R-MATRIX THEORY OF REACTIVE ATOM–DIATOM COLLISIONS

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For chemical reactions, R-matrix theory is demonstrated to be well suited both as a computational tool and for investigations of the reaction mechanism. Transition probabilities are calculated for three different potential surfaces and the results discussed in terms of resonance states.

1. Introduction

At present there exist quite a number of quantum mechanical methods to calculate numerically transition probabilities for collinear atom–diatom collisions by directly solving the Schrödinger equation. Since these methods are especially tailored to the one-dimensional problem and yet require a large amount of computer time, the treatment of real chemical systems seems to be practically possible only by introducing simplifications based on physical models. In general, these models assume either a pure direct-reaction or a pure compound mechanism. However, in a chemical reaction both of these mechanisms contribute, their relative importance not yet being clear.

As is well known, there are some fully worked out formal reaction theories such as R-matrix theory (RMT) [1] or Feshbach's projection-operator theory [2] which not only allow a clear separation between these two mechanisms but also make explicit their influence on each other and even are able to take into account more complicated reaction mechanisms of an intermediate nature [3]. Thus, it is felt, that by using these theories in dynamical calculations much insight could be gained into the mechanism of a chemical reaction and possibly new computational methods might be developed.

RMT seems to be well suited for this purpose, since it is formulated in terms of a set of discrete states $|X_\lambda\rangle$ which are usually interpreted as complex; it is also apt to describe direct reactions. To test this

presupposition numerical calculations of collinear atom–diatom collisions were carried through for three different potential surfaces.

2. Calculation of transition probabilities

The three potential surfaces used, are Wall–Porter potentials [4] which differ only in the parameter a that determines the barrier height. Surface I is the H_2 +H surface with $a = 0.128$ and for surfaces II and III the values of a are 0.064 and 0.0, respectively.

The method of calculation of the transition probabilities is similar to that used in the work of Crawford [5]. The $|X_\lambda\rangle$, the fundamental states of the R-matrix theory, were obtained by diagonalizing the hamiltonian in a set of basis states fulfilling the special boundary conditions of this theory. These basis states were constructed from a primitive basis set P_m^l made up of gaussian functions multiplied by polynomials:

$$P_m^l = (a_m x + b_m y)^l \exp\{-[(x-x_m)^2 + (y-y_m)^2]/2\sigma_m^2\},$$

$$l = 0, 1, \dots N, \quad m = 1, \dots M, \tag{1}$$

where x, y are the coordinates of an arbitrary point on the potential surface, x_m, y_m the coordinates of the center of the gaussian function and σ_m its width. The centers were located directly on the reaction path and at each center, the values of a_m, b_m, σ_m were chosen such that combinations of P_m^l with different l describe the oscillations of the system perpendicular

to the reaction path. After having obtained the $|X_\lambda\rangle$ and thus the energies E_λ and widths $\gamma_{\lambda c}$ from the R-matrix, the S-matrix and transition probabilities are calculated as usual [1, 5]. Apart from the modifications of the primitive basis set and the value of B_c, all parameters of the calculation, especially the choice of the internal region, were the same as in ref. [5].

To study how the modifications of the basis set described above influence the results, calculations with different basis sets were carried out for the potential surface I (the same as used by Crawford). As starting point a calculation was carried through using the same basis set as Crawford but with varying values of σ_m from center to center, thus taking explicitly into account the varying width of the valleys of the potential surface. The results show that the agreement with the exact results of Diestler [6] is much improved upon Crawford's calculation with constant values of σ_m. This agreement is further improved by allowing for all the modifications described above and by increasing the number of gaussian centers from 10 to 14 retaining however $N = 1$. If finally N is increased from $N = 1$ to $N = 2$, which means that the second excited state of the oscillations perpendicular to the reaction path is also taken into account, we get the results shown in fig. 1.

From fig. 1 it may be seen that up to kinetic energies of $E \approx 0.8$ eV, we get a quite good agreement with the exact calculations of Diestler. For higher energies the agreement is much worse due to the fact that the $|X_\lambda\rangle$ were calculated from the Raleigh–Ritz variational method which yields a decreasing accuracy for increasing values of E_λ. This improvement is, however, not as suggested by Crawford due to the greater number of states $|X_\lambda\rangle$ taken along in the R-matrix but instead due to the improved accuracy of the states $|X_\lambda\rangle$. This can be seen from curve 4 of fig. 1, which was calculated using only the first five states $|X_\lambda\rangle$ (table 1) in the R-matrix. Since both curves differ only very little from each other and since the two lowest states $|X_\lambda\rangle$ cancel each other in their influence on the transition probability [5], it is concluded that all the low energy behavior of the $H_2 + H$ reaction is given by only three states $|X_\lambda\rangle$.

