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MODEL FOR THREE BODY REACTIONS

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MODEL FOR THREE BODY REACTIONS

by

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ABSTRACT

Exact quantum mechanical reactive cross sections are reported for a three dimensional angle dependent model surface. The surface simulates an atom-heteronuclear diatom system $A + BC \rightarrow AB + C$ where atom B is much heavier than A or C. The molecules BC and AB are taken to be rotating vibrators which can dissociate. Results for two angle dependent potentials are given.

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Exact quantal calculations for models serve important functions by providing insight which can aid in treating more complex problems, providing "benchmark" calculations so that various methods for treating difficult problems may be tested and compared inexpensively and suggesting simple pictures which are useful in correlating complex phenomena. This has been especially true in the case of quantum mechanical reactive scattering studies.¹ With a view toward future treatments of full three dimensional reactive scattering using smooth potentials, exact quantum mechanical reactive scattering cross sections for a full three dimensional angle dependent model rearrangement collision process have been computed.

The model was chosen to simulate reactions of an atom with a heteronuclear diatomic BC, with the mass of B being much larger than that of the other two. The interaction surface employed represents a system where atoms A and B are attracted whereas A and C repel one another. The diatomic molecules are treated as rotating vibrators and their internal states numerically determined. Total reactive cross sections summed over all possible final states have been obtained.

The model potential is given by

$$V(r, R, \theta) = \begin{cases} 0, & r < R_0, R > R_0 \\ 0, & r > R_0, R < R_0 \\ V_0 + V_1 P_1(\cos\theta), & r < R_0, R < R_0 \\ V_0, & r > R_0, R > R_0 \\ \infty & \text{elsewhere,} \end{cases}$$

where r is the distance between B and C, R is the distance between B and A, θ is the angle formed by the triangle A-B-C, V_0 is the binding energy of the diatomic molecules, v_0 is a barrier and v_1 is taken to be approximately $v_0/2$. Thus the barrier varies from $3v_0/2$ for equal θ equal 0° to $v_0/2$ for θ equal π .

For the scattering calculations, coupled channel τ operators were employed.^{1,2} The zero point energy of the molecule was 0.0747 eV and calculations were performed over an energy range from 0.16 to 0.56 eV. A total of 5 vibrational states were employed in all these calculations (at least three vibrational states were closed channels). For the open channel vibrational states, all open rotational states plus two closed rotational states were included while for the higher vibrational states, only one rotational state was required (namely that state which satisfied the "angle independent" reactive selection rule $\Delta j = (\ell_i - j_i)$, $\Delta \ell = (j_i - \ell_i)$). At the higher energies, this resulted in inclusion of 4 molecular j values for the ground vibrational state, 3 molecular j values for the first excited vibrational state and one molecular j value for each of the next three vibrational states (this is of course for both the α and β arrangement molecules).

The total cross section as a function of total energy is shown in Figure 1. An interesting propensity rule for reaction was found to be $\Delta j = (\ell_i - j_i)$ and similarly $\Delta \ell = (j_i - \ell_i)$ for the potential $2.3 + 1.33 \cos \theta$. For an angle independent potential, this would be a rigorous selection rule and in fact, the results for an angle independent potential with $v_0 > 0$ are quite similar to those for the

present angular dependent potential with the same v_0 . The angle dependence of this potential leads to a variation in barrier height from 3.63 for $\theta = 0^\circ$ to 0.97 for $\theta = \pi$ (in units of energy equal to the zero point energy of the molecule). If one assumes that the region in Figure 1 for energies $E \lesssim 2$ corresponds to primarily tunneling reaction, then the results suggest an effective barrier for the angle dependent problem of ~ 2.2 . This is essentially the same as what would occur if v_1 were zero. One interpretation of this is to suggest a preferred attack of $\theta \sim \pi/2$ for reaction to occur (since then $v_1 \cos \theta = 0$).

In Figure 2 we present some example results on the dependence of $|T|^2$ for reaction on the total angular momentum quantum number J . For these calculations, the potential is taken to be $1.33 \cos \theta$ so that now the potential changes from a barrier of 1.33 for $\theta = 0^\circ$ to a well of -1.33 for $\theta = \pi$. Again, for the angle independent potential $v_0 = 0, v_1 = 0$, the $|T|^2$ values are independent of the value of J and this has been shown to lead to completely isotropic scattering.³ In the present case, it is clear that the scattering will now be angle dependent (on the angle θ between the incident and exit wave vectors). The appearance of $|T|^2$ values essentially equal to one suggests that orientations of the system with angles θ satisfying $0 \leq \theta < \pi/2$ must be important since it is known that for similar collinear models, reaction probabilities for potential wells are usually quite small.^{1,4} This is associated with the dependence of the reaction probability on the length of time atom A is within a distance R_0 of atom B. The presence of a well speeds up atom A so that it

leaves the reaction zone before atom B thereby reducing the reaction probability.

More detailed results and analysis will be presented in a paper to be published elsewhere.

