features of the DWBA*

In this section we summarize the essential theoretical methodology of the *DWBA* for the exchange reactions $A + BC \rightarrow AB + C$. The stationary wave function ψ_α satisfies the Schrödinger equation

$$(\hat{H} - \mathscr{E})\psi_\alpha = 0. \tag{1}$$

For the total Hamiltonian $\hat{H}$ the solutions with energy $\mathscr{E}$ and outgoing (+) or incoming (—) spherical wave boundary conditions are written $\psi_\alpha^{(+)}$ and $\psi_\alpha^{(-)}$, respectively; these functions satisfy the Lippman-Schwinger integral equations[11]

$$\psi_\alpha^{(\pm)} = X_\alpha + (\mathscr{E} - \hat{H}_\alpha \pm \mathrm{i}\,\varepsilon)^{-1}\, V_\alpha \psi^{(\pm)}. \tag{2}$$

α corresponds to the quantum numbers for a particular rotation — vibration state of molecule BC in the reactant channel; the index β has the same connotation for the product molecule AB in the final channel. V_α is the initial state interaction potential and V_β is correspondingly defined for the final channel. As the atom-molecule distance R goes to infinity, $\psi^{(\pm)}$ approaches the required asymptotic forms; e. g., for $\psi_\alpha^{(+)}$ and $\alpha \neq \beta$

$$\psi_\alpha^{(+)} \underset{R_\beta \to \infty}{\sim} R_\beta^{-1} \sum_{n_\beta} X_{n_\beta} f_{\alpha\beta}(\Omega)\, \mathrm{e}^{\mathrm{i}\, \hat{P}_\beta R_\beta / \hbar}, \tag{3}$$

with the scattering amplitude in the direction $\hat{P}_\beta$

$$f_{\alpha\beta}(\Omega) = \left(\frac{-\mu_\beta}{2\pi \hbar^2}\right) \langle X_\beta | V_\beta | \psi_\alpha^{(+)} \rangle, \tag{4}$$

Here $\hat{P}_\beta$ is the momentum of C relative to AB and the reduced mass (C, AB) being μ_β. The differential scattering cross section is given as the absolute square of the scattering amplitude multiplied by the ratio $\hat{P}/\mu$ of products and reactants,

$$\frac{\mathrm{d}\sigma_{\alpha\beta}}{\mathrm{d}\Omega} = \frac{\hat{P}_\beta \, \mu_\alpha}{\hat{P}_\alpha \, \mu_\beta} |f_{\alpha\beta}(\Omega)|^2. \tag{5}$$

Formaly we can conceive

$$\langle X_\beta | V_\beta | \psi_\alpha^{(+)} \rangle = \langle X_\beta | \hat{T} | X_\alpha \rangle = T_{\alpha\beta}, \tag{6}$$

as the matrix element of the operator $\hat{T}$[12].

Because of the complicated functional dependence of the potential, the solution of Eq. (2) and the calculation of the differential cross section (5) is very difficult even for simple chemical elementary reactions. As a starting point for a practical approximation, it is appropriate for both parts V_α and V_β of the interaction potential to be written in the following separated forms

$$\begin{aligned} V_\alpha &= U_\alpha + W_\alpha, \\ V_\beta &= U_\beta + W_\beta. \end{aligned} \tag{7}$$

Here U_α is chosen to account for the atom-molecule interaction as completely as possible. The wave functions $\varphi_\alpha^{(\pm)}$ for the scattering from potential U_α satisfy the integral equation

$$\varphi_\alpha^{(\pm)} = X_\alpha + (\mathscr{E} - \hat{H}_\alpha \pm \mathrm{i}\varepsilon)^{-1} \, U_\alpha \varphi_\alpha^{(\pm)}; \tag{8}$$

with an analogous equation for the scattering from U_β. Eq. (2) with the use of Eq. (8) will be[12]

