SEMICLASSICAL *S* MATRIX THEORY FOR A COMPOUND STATE RESONANCE IN THE REACTIVE COLLINEAR $H + H_2$ COLLISION*

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The broad compound state resonance found in quantum mechanical calculations of the collinear $H + H_2$ reaction is shown to correspond semiclassically to multiple collisions of the atoms within the collision complex. The quantitative agreement between QM and SC results is quite reasonable.

1. Introduction

The semiclassical theory of inelastic and reactive collisions developed by Miller [1, 2] and Marcus [3, 4] has been applied to a variety of problems involving vibrational–translational and rotational–translational energy transfer, with encouraging results [1–6]. Application has also been made to the $A + BC \to AB + C$ reactive collision problem [7–10]. The collinear reactive $H + H_2$ problem in particular has been studied in considerable detail, both semiclassically [8, 9] and quantum mechanically [11, 12].

The quantum reactive calculations have been used, as they have in the inelastic nonreactive calculations, to test the semiclassical theory. The quantum and semiclassical results agreed well in the tunneling region, i.e., at translational energies below the classical threshold [9]. However, at higher energies the semiclassical method appeared to reproduce only the average behavior of the transition probability [8]. Specifically, a strong oscillation in the exact quantum mechanical reaction probability versus total energy plot, associated with a Feshbach compound-state resonance, was not reproduced by the several numerical applications which have been made of the theory [8].

In this communication we show that this quantum mechanical resonance effect is described quite adequately if one includes the classical trajectories in which the atoms of the collision complex undergo multiple collisions with each other. The previous calculations neglected the latter. The interference by these additional trajectories produces the oscillation in the quantum transition probability. A complete description of the results and method will be published later.

2. Description of the collision system and classical results

The classical hamiltonian for this system in the center of mass system of coordinates is [7]

$$H = (P^{\mathrm{I}})^2/2\mu + (p^{\mathrm{I}})^2/2m + V(R^{\mathrm{I}}, r^{\mathrm{I}}) = E\,, \qquad (1)$$

where R^{I} denotes the distance between A and the center of mass of BC in a reaction $A + BC \to AB + C$, where A, B, and C are hydrogen atoms; r^{I} denotes the BC distance. P^{I} and p^{I} are canonically conjugate to R^{I} and r^{I}, respectively. Similarly, R^{II} denotes the distance between C and the center of mass of AB, r^{II} denotes the AB distance, etc. Without danger of confusion, the region where A is far from BC will be called asymptotic region I, and the region where C is far from AB is called II. In present case μ is $2m_{\mathrm{H}}/3$, m is $m_{\mathrm{H}}/2$ and m_{H} is mass of hydrogen atom.

A Wall–Porter potential [13] was used for V. In each asymptotic region I and II it has the property of

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reducing to a Morse potential for the vibrational coordinate. Hamilton's equations were obtained directly from eq. (1) and were integrated numerically from some initial time t_i. The initial values of the coordinates and momenta were[†]: R_i^I = large, $P_i^I = -\{2\mu[E - \epsilon(n_i^I)]\}^{1/2}$, $r_i^I = r_<^i$, and $p_i^I = 0$, where $\epsilon(n)$ is the energy of the Morse oscillator [7] in state n, n is the classical analogue of the quantum number, and $r_<^i$ is the lower turning point of the Morse oscillator at R_i^I. The integration was terminated at some final time t_f such that the final values were R_f^γ = large, $P_f^\gamma = \{2\mu[E - \epsilon(n_f^\gamma)]\}^{1/2}$, $r_f^\gamma = r_<^f$, and $p_f^\gamma = 0$, where γ is I or II according as the trajectory ends in region I or II; $r_<^f$ is the lower turning point of the Morse oscillator. For notational simplicity the γ will be omitted in n_f^γ and in a conjugate variable $\bar{w}_f^\gamma$, but will be retained in R_f^γ and P_f^γ.

