Quantum Reactive Scattering Calculation for Four-Atom Chemical Reaction Systems: Application of a Fixed-Angle Approximation

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An approximate quantum mechanical method is described for calculating reaction probabilities for the general four-atom chemical reaction AB+CD→A+BCD. By applying a fixed-angle approximation, reaction probabilities are calculated for the H_2+CN→H+HCN reaction on a semiempirical potential energy surface. The calculated results are compared favorably with those of quasiclassical trajectory calculations.

Quantum calculation of reactive scattering is one of the important problems in theoretical chemistry. Significant progress has recently been made for atom–diatom reactions using various methods including hyperspherical,$^{1-3)}$ L_2 algebraic,$^{4-6)}$ and time-dependent methods.$^{7)}$ The three-dimensional quantum scattering calculation on a single potential energy surface is now a solved problem, although actual calculations are restricted to reactions involving light atoms such as hydrogen.

Very recently, the extension of quantum reactive scattering theory to reactions involving four atoms has been done. Bowman's group$^{8-10)}$ and Clary's group$^{11)}$ have independently developed the computational technique to calculate reaction probabilities for the AB+CD→A+BCD reaction in collinear geometry. They have applied the method to the realistic reaction CN+H_2→H+HCN and reported converged reaction probabilities on the semiempirical potential surface which has been based in part on ab initio molecular orbital calculations. An extension to the reactions with nonlinear geometry has also been done. Sun and Bowman$^{12-14)}$ have used a reduced dimensionality approximation which treats bending vibrations adiabatically. They have applied the method to a study of mode specificity in the H_2+OH→H+H_2O reaction, which has a nonlinear geometry at the saddle point. Clary$^{15)}$ has developed another technique to calculate cross sections for AB+CD→A+BCD reaction with nonlinear geometry. His method accounts explicitly for the rotations of AB, the vibration of CD, the bending vibration in ABC, and the local stretching vibration in ABC. The method has been applied to the H_2+OH→H_2O+H reaction and its isotopic variants,$^{15-18)}$ the Cl+H_2O→HCl+OH reaction$^{19,20)}$ and the OH+CO→H+CO_2 reaction.$^{21)}$ Zhang and Zhang$^{22)}$ have developed a five-dimensional time-dependent wave packet method and calculated initial state-specific total reaction probabilities for the H_2+OH→H+H_2O reaction. Miller and his co-workers$^{23)}$ have done full-dimensional quantum calculations for the H_2+OH→H+H_2O reaction using a direct procedure without solving the reactive scattering problem.

Obviously, an exact quantum scattering method should be used to study polyatomic reaction systems having more than three atoms. Unfortunately, there are some difficulties in doing such a calculation because of the huge number of channels. Thus, it seems reasonable to develop approximate quantum methods, especially for polyatomic reactions. Additionally, we think that such an approximate method is important for quantitative understanding of the reaction dynamics. In this paper, we apply a fixed-angle approximation to the four-atom reaction, AB+CD→A+BCD. In this approximation the orientation angles are fixed during collision in each arrangement channel. A general concept of the fixed-angle approximation is very similar to that of the infinite-order-sudden approximation (IOS),$^{24,25)}$ which is frequently used for atom–diatom reactions. The IOS approximation has been found to be very useful for estimating vibrationally state-to-state reaction probabilities.$^{26)}$ Furthermore, it is known that the method gives very accurate results, especially for heavy-atom transfer reactions. For the four-atom reaction, AB+CD→A+BCD, there are three internal angular motions and three internal stretching motions. In this calculation, these three rotational motions are fixed during collision, while the other three stretching modes are fully treated quantum-mechanically.

Computational Procedure

The theory presented here is for the AB+CD→A+BCD reaction. Two arrangement channels, AB+CD and A+BCD, are denoted by i and f, respectively. Figure 1 shows the coordinate system used in these calculations for each arrangement channel. R'_i is the distance between the centers of masses of AB and CD, and r_i' and z_i' are AB and CD internuclear distances, respectively. R'_f is the distance between A and the center of mass of the BCD molecule. r_f' is the distance from B to the center of mass of CD. z_f' is the internuclear distance of CD. It is noted that the definition of z_i' and z_f' does not change in each arrangement channel. The angles that R' makes with r' and z' are denoted as γ and θ, respectively. The torsional angle ϕ is the angle that r makes with z. The approximation is now made of holding the orientation angles fixed in the dynamics calculation. First, the torsional angle ϕ is assumed to be zero for computational simplicity. This means that the collision system is confined to a single plane and the molecular orientation is defined by the set of two angles γ and θ in each arrangement channel. In addition, an orbital angular momentum is completely neglected in this theory.