$$\psi_\alpha^{(+)} = \varphi_\alpha^{(} + (\mathscr{E} - \hat{H}_\alpha - U_\alpha + \mathrm{i}\varepsilon)^{-1} \, W_\alpha \psi_\alpha^{(+)}, \tag{9}$$

and the elements of the T-matrix (6) can be given in the following form

$$T_{\alpha\beta} = \langle X_\beta | U_\beta | \varphi_\alpha^{(+)} \rangle + \langle \varphi_\beta^{(-)} | W_\beta | \psi_\alpha^{(+)} \rangle = T_{\alpha\beta}^{(0)} + T_{\alpha\beta}^{(1)}. \tag{10}$$

The term $T_\alpha^{(0)}$ describes the scattering from potential U_α and $T_\alpha^{(1)}$ gives the correction due to the presence of W_α.

The eigenfunctions of $\hat{H}_\alpha$ and $\hat{H}_\beta$ (which describe the free reactants and products) are separable into a translational part and another part for the inner state of the molecules BC and AB. The system of coordinates (r, R) and (s, S) are the complete set for three — particle system for the entrance and exit channels, respectively (see Fig. 1). Therefore $\hat{H}_\alpha$ and $\hat{H}_\beta$ have the two following expressions

$$\hat{H}_\alpha = \frac{-\hbar^2}{2\mu_{\mathrm{BC}}}\nabla_r^2 - \frac{\hbar^2}{2\mu_\alpha}\nabla_R^2 + V_{\mathrm{BC}}(r),$$

$$\hat{H}_\beta = \frac{-\hbar^2}{2\mu_{\mathrm{AB}}}\nabla_s^2 - \frac{\hbar^2}{2\mu_\beta}\nabla_S^2 + V_{\mathrm{AB}}(s), \tag{11}$$

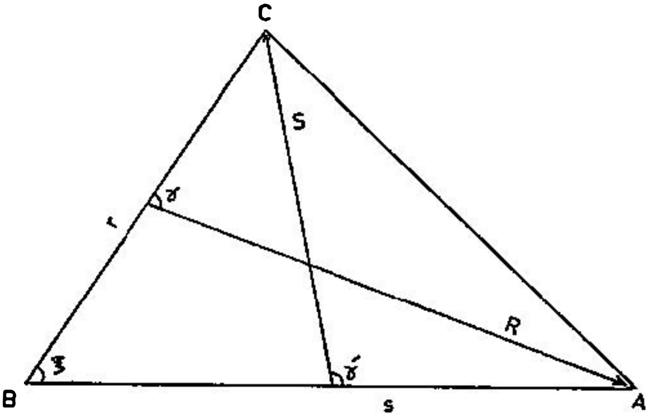

Fig. 1. Relative coordinates pertaining to the A + BC → AB + C reaction.

where μ_α, μ_β are the reduced channel masses and μ_{BC}, μ_{AB} are the reduced internal masses. $V_{\mathrm{BC}}(r)$ and $V_{\mathrm{AB}}(s)$ are the intermolecular potentials for the free molecules. The total Hamilton operator is

$$\hat{H} = \hat{H}_\alpha + V_\alpha = \hat{H}_\beta + V_\beta, \tag{12}$$

where V_α and V_β are calculated from the total potential $V(R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}})$ through

$$V_\alpha = V - V_{\mathrm{BC}}, \qquad V_\beta = V - V_{\mathrm{AB}}. \tag{13}$$

We turn back to the integral equation (9) for the wave function and try to examine it by perturbation. Therefore we replace W_α by λW_α and rewrite (9) using the definition

$$(\mathscr{E} - \hat{H}_\alpha - U_\alpha + \mathrm{i}\varepsilon)^{-1}\, W_\alpha = \hat{K}_\alpha \tag{14}$$

in the form

$$\psi_\alpha^{(+)} = \varphi_\alpha^{(+)} + \lambda \hat{K}_\alpha \psi_\alpha^{(+)}. \tag{15}$$