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REFERENCES

1. For example, H. Hulburt and J. O. Hirschfelder, J. Chem. Phys. 11, 273 (1944); K. T. Tang, B. Kleinman and M. Karplus, ibid. 50, 1119 (1969); D. J. Diestler, ibid. 50, 4746 (1969), M. Baer and D. J. Kouri, ibid. (to be published) are a few representative references for studies of simple collinear models. For the system H-H₂ collinear (which is, of course, a model), examples include D. G. Truhlar and A. Kuppermann, J. Chem. Phys. 52, 3841 (1970); E. M. Mortenson and L. D. Gucwa, ibid. 51, 5695 (1969); D. J. Diestler, ibid. 54, 4547 (1971). Most recently, preliminary results for H-H₂ reactive scattering in a plane have been reported by R. P. Saxon and J. C. Light, J. Chem. Phys. 55, 455 (1971). This represents only a small sampling since all exact quantum calculations to date represent model calculations.
2. M. Baer and D. J. Kouri, Phys. Rev. (to be published).
3. M. Baer and D. J. Kouri, J. Chem. Phys. (to be published).
4. N. S. Evers and D. J. Kouri, J. Chem. Phys. (to be published).

FIGURE CAPTIONS

Figure 1. Total reactive cross section (summed over all final states) in units of Å^2 plotted versus total energy in units of the molecular zero point energy (0.0747 eV). The initial state is $n = 1$, $j = 0$ (ground state). The potential parameters are $v_0 = 2.3$ and $v_1 = 1.33$ ground state units. V_0 is taken as 5 eV, the masses of particles A and C are 1 H atom mass and R_0 is 0.5 Å .

Figure 2. Reaction probabilities for $J = 0$ and $J = 2$ as a function of total energy (expressed in units of the initial state = 0.157 eV). The potential parameters are $v_0 = 0$, $v_1 = 1.33$. The curve (---) is for $n = 1$, $j = 1$, $\ell = 1$, $J = 0$ and the curve (—) is for $n = 1$, $j = 1$, $\ell = 1$, $J = 2$. The masses of A and C, V_0 and R_0 are the same as for Figure 1.



FIGURE 1

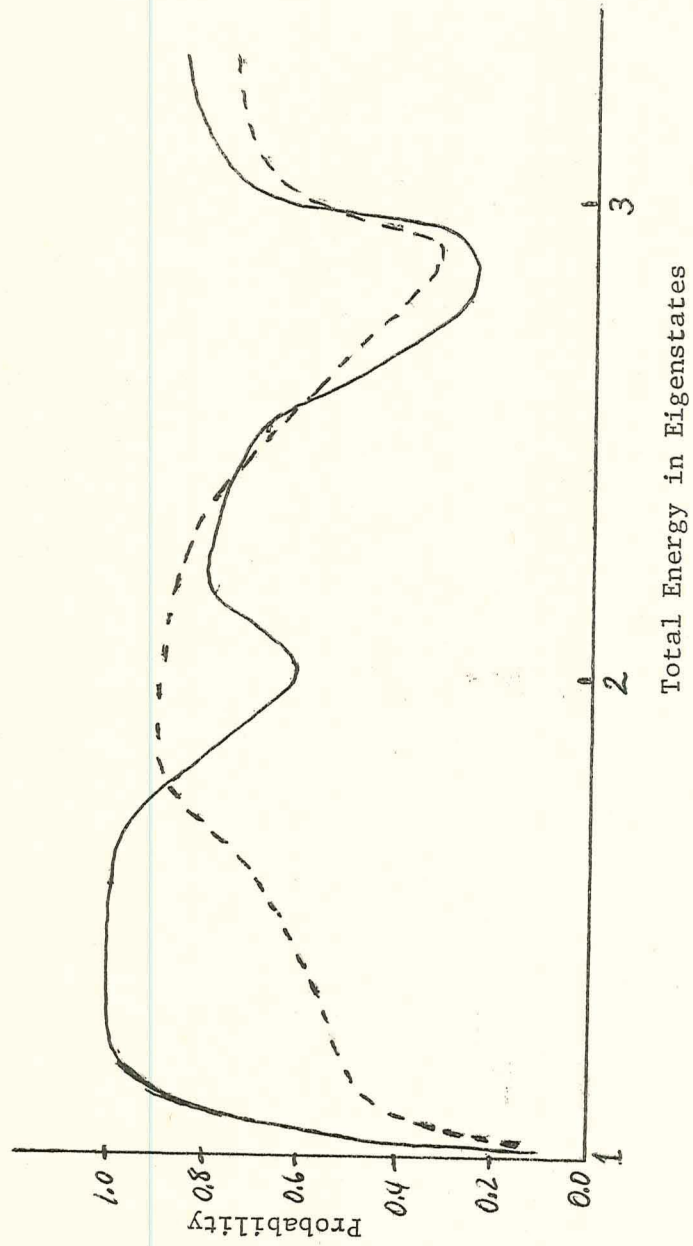


FIGURE 2