By neglecting the angular operators, the Hamiltonian in mass-scaled Jacobi coordinates (for zero total angular momentum) can be written as follows;

$$H_i=-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R_i^2}+\frac{\partial^2}{\partial r_i^2}+\frac{\partial^2}{\partial z_i^2}\right)+V(R_i,r_i,z_i;\theta_i\gamma_i), \quad (1a)$$

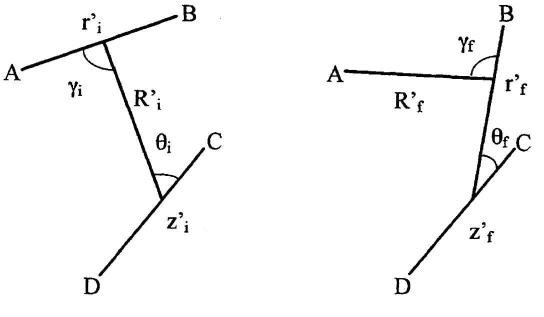
and

$$H_f=-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R_f^2}+\frac{\partial^2}{\partial r_f^2}+\frac{\partial^2}{\partial z_f^2}\right)+V(R_f,r_f,z_f;\theta_f,\gamma_f). \quad (1b)$$

Here, μ, R_i, r_i, z_i, R_f, r_f, and z_f are defined by the following equations;

$$\mu=\left(\frac{m_A m_B m_C m_D}{m_A+m_B+m_C+m_D}\right)^{1/3}, \quad (2)$$

$$\begin{aligned} R_i&=(\mu_{AB,CD}/\mu)^{1/2}R'_i,\\ r_i&=(\mu_{AB}/\mu)^{1/2}r'_i,\\ z_i&=(\mu_{CD}/\mu)^{1/2}z'_i, \end{aligned} \quad (3a)$$



Initial Channel *Final Channel*

Fig. 1. Coordinate system for the AB+CD (i-channel)→A+BCD (f-channel) reaction.

$$\begin{aligned} R_f&=(\mu_{A,BCD}/\mu)^{1/2}R'_f,\\ r_f&=(\mu_{B,CD}/\mu)^{1/2}r'_f,\\ z_f&=(\mu_{CD}/\mu)^{1/2}z'_f, \end{aligned} \quad (3b)$$

$$\begin{aligned} &\mu_{AB,CD}=(m_A+m_B)(m_C+m_D)/(m_A+m_B+m_C+m_D),\\ &\mu_{AB}=m_A m_B/(m_A+m_B),\\ &\mu_{CD}=m_C m_D/(m_C+m_D),\\ &\mu_{A,BCD}=m_A(m_B+m_C+m_D)/(m_A+m_B+m_C+m_D),\\ &\mu_{B,CD}=m_B(m_C+m_D)/(m_B+m_C+m_D). \end{aligned} \quad (3c)$$

Here, m_i is the mass of the atom i. From Fig. 1 it is easily found that the system is essentially the same as the atom–diatom system if the nonreactive diatom CD is treated as a single atom. Thus, a matching condition between two arrangement channels is essentially the same as the case for the atom–diatom system. Solutions of the Schrödinger equations for the initial and final arrangement channels are matched along a surface defined by

$$r_f = B_{fi}r_i, \quad (4)$$

where B_{fi} is a matching parameter and dependent on both γ_i and θ_i. In the original IOS approximation for atom–diatom reactions, the procedure for calculating the matching parameter is somewhat arbitrary. Nakamura et al.[27)] have proposed a physically reasonable procedure to calculate B_{fi}, so we here adapted their procedure. Details are described in the following section.