An analogous conclusion can also be drawn for the transition probabilities at higher energies E. In the same way as just described it can be shown that at a certain energy E the X_λ with values of E_λ in the vicini-
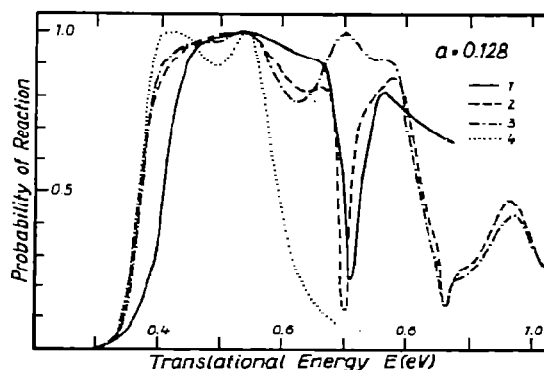

Fig. 1. Transition probabilities for the $H_2 + H$ Wall–Porter potential surface from various R-matrix calculations (curves 2 to 4) and from the exact calculations of Diestler (curve 1). Curve 2 is calculated including all the states $|X_\lambda\rangle$ into the R-matrix sum whereas in the calculation of curve 3 the narrow state $|X_\mu\rangle$ is missing and for curve 4 only the 5 lowest states $|X_\lambda\rangle$ are taken into account. All calculations were done with $N = 2$. The value of the boundary condition parameter is $B_c = -4$.

ty of E give the most important contribution to the transition probability.

For the potential surfaces II and III we find exactly the same results. Again, as can be seen from figs. 2 and 3, the agreement with the exact calculations of Diestler is quite good and at any energy a very restricted number of X_λ is sufficient to calculate the main contribution to the transition probability.

3. Interpretation

Through the usual reasoning of R-matrix theory the complex-formation mechanism manifests itself in isolated resonances or in overlapping resonances with uncorrelated signs of the $\gamma_{\lambda c}$ whereas the direct-reaction mechanism shows up in correlations of the signs, the correlations extending over a great number of the $\gamma_{\lambda c}$. The above established fact, that a restricted number of $|X_\lambda\rangle$ yields nearly all of the transition probability at a certain energy would thus imply that the reaction proceeds mainly via complex formation, the complex states being given by the $|X_\lambda\rangle$. However in the case of the $H_2 + H$ potential we find, that apart from a resonating behaviour [7, 8] at $E \approx 0.7$ eV and possibly in the threshold region [8] the transition

Table 1

The parameters of the lowest states $|X_\lambda\rangle$ of the $N = 1$ and $N = 2$ calculations for potential surface I. $\gamma_{\lambda 0}$ denotes the width for decay into the ground state channel ($c = 0$). Γ_λ is calculated in the single level approximation [1, 5] and the symmetry character refers to reflections at the symmetry axis of the potential surface. The value of the boundary condition parameter is $B_c = -4$

$N = 2$				$N = 1$			
E_λ (eV)	$\gamma_{\lambda 0}$ (eV$^{1/2}$)	Γ_λ (eV)	symm.	E_λ (eV)	$\gamma_{\lambda 0}$ (eV$^{1/2}$)	Γ_λ (eV)	symm.
0.301	0.059	0.094	+	0.302	0.060	0.095	+
0.306	0.064	0.107	−	0.307	0.064	0.108	−
0.416	0.041	0.053	÷	0.417	0.041	0.052	+
0.497	0.050	0.037	−	0.500	0.049	0.084	−
0.598	0.047	0.081	+	0.599	0.046	0.079	+
0.698	0.015	0.017	+	0.739	0.020	0.017	+
0.731	0.045	0.083	−	0.739	0.045	0.085	−

Fig. 2. Transition probabilities for surface II. The labelling of the curves is the same as in fig. 1. The value of B_c is −2.
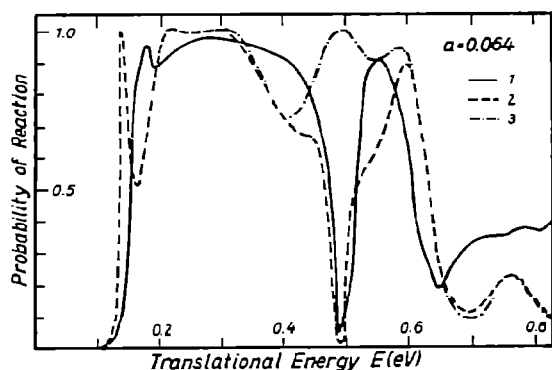