Through iteration of (15) we obtain a formal development of the wave function in powers of λ

$$\psi_{\alpha}^{(+)} = \sum_{j=0}^{\infty} \lambda^j K_{\alpha}^j \varphi^{(+)}. \tag{16}$$

The series (16) represents a general Born series, which can serve as a starting point for approximations of faster convergence. The convergence of (16) is determined through the analytical properties of the series in the complex λ-plane[13]. A problem may appear here, the operator $\hat{K}_{\alpha}$ in (16) for scattering problems of more than two particles is not compact, thus the series will diverge[14]. This defect is eliminated through Faddeev's theory for three-particle problems[15,16].

We put the zero-order approximation wave function $\varphi_{\alpha}^{(+)}$ for $\psi_{\alpha}^{(+)}$ in Eq. (10), so we obtain the distorted wave Born approximation of the first-order for the T-matrix

$$T_{\alpha\beta}(DWB) = \langle X_{\beta} | U_{\beta} | \varphi_{\alpha}^{(+)} \rangle + \langle \varphi_{\beta}^{(-)} | W_{\beta} | \varphi_{\alpha}^{(+)} \rangle. \tag{17}$$

3. *Performance of the calculations*

We chose for U_{α} and U_{β} in the static approximation calculated central potentials and obtain the distorted waves as products of elactis scattering waves F and unperturbed molecular wave functions η

$$\begin{aligned} \varphi_{\alpha}^{(\pm)}(r, R) &= F_{\alpha}^{(\pm)}(R)\, \eta_{\alpha}(r), \\ \varphi_{\beta}^{(\pm)}(s, S) &= F_{\beta}^{(\pm)}(S)\, \eta_{\beta}(s). \end{aligned} \tag{18}$$

For the case of reactions in which we are interested, the first term in Eq. (17) disappears and it remains a matrix element of the type

$$\begin{aligned} T_{\alpha\beta}(DWB) &\cong \langle \varphi_{\beta}^{(-)} | W_{\beta} | \varphi_{\alpha}^{(+)} \rangle = \\ &= \int \mathrm{d}^3 r \int \mathrm{d}^3 R\, \varphi_{\beta}^{(-)*}(s, S)\, W_{\beta}(r, R, \gamma)\, \varphi_{\alpha}^{(+)}(r, R), \end{aligned} \tag{19}$$

to be calculated. γ is the angle between r and R. The six-dimensional integral of Eq. (19) is developed in a series form by the use of the partial wave expression[12]

$$F_{k}^{(+)}(R) = (kR)^{-1} \sum_{l=0}^{\infty} (2l + 1)\, \mathrm{e}^{\mathrm{i}\delta_l}\, G_l(R)\, P_l(\cos\vartheta), \tag{20}$$

for $F_{\alpha}^{(+)}$ and $F_{\beta}^{(-)}$ and the application of the addition theorems for the spherical functions[17], with the boundary condition $G_l(0) = 0$ and the asymtotic relation

$$G_l(R) \xrightarrow[R\to\infty]{} \sin\left(kR - \frac{l\pi}{2} + \delta_l\right).$$

All informations on the scattering process are contained in the scattering phase δ_l, through which the asymptotic relation of $F_k^{(+)}$ is determined. Then we have

$$T_{\alpha\beta}(DWB) = \sum_{l=0}^{\infty} (2l + 1)\, A_l P_l (\cos \vartheta), \tag{21}$$

where ϑ and A_l are the scattering angle and the five-dimensional integral, respectively. This treatment has been followed by Karplus and Tang[2,3].