The variables used to specify the initial coordinates and momenta are the total energy E, the initial state of the oscillator n_i (which equals an integer), and $\bar{w}_i$ defined by [1–4]

$$\bar{w}_i = w_i - \mu\nu(n_i)R_i^I/2\pi P_i^I\,, \tag{2}$$

where w_i is the initial angle of the oscillator, obtainable from eq. (5) of ref. [7] (q is our $2\pi w$) for a Morse oscillator, and ν is the frequency of the oscillator [7].

The phase φ was integrated along with Hamilton's equations and is given by [1–4]

$$\varphi = \int_{t_i}^{t_f} [P^I(t)\dot{R}^I(t) + p^I(t)\dot{r}^I(t)]\,dt + P_i^I R_i^I - P_f^\gamma R_f^\gamma\,. \tag{3}$$

Apart from certain multiples of $\pi/2$ the phase Δ appearing in the integral representation of the S matrix [4] equals a quantity we shall denote by Φ:

$$\Phi = \varphi - 2\pi(n_f - m)\bar{w}_f\,, \tag{4}$$

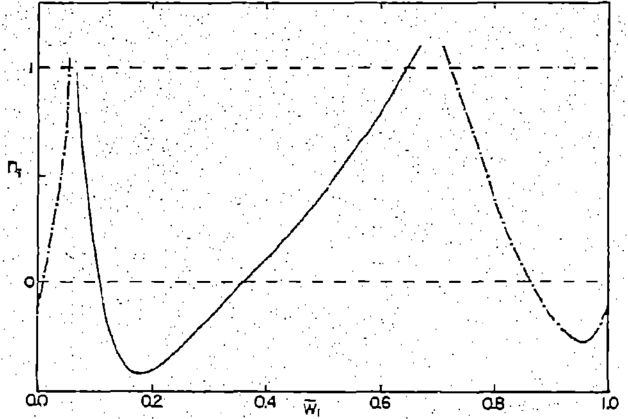

Fig. 1. Final vibrational quantum number for E = 22.0 kcal/mole and n_i = 0. Reactive trajectory results are shown with solid line (—); nonreactive results with dotted dash (–.–.–). Horizontal dashed line (– – –) is graphic solution to eq. (5) for m = 0,1. For m = 0 there are two real roots on the reactive and nonreactive branches.

where m is the desired final integer vibrational quantum number for a transition $n_i \to m$, and where $\bar{w}_f$ is the same as (2) with i and I replaced by f and γ.

3. Classical results

A typical distribution of final vibrational quantum number (n_f) for n_i = 0 in the range 16 to 29 kcal/mole is shown in fig. 1. The dashed line indicates the solution of

$$n_f - m = 0\,, \tag{5}$$

for m = 0 and 1. Eq (5) is the stationary phase condition of the integral representation of the S matrix, i.e., it is the solution of $d\Phi/d\bar{w}_f = 0$ [2, 4]. In fig. 1 there are seen to be two such roots (stationary phase points) on the reactive branch and two on the nonreactive branch.

Between the reactive branch and the nonreactive branch is a region in which the atoms execute multiple collisions. Between these two reactive–nonreactive branches we have found that there is another reactive–nonreactive branch, each branch containing two stationary phase points. Between each of these is still another branch, and so on.

[†] In actual practice all numerical integrations were begun at a fixed R_i^I outside the interaction region and at various values of r_i^I corresponding to an initial uniform distribution of the vibrational phase. Analytical integration was then used to reach $r_<^i$ and the variable R_i^I in each case. The reason for beginning with $r_<^i$ is described in ref. [4]. The same remarks apply to the final values of the trajectories, which were in practice terminated at a fixed R and integrated analytically until a lower vibrational turning point $r_<^f$ was reached (cf. ref. [4]).