The relations between the initial and final orientation angles can be written as follows;

$$\cos\gamma_f=\frac{\cos\gamma_i-(1-B_{fi}^2)\tan\alpha_i\cot\beta_{fi}}{B_{fi}\sqrt{1+(1-B_{fi}^2)\tan^2\alpha_i}}, \quad (5)$$

$$\tan\alpha_i=\frac{\sin\beta_{fi}}{B_{fi}^2-\cos^2\beta_{fi}}\left\{-\cos\beta_{fi}\cos\gamma_i+\sqrt{B_{fi}^2-\sin^2\gamma_i\cos^2\beta_{fi}}\right\}, \quad (6)$$

$$\tan\alpha_f=\frac{B_{fi}}{\sqrt{1+(1-B_{fi}^2)\tan^2\alpha_i}}\tan\alpha_i, \quad (7)$$

$$\beta_{fi}=\tan^{-1}\left(\frac{m_B(m_A+m_B+m_C+m_D)}{m_A(m_C+m_D)}\right)^{1/2}, \quad (8)$$

$$\theta_f=\theta_i+\sin^{-1}\left[\frac{1}{B_{fi}}\left(\frac{\mu_{AB}}{\mu_{AB,CD}}\right)^{1/2}\frac{\sin\gamma_i}{\tan\alpha_i}\right]. \quad (9)$$

Equations 5, 6, and 7 are exactly the same as the atom–diatom case. The definition of the skew angle β_{fi} is slightly different from the atom–diatom case. Equation 9 is an additional condition arising from the system having two orientation angles.

To solve the Schrödinger equation the Hamiltonian of which is given by Eq. 1, we used two coordinate systems to check the numerical accuracy of our computational codes. One is the hypercylindrical coordinate system that is described in detail in Ref. 8 and the other is the natural collision coordinate system.[28] In the natural collision coordinates, the Hamiltonian can be written as follows;

$$H=-\frac{\hbar^2}{2\mu}\left(\frac{1}{\eta^2}\frac{\partial^2}{\partial u^2}+\frac{1}{\eta}\frac{\partial}{\partial v}\eta\frac{\partial}{\partial v}+\frac{\partial^2}{\partial z^2}\right)+V(u,v,z;\gamma,\theta), \tag{10}$$

where the definitions of u, v, and η are described in Ref. 28. Equation 10 is essentially the same as the atom–diatom case except for an additional vibrational mode z.

The R-matrix propagation method[28] was used to solve the close-coupling equations numerically. For both coordinate systems, the two-dimensional eigenvalue problems are solved by using a standard basis-set expansion method. Convergence tests are carefully done by increasing the number of channels. About one hundred channels for close-coupling equations are found to be needed to obtain converged reaction probabilities. As a result, an excellent agreement was obtained for both coordinate systems.

Application

We apply the method described in the previous section to the $CN+H_2 \rightarrow HCN+H$ reaction. According to an ab initio molecular orbital calculation,[29,30] the geometry of the transition state is collinear for this reaction. The analytic potential energy surface has been developed by Sun and Bowman semiempirically.[9] Their potential surface function approximately reproduces the saddle point properties that have been calculated by the ab initio molecular orbital method.[29,30] The classical barrier height and exoergicity for this potential energy surface are 0.18 and 0.89 eV, respectively.

As mentioned in the previous section, the matching parameter B_{fi} depends on the orientation angles. The value of B_{fi} is calculated as follows. At first, the initial angles γ_i and θ_i are specified. Second, z is fixed at the saddle point value. Then, we can draw a contour map of potential energy surface as functions of R_i and r_i. Once the contour map can be drawn in two dimensions, the same procedure proposed by Nakamura et al.[27] is applicable. As a result, it was found that B_{fi} weakly depends on both γ_i and θ_i. This probably comes from the properties of the potential energy surface of the H_2+CN reaction. Thus we used the same value of $B_{fi}=2.2$ for all sets of the orientation angles, γ_i and θ_i.

In principle, the initial orientation angles γ_i and θ_i are free parameters as mentioned in the previous section. Once the two angles are fixed, the final orientation angles γ_f and θ_f can be calculated from Eqs. 5, 6, 7, 8, and 9. However, this is not realistic because θ_f defines the geometry of the product BCD molecule. In the case of the H_2+CN reaction, the product HCN molecule is linear. Then the initial orientation angle θ_i should be so chosen that θ_f becomes 0°. In other words, the orientation angle γ_i is only a free parameter, while the angle θ_i is not a free parameter. The relations between the initial orientation angles and the final orientation angle are plotted in Fig. 2.