Another method have been worked out by Miller[10] which is practically better, and hence has been used in the present work. By taking advantage of the fact that the potential is independent of the three Euler angles which orient the triangle of particles, Miller[10] reduced the necessary integrals (19) to three-dimensional ones after a series of algebraic manipulations. Before we give the resultant expression we write the molecular wave functions as

$$\eta_\alpha (\vec{r}) = g_\alpha (r)\, Y_{J\alpha M\alpha} (\hat{r}), \tag{22}$$

with $Y_{J\alpha M\alpha}(\hat{r})$ the orthonormalized spherical functions[17], $\hat{r} = \vec{r}/r$ and a corresponding definition for $\eta_\beta (\vec{s})$. For (17) and (19) we obtain after Miller

$$T_{\alpha\beta}(DWB) = \sum_{j=0}^{\infty} (2j + 1)\, S^J_{\alpha\, M_\alpha \leftarrow \beta M_\beta}\, d^J_{M_\alpha M_\beta} (C), \tag{23}$$

with the rotation-matrices[18] $d^J_{M_\alpha M_\beta}(\vartheta)$ and

$$S^J_{\alpha\, M_\alpha \leftarrow \beta M_\beta} = \sum_{ll'MM'} C(J_\alpha, Jl;\, M_\alpha, -M_\alpha)\, C(J_\alpha, Jl;\, M, -M)$$

$$C(J_\beta, Jl';\, M_\beta, -M_\beta)\, C(J_\beta, Jl';\, M, -M)\, e^{i[\delta\alpha(l) + \delta\beta(l')]}\, I^J_{\alpha\, l M \leftarrow \beta\, l' M'}, \tag{24}$$

$$I^J_{\alpha\, l M \leftarrow \beta\, l' M} = 2 \int d^3\tau\, G_{\beta l'}(S)\, g_\beta (s)\, Y_{J\beta M'}(\gamma', 0)\, d^J_{M' M}(\gamma s)\, W_\beta (r, R, \gamma)\, \cdot$$

$$\cdot\, G_{\alpha l}(R)\, g_\alpha (r)\, Y_{J\alpha M}(\gamma, 0), \tag{25}$$

where $\int d^3\tau$ is the integral over the three coordinates specifying the size and shape of the triangle of particles A, B, C[10] and $C(J_1, J_2;\, M_1, M_2)$ are the Clebsch-Gordan coefficients[18]. Eq. (24) is the *DWBA* for the *S*-matrix elements. The sume over l, l', M, M' are all finite and run on the following values

$$l = |J - J_\alpha|, \ldots, |J + J_\alpha|$$

$$l' = |J - J_\beta|, \ldots, |J + J_\beta|$$

$$M = 0, \pm 1, \ldots, \pm \mathrm{Min}\,(J, J_\alpha)$$

$$M' = 0, \pm 1, \ldots, \pm \mathrm{Min}\,(J, J_\beta). \tag{26}$$

The appearance of the rotation matrix $d^l_{M'M}(\gamma s)$ inside the integrand is a consequence of the different entrance and exit channel coordinates for the case of a rearrangement.

Because of some difficulties in calculation techniques, we considered in the present work a nonrotating initial and final molecule, i. e., $J_\alpha = J_\beta = 0$. Therefore the Clebsch-Gordan coefficients in Eq. (24) demand that $l = l' = J$, $M = M' = 0$, so that the only remaining sum is that over J, and the integral (25) will be simpler.

From Eqs. (4), (5), (6) and (23) the differential scattering cross section is given by

$$\frac{\mathrm{d}\sigma_{\alpha\beta}}{\mathrm{d}\Omega} = \frac{\hat{P}_\beta \, \mu_\alpha \, \mu_\beta}{\hat{P}_\alpha (2\Pi \hbar^2)^2} |T_{\alpha\beta}(DWB)|^2, \tag{27}$$

where $T_{\alpha\beta}(DWB)$ is calculated through Eqs. (24) and (25). The total reaction cross section is obtained by integrating Eq. (27) over all angles.

4. Results for the process $H + H_2 \rightarrow H_2 + H_2$ and discussions

4.1. *Using a complete DWBA*

The calculations for the reaction H + H_2 in molecular ground state are carried out using the potential energy surface of Porter and Karplus (*PK*)[19] in order to permit comparison with classical and close-coupling calculations. Although this elementary process is not directly observable because the particles are identical, it is of theoretical interest as a model to test approximation methods and to study quantum effects.