Fig. 3. Transition probabilities for surface III. The labelling of the curves is the same as in fig. 1. The value of B_c is −1.

probability and phase shifts show a smooth behaviour indicating a direct reaction mechanism. Moreover, the trajectory calculations on the $H_2 + H$ potential surface suggest [9] that this reaction proceeds mainly by a direct mechanism. Thus we establish the fact, till now unknown in R-matrix theory, that a small number of states $|X_\lambda\rangle$ is able to describe not only the complex-formation but also the direct-reaction mechanism, provided the boundary conditions are suitably chosen. These states $|X_\lambda\rangle$ have to be correlated very strongly to give the relatively smooth curves of the transition probability seen in the figures.

We now try to interpret the dip found in the transition probability of the $H_2 + H$ reaction at $E \approx$ 0.7 eV. As can be seen from fig. 1, there is a relatively "narrow" state $|X_\mu\rangle$ at the energy $E = 0.697$ eV. In order to test whether this state is responsible for the resonating behaviour at this energy, the transition
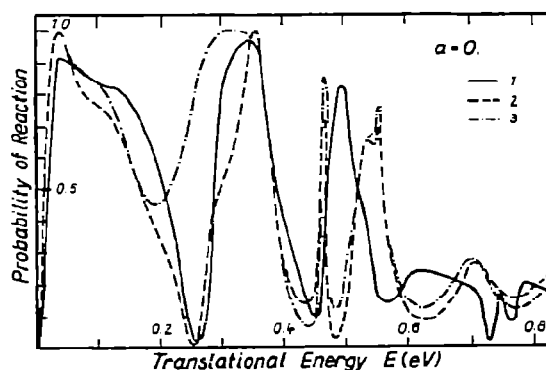
probability and phase shifts were calculated using the same states $|X_\lambda\rangle$ but without including the single state $|X_\mu\rangle$ into the R-matrix sum. Curve 3 of fig. 1 shows clearly that in this case the dip in the transition probability is totally missing. This suggests that the fluctuation at $E \approx 0.7$ eV is caused by the interference of an isolated resonance with a relatively energy independent background caused by the other overlapping and strongly correlated $|X_\lambda\rangle$ and that furthermore this resonance is due to a complex state described entirely by the single state $|X_\mu\rangle$. The lifetime τ_h of this state is in the single level approximation

$$\tau_h = 2\hbar/\Gamma_\lambda = \hbar/P_c\gamma_{\lambda c}^2 ,$$

where P_c is the penetration factor [1, 5], given by τ_h = 4.8 × 10^{-14} sec. Thus τ_h is about five times as long as the corresponding lifetimes of the other $|X_\lambda\rangle$. It should be noted that X_μ has positive symmetry with

regard to reflections of the coordinate systems at the symmetry axis of the potential surface.

There is a number of further facts which show that $|X_\mu\rangle$ is really a complex state in the usual sense. The small values of $\gamma_{\mu c}^2$ suggest that the wavefunction $|X_\mu\rangle$ is concentrated mainly in the inner part of the internal region around the saddle point. Moreover from table 1 it can be seen that from the lowest lying states $|X_\lambda\rangle$ only the state $|X_\mu\rangle$ is sensitive in going from $N = 1$ to $N = 2$. This means that this state has a more complicated wavefunction, higher excitations of the motion perpendicular to the reaction path playing a more important role. Finally, varying the boundary conditions in the range of $B_c = -2$ to $B_c = -9$ we find that the corresponding resonance energy (in the single level sense) changes by about 0.3% and the value of $\gamma_{\mu\sigma}$ by about 8%. This demonstrates [1] that the state $|X_\mu\rangle$ is really a physical state and not only serves as a formal mathematical basis state.

Exactly the same results are obtained for the potential surface II. Here, the state $|X_\mu\rangle$ causing the interference structure lies at $E = 0.49$ eV and has a lifetime of 9.6×10^{-14} sec. Again it is a state of positive symmetry.

For surface III the situation is somewhat less clear. Again, the minimum at $E = 0.26$ eV is caused by a complex state of positive symmetry but even neglecting the influence of this state the transition probability has still a resonating character (see curve 3 of fig. 3). This could be due to a kind of Ericson fluctuation [10] caused by the states $|X_\lambda\rangle$ which then would have to be interpreted as very short lived complex states

coupled strongly to the continuum. This point is under further study and will be treated in a forthcoming paper, where along with further material, the behaviour at threshold and the relationship to the concept of the dynamical Eyring sea will also be discussed.

Acknowledgement

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