Figure 3 shows the total reaction probability for the H_2 $(v=0)+CN$ $(v'=0)\rightarrow H+HCN$ reaction as functions of the initial orientation angle γ_i and the total energy in a three-dimensional perspective plot. The total energy is measured from the reactant bottom. The total reaction probabilities are summed over all final states. It is found that the reaction threshold shifts toward higher total energy as the initial orientation angle γ_i increases. This behavior is simply explained by the fact that the classical barrier height becomes larger as γ_i increases. Thus, the γ_i-dependent probability shown in Fig. 3 corresponds to what has been called the steric factor.

Figure 4 shows angle-averaged reaction probabilities, P_{ave}, as a function of the translational energy for the $H_2+CN \rightarrow H+HCN$ reaction. The reaction probabilities are calculated by the following equation:

$$P_{\mathrm{ave}}=\frac{1}{2}\int_0^{\pi}P(\gamma_i)\sin\gamma_i d\gamma_i, \tag{11}$$

where $P(\gamma_i)$ is the γ_i-dependent reaction probability. Figure 4 demonstrates the effects of the initial vibrational quantum numbers of H_2 and CN on the total reaction probabilities. It should be noted that excitation of the initial vibration of CN does not affect the reaction probability. On the other hand, the reactivity is greatly increased by vibrational excitation of H_2. This finding has already been pointed out by Sun and Bowman[9] and by Brooks and Clary[11] in their collinear calculations. This approximate theory also gives the same conclusion even if the effects of non-collinear collisions are taken into consideration.

Full-dimensional quantum results are not available for the H_2+CN reaction. However, it is possible to do

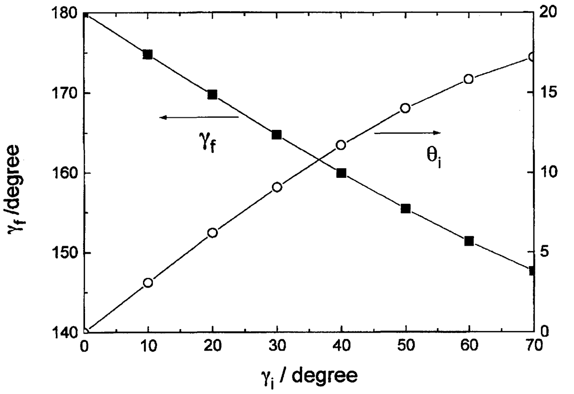


Fig. 2. γ_i-dependence of γ_f (filled squares) and θ_i (open circles) for the $H_2+CN \rightarrow H+HCN$ reaction on the potential energy surface employed in the present calculations. Once the value for B_{fi} is given, γ_f is calculated as a function of γ_i from Eq. 5. θ_i is calculated as a function of γ_i from Eq. 9 assuming $\theta_f=0°$ because the product HCN is a linear molecule.

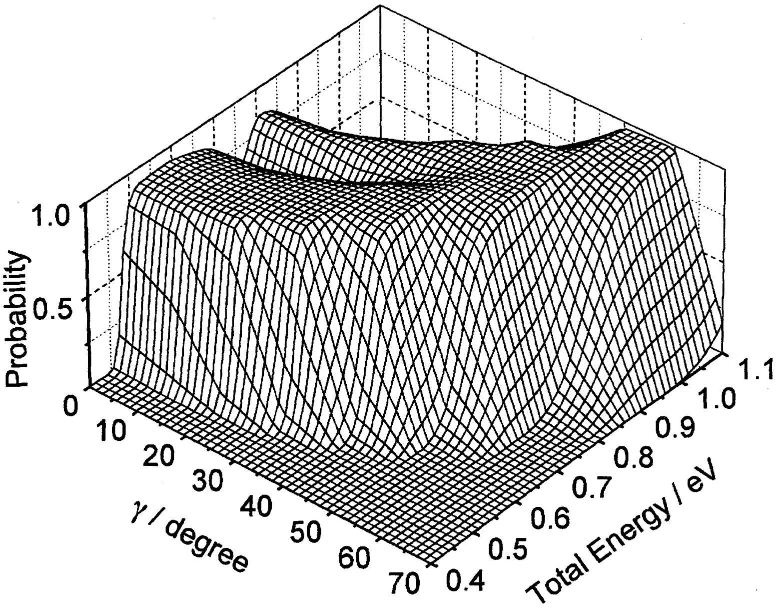


Fig. 3. Three-dimensional perspective plot of total reaction probabilities for the H_2 (v=0)+CN (v'=0)→H+HCN reaction.