In Fig. 2 we present our results for the relative energy dependence of the total reaction cross section σ together with the quasiclassical calculations of Karplus-Porter-Sharma (*KPS*)[20], the close-coupling results of Wolken and Karplus (*WK*)[21] and the unperturbed molecule function *DWB* calculations of Karplus and Tang (*KT*)[2,3] for comparison. We notice the high value of the threshold energy nearly for all the calculations. The most important point is that the *DWBA* quantum calculations, whether ours or by *KT* yield a significantly higher effective threshold than does the quasiclassical treatment. This is reasonable when one considers that the same initial molecular zero-point energy is present in both approaches, but that the quantum constraints in the saddle-point region may provide a limit on the vibrational energy available for crossing the barrier which does not exist for the classical trajectories. Above threshold, σ rises in a nearly linear manner for all calculations. Our results achieve a maximum value at $\mathscr{E}_{rel} = 0.93$ eV after that σ begins to decrease gradually with increasing energy. As we see in the figure, the *KT* cross section corresponds to a higher threshold than ours. By contrast, the close-coupling results while nearer in behaviour to the classical cross section, has a significantly lower threshold. This suggests that there is an important tunneling contribution in the H + H_2 reaction. The fact that the *KT* threshold is higher than the present value and their results have lower values than ours may be explained through the two different approaches used in evalua-

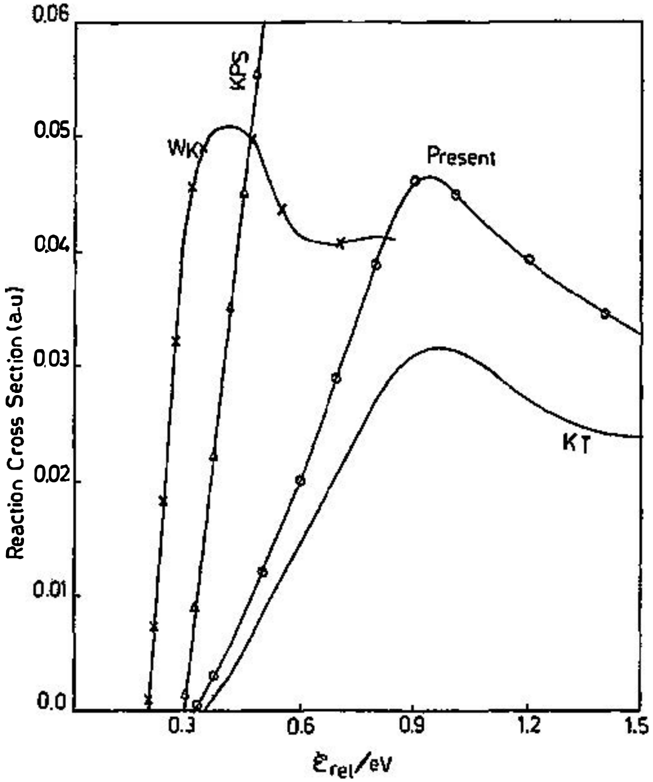

Fig. 2. Total reaction cross sections (0 → 0) from the present study (—0—), close coupling technique *WK* (—x—), classical *PKS* (— △ —) and *DW* calculations of *KT* (———).

ting the *T*-matrix elements if both calculations are numerically correct (one always worries about errors in such long and complicated calculations).

Also we compare in Fig. 3 the present results for the differential cross section (in arbitrary units) at an energy of 0.5 eV as a function of the scattering angle Θ with the classical and *DWB* calculations of *PKS* and *KT*, respectively. The results correspond to backward scattering$^{2)}$ in the centre of mass system; i. e., the incoming atom strikes the molecule, picks up an atom, and the newly formed molecule goes back dominantly in the direction from which the atom came. The form of the three curves is identical, they all have their maximum at $\Theta = 180°$. Such strongly backward peaked cross sections are expected when the quantum mechanical wave function or classical path of the incoming atom is strongly distorted by a repulsive barrier. They contrast sharply with the Born approximation which yields an oscillating cross section with its maximum in the forward direction.