full-dimensional quasiclassical trajectory (QCT) calculations. In the QCT method, the classical equations of motions are solved numerically and the initial conditions are selected by a standard Monte Carlo procedure. The details of the QCT method for diatom–diatom reactive collisions have been described in Ref. 31. To compare the QCT results with these approximate quantum results, the initial impact parameter and the initial rotational energies for the reactants, H_2 and CN, are set to be zero. The initial orientation angles between two diatomic molecules and the initial vibrational phases are selected randomly. The numerical integrations of the classical equations are done using a standard Runge–Kutta method. Typically, several hundreds of trajectories are calculated for each translational energy. Since we are interested in the total reaction probability, the assignments of final states are not done.

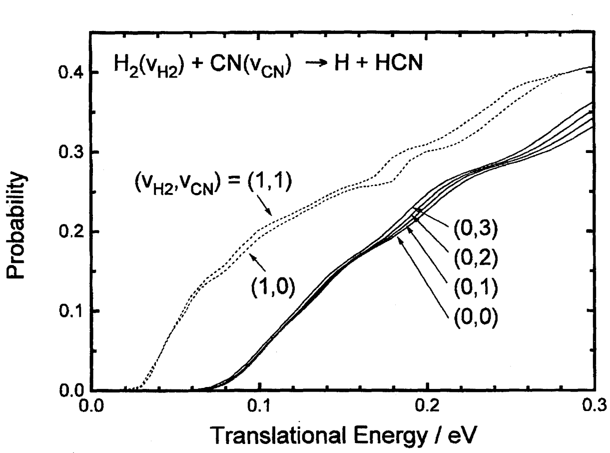


Fig. 4. Angle-averaged reaction probabilities as a function of translational energy for the H_2 (v_{H2})+CN (v_{CN})→H+HCN reaction.

Figure 5 shows the reaction probabilities obtained by the QCT calculations. A fairly good agreement with our quantum results is obtained at low translational energies less than about 0.2 eV. However, the quantum probabilities give larger values in the high translational energy region. Both the QCT results and the quantum results show that vibrational excitation of H_2 increases the reaction probabilities and that the vibrational excitation of CN does not increase the reaction probabilities. It is known that the QCT results are inaccurate at the reaction threshold region because the classical theory does not take into account quantum-mechanical tunneling. The difference between the quantum and

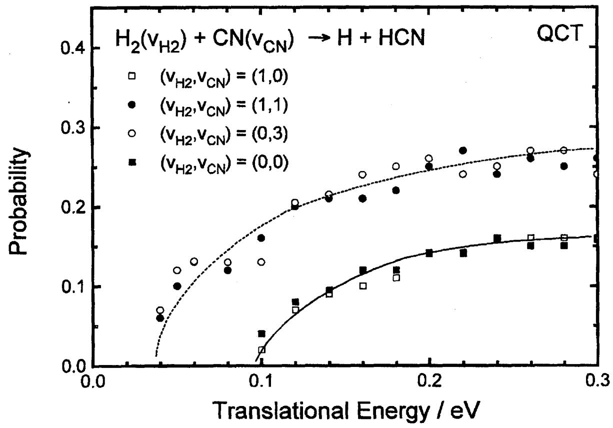


Fig. 5. QCT reaction probabilities as a function of translational energy for the H_2+CN→H+HCN reaction. Filled squares are for H_2 (v_{H2}=0)+CN (v_{CN}=0), open squares for H_2 (v_{H2}=0)+CN (v_{CN}=3), filled circles for H_2 (v_{H2}=1)+CN (v_{CN}=1), and open circles for H_2 (v_{H2}=1)+CN (v_{CN}=0). Solid and dashed lines are smoothed lines.

classical results is easily recognized from the functional forms of the probabilities at the reaction threshold region as shown in Figs. 4 and 5. In this stage of investigation, quantitative comparisons of our approximate quantum results with the QCT results is not possible, because there are no full-dimensional quantum calculations for the H_2+CN→H+HCN reaction. Nevertheless, a qualitative agreement with the QCT results should be emphasized.