It is of considerable interest to obtain an idea of the configurations of the three nuclei which make the dominant contributions to the reaction. Therefore we choose r, s as integration variables in Eq. (25) and ξ the angle between r and s (see Fig. 1) and obtain

$$\int d^3\tau = \int_0^\infty dr \int_0^\infty ds\, r^2 s^2 \int_{-1}^{1} d(\cos\xi). \tag{28}$$

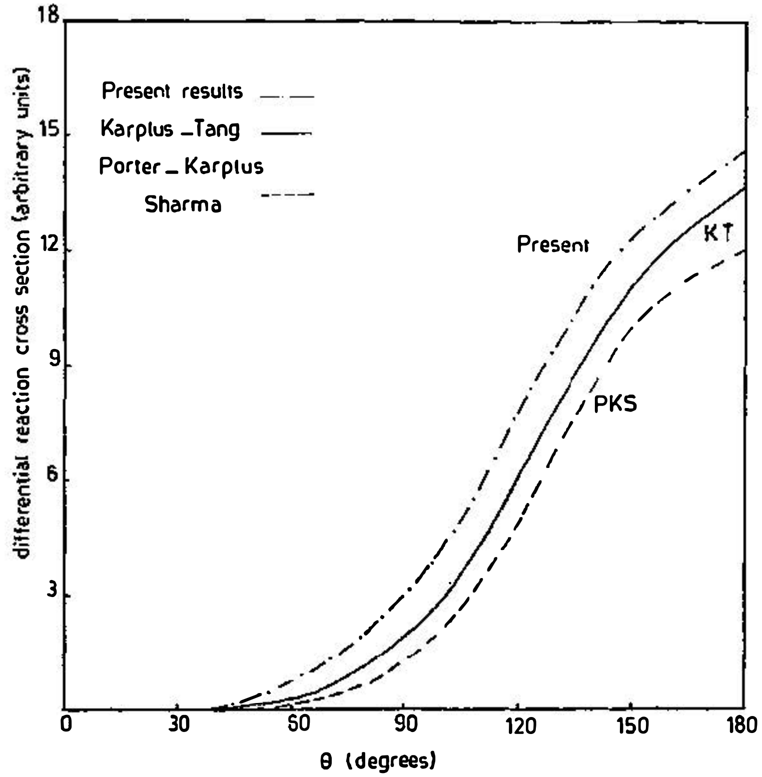

Fig. 3. Differential cross section as a function of the scattering angle Θ for an incident energy 0.5 eV.

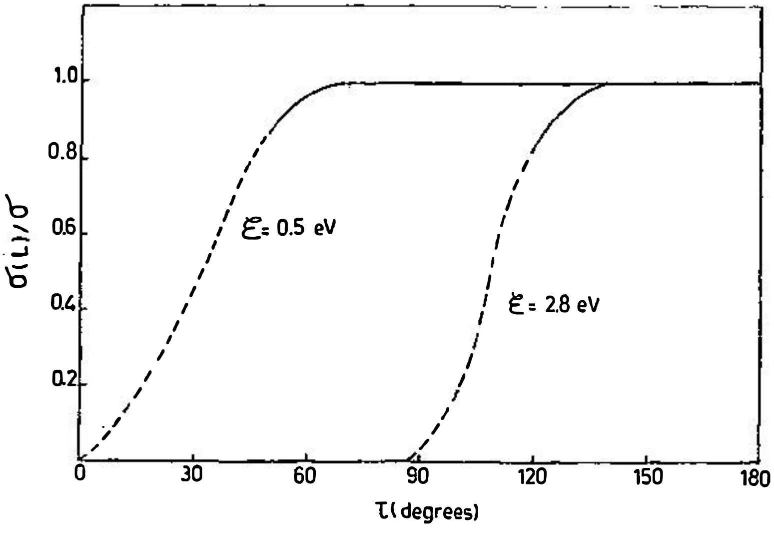

Fig. 4. Relative contribution of H_3 configurations to the total reactive cross section ($J = 0$, $J' = 0$) for two energies.