Figure 6 shows the angle-averaged reaction probability for the reverse reaction, H+HCN $(v_s, v_a) \rightarrow H_2$+CN, where v_s and v_a are the symmetric and antisymmetric stretching vibrational quantum numbers of HCN, respectively. The symmetric stretch is predominantly the CN local stretch, while the antisymmetric stretch is mainly assigned to the local CH stretch. From Fig. 6 it is found that the reactivity is increased by excitation of the antisymmetric vibration and that the effect of excitation of the symmetric vibration on the reaction probability is small. Therefore, the computational results shown in Figs. 4 and 6 indicate that the CN vibration is adiabatically correlated to the symmetric stretching of HCN.

Although our quantum calculations are approximated and the potential energy surface used is semiempirical, it is still informative to compare these computational results with available experimental results qualitatively. Sims and Smith[32] have measured thermal rate constants for the H_2+CN $(v=0,\ 1)$→H+HCN reactions. They have shown that vibrational excitation of CN does not increase the reaction rate. Thus, their results can be explained qualitatively by the calculated reaction probabilities shown in Fig. 4. Unfortunately, there are no experimental measurements of the rate constants with H_2 vibrationally excited. From our computational results, it is expected that the reaction probabilities are significantly increased by vibrational excitation of H_2.

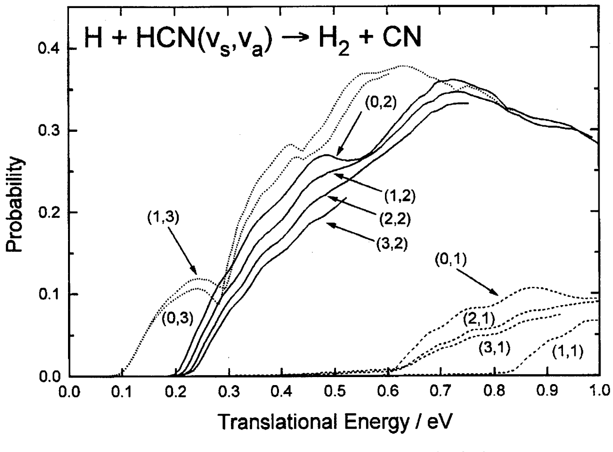


Fig. 6. Angle-averaged reaction probabilities as a function of translational energy for the H+HCN $(v_s, v_a) \rightarrow H_2$+CN reaction.

Discussion

In this paper, we have applied the fixed-angle approximation to the general four-atom reaction system, AB+CD→A+BCD. The fixed-angle approximation should be generally valid at high collision energies and work well for heavy-atom transfer reactions by analogy with the atom–diatom case.[27] In spite of these limitations, the approximation have been applied to many atom–diatom reaction systems because the order of the coupled-equations can be considerably reduced. Ideally, full-dimensional quantum reactive scattering calculations should be done for the four-atom reaction system. However, a large number of rotational channels in the four-atom reaction system including heavy atoms make the full-dimensional quantum calculations unrealistic. This approximate theory can handle such a system since only vibrational degrees of freedom are considered.

At low collision energies, the fixed-angle approximation is not valid; though an adiabatic-bend approximation rather works well.[27] In the adiabatic-bend approximation, the rotational motions during collision are treated as adiabatic bending vibrations. A detailed theory has been developed by Bowman and his coworkers and applied to the H_2+CN→H+HCN[9] and H_2+OH→H+H_2O[12—14] reactions as mentioned in the introduction.

It is possible to calculate a so-called steric factor by using the fixed-angle approximation as is demonstrated in Fig. 3. The steric factor provides useful information for understanding the reaction dynamics qualitatively. In addition, this approximate theory can also be applied to the non-collinear dominated reaction other than H_2+CN→H+HCN.

In this calculations, only the reaction probabilities have been calculated because the effect of the orbital angular momentum is not taken into account. Inclusion of such an effect may be straightforward. Therefore, calculations of reaction cross sections and rate constants become possible. In the near future, we plan to apply such a theory to various four-atom reaction systems.

Summary

We have developed an approximate theory for the general four-atom chemical reaction system, AB+CD→A+BCD, in which the orientation angles are fixed during collision in each arrangement channel. The theory has been applied to the H_2+CN→H+HCN reaction on the model potential surface developed by Sun and Bowman. The angle-dependent reaction probabilities have been calculated, giving a qualitative picture for a so-called steric factor.

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