To establish which angle ξ is significant in the integration we displace W_β in Eq. (25) by

$$W_\beta^\tau(s, r, \xi) = W_\beta(s, r, \xi)\,\Theta(\tau - \pi + \xi), \tag{29}$$

with Θ the Heaviside function $[\Theta(x) = 0, x < 0; \Theta(x) = 1, x > 0]$. After the substitution of (29) in (25) and using Eqs. (23) and (24), the calculated total reaction cross section $\sigma(\tau)$ provides a semi-classical measure of the contribution to reaction for atom, molecule orientations with angles in the range between 0 and τ. In Fig. 4 we represent the relative contributions of different configurations to reaction cross sections $\sigma(\tau)/\sigma$ for two different relative energies. For $\mathscr{E} = 0.5$ eV, contribute the configurations with $\tau < 50°$ to about 85% of the reaction cross section; i. e., nearly collinear collisions dominate. Whereas for $\mathscr{E} = 2.8$ eV the essential contribution takes place between 90° and 120°.

TABLE 1.

Energy (eV)	Integration variables		
	r, s	s, S	R, S
0.5	0.012	0.012	0.012
0.7	0.0697	0.0686	0.0688
0.9	0.0874	0.0862	0.0867
1.1	0.0727	0.0701	0.0715
1.3	0.0621	0.0613	0.0616
1.5	0.0574	0.0547	0.0563
1.7	0.0498	0.0453	0.0467
1.9	0.0466	0.0424	0.0435

Total reaction cross section in a. u. (1a. u. $= a_0^2 = 2.8 \cdot 10^{-21}\mathrm{m}^2$) for different linear *DWBA*. Calibration with the complete *DWBA* at $\mathscr{E} = 0.5$ eV to choose λ.

For comparison, we give in Table 1 the results for total reaction cross section obtained by *KT* for two different methods (the unperturbed molecule functions and the adiabatic perturbed molecule functions) at three different relative energies. The comparison with our results is only for the total reaction cross section at $\mathscr{E} = 0.5$ eV in column a in the table. Our calculated $\sigma_{reac} = 0.012$ a. u. is greater by a factor about 1.33. After the appearence of this discrepancy we tested our program to ensure our result. Also there is a profound difference in the results between the two approximate models in the table itself. At 0.5 eV the adiabatic perturbation of the molecule by the incoming atom yields a 20-fold increase in σ over that corresponding to an unperturbed molecule, and seem to be in better agreement with the classical calculations.

4.2. *Using the linear DWBA*

To carry out extensive calculations and to investigate the rotation stimulation of product molecules, *KT* introduced a simpler approximation, the so-called linear *DWBA*$^{2)}$. This was to assume, as justified in part by the *DWB* results, that reaction occurs only when the three atoms are in the neighbourhood of linear geometry. The matrix element $T_{\alpha\beta}$ (*DWB*) is then approximated by the expression

$$T_{\alpha\beta}(DWBL) = \lambda\, \langle \varphi_\beta^{(-)} | W_\beta \delta(\gamma - \pi) | \varphi_\alpha^{(+)} \rangle$$

where γ is the angle (R, r) or (S, s) and λ is the δ-function strength parameter. A fixed value of λ was chosen so that $T_{\alpha\beta}(DWBL) = T_{\alpha\beta}(DWB)$ at 0.5 eV and was kept fixed at the same value for all of the calculations[2,3]. In the following we show that one can obtain different linear approximations for the applied integration variables. Therefore we go out from Eq. (25) with the integration variables R, r, γ. Then we have integrals of the type

$$I = \int_0^\infty \mathrm{d}R \int_0^\infty \mathrm{d}r \int_{-1}^{1} \mathrm{d}(\cos\gamma)\, r^2 R^2 f(R, r, \cos\gamma), \tag{30}$$

to be calculated. When we introduce in Eq. (30) the δ-function $\lambda\delta(\cos\gamma + 1)$, ($\cos\gamma = -1$ for linear configuration), so we obtain

$$I_{Linear} = \lambda \int_0^\infty \mathrm{d}R \int_0^\infty \mathrm{d}r\, r^2 R^2 f(R, r, -1), \tag{31a}$$

and after conversion of the integration variables to r and s

$$I_{Linear} = \lambda \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}s\, r^2 R^2 f(R, r, -1). \tag{31b}$$

Also one can proceed with integration variables r, s, $\cos\xi$ in Eq. (30) and multiply the integrand by the δ-function $\lambda\delta(\cos\xi + 1)$ to obtain another expression

$$I'_{Linear} = \lambda \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}s\, r^2 s^2 f(R, r, -1). \tag{31c}$$

To examine these effects we carried out calculations for the reaction H, H_2 for three different linear approximations over a wide range of energy and the results are given in Table 2. The deviations in the whole region between the calculated total reaction cross sections is being less than 10% as shown in Table 2, which means that the agreement of the results is good for the three different approximations. The question for the best linear approximation will in general have no

TABLE 2.

Relative energy (eV)	σ_{react} (a. u.)	
	a	b
0.21	—	0.0001
0.33	—	0.027
0.50	0.009	0.200

Quantum *DWBA* total reaction cross section for $H + H_2 \rightarrow H_2 + H$ by Karplus and Tang.
a. unperturbed molecule functions.
b. adiabatic perturbed molecule functions.

answer. It is also observed that the application for higher energies gives smaller total reaction cross section. This observation reflects itself also in Fig. 2 when we compare the energy dependence of the total reaction cross section for both linear and complete *DWBA* calculations. In fact the linear *DWB* calculations give results having the same qualitative behaviour as the results obtained from calculations with complete *DWB*. Meanwhile, there is a noticable quantitative difference between both results. We may estimate that the linear *DWBA* is not necessary for calculations of chemical elementary reactions, since the complete *DWBA* is quite enough and suitable to examine the reaction attributes of these processes.

5. *Concluding remarks*

A *DWBA* has been used to examine rearrangement scattering in the $H + H_2$ system. The *T*-matrix elements were calculated by the method of Miller. The results for a variety of reaction attributes (energy dependence of total reaction cross section and differential cross section) suggest by their similarity to the available quasiclassical calculations with the same interaction potential that quantum effects are not very important. However, the energy dependence of the total reaction cross section is different in the quantum and the quasiclassical treatments; in particular the effective threshold is higher in the quantum calculation. This result has been arrived at by Karplus and Tang in their *DWBA* calculations. The results for the differential cross section correspond to backward scattering in the centre of mass system. These results contrast sharply with the Born approximation which yields an oscillating cross section with its maximum in the forward direction. A linear *DWBA* was used to calculate the total reaction cross section for three different types. The deviations in the whole region of applied relative energies between the calculated results is being less than 10%.

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PRORAČUN RASPRŠENJA ATOM-DIATOMNA MOLEKULA U KVANTNOJ BORNOVOJ APROKSIMACIJI S DISTORDIRANIM VALOVIMA

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Koristeći Bornovu aproksimaciju s distordiranim valovima proučavano je raspršenje s premještanjem u reakciji izmjene $H + H_2 \rightarrow H_2 + H$. Međudjelovanje triju čestica opisano je Porter-Karplusovom potencijalnom površinom kako bi se omogućila usporedba s kvaziklasičnim i računom bliskog vezanja. Elementi T matrice proračunati su metodom Millera.