These different branches were grouped according to the number of additional collisions that the atoms executed in the interaction region. That is, those trajectories that pass directly over the col in the potential energy surface were designated as being of order zero. Those that execute an additional collision are of first order, etc. There are 2 zero order, 4 first order, and 8 second order stationary phase points, as well as higher order points.

It was also found in the present work that between the two stationary phase points on each branch in this system there exists a $\bar{w}_i$ where $d\bar{w}_f/d\bar{w}_i = 0$. The inverse of the jacobian is related to the pre-exponential factor of the primitive semiclassical wavefunction. The latter is infinite at the $\bar{w}_i$ where this jacobian sign change occurs, although it is well-defined away from such a region. Unlike the case considered heretofore in the derivation of a uniform approximation for the S matrix from the integral representation [5, 14], the value of $d^2\Phi/d\bar{w}_f^2$ is negative now for *both* stationary phase points, a fact used in the next section.

4. A uniform approximation

As was observed in the previous section, this system has a very large (possibly infinite) number of stationary phase points, and between each pair is a jacobian sign change. This situation makes difficult the rigorous derivation of a uniform approximation, and we obtain it on an intuitive basis.

A stationary phase evaluation of the integral expression for the S matrix yields for the present case

$$S_{n_i m} = \sum_{\text{branches}} \{p_1^{1/2} \exp[i(\Delta_1^c - \tfrac{1}{4}\pi)] + p_2^{1/2} \exp[i(\Delta_2^c - \tfrac{1}{4}\pi)]\}\,, \tag{6}$$

where the sum is over all branches, each branch containing two stationary phase points. The $-\pi/4$ in *both* terms (instead of the more usual $-\pi/4$ and $+\pi/4$) is a result of the fact that $d^2\Phi/d\bar{w}_f^2$ is negative for both stationary phase points. Δ^c arose from the phase of the wavefunction [3, 4] and includes the phase of the pre-exponential factor, while p_1 and p_2 denote the classical probabilities:

$$\Delta^c = \Phi - N(\pi/2)\,, \quad p_j = |dn_f/d\bar{w}_i|_j^{-1} \quad (j = 1,2)\,, \tag{7}$$

where N is the number of times the trajectory touches a caustic, i.e., the number of times that "adjacent trajectories cross", between $t = t_i$ and $t = t_f$ [4, 15]. Analysis of the wavefunction near the point $\bar{w}_i$ where the jacobian sign change occurs shows that Δ_1^c should approach $\Delta_2^c + \frac{1}{2}\pi$ as this point is approached from either side along each branch.

The calculation of N may be conveniently carried out in the following manner. The van Vleck determinant [16], whose square root is the pre-exponential factor of the semiclassical wavefunction [3, 4], is shown in a later paper to equal

$$D = \begin{vmatrix} \partial\bar{w}_i/\partial R^I & \partial\bar{w}_i/\partial r^I \\ \partial t/\partial R^I & \partial t/\partial r^I \end{vmatrix}\,. \tag{8}$$

D becomes infinite on a caustic. The inverse of D can be shown to be

$$D^{-1} = \begin{vmatrix} (\partial R^I/\partial\bar{w}_i)_t & (\partial r^I/\partial\bar{w}_i)_t \\ P^I/\mu & p^I/m \end{vmatrix}\,. \tag{9}$$

D and D^{-1} vary along a trajectory. One can show that N is the number of times D^{-1} changes sign throughout the trajectory between t_i and t_f[†].

Eq. (7) gives the *absolute* value for the phase Δ^c. This Δ^c is also independent of any extra periods that the oscillator may go through after passing through the interaction region.

We wish to employ a uniform approximation whose asymptotic form is eq. (6). Two expressions which have this asymptotic form are[‡]

$$S_{n_i m} = \sum_{\text{branches}} e^{iA}[(p_1^{1/2} + p_2^{1/2})\zeta^{1/2}\,\mathrm{Ai}(-\zeta) - i(p_1^{1/2} - p_2^{1/2})\zeta^{-1/2}\,\mathrm{Ai}'(-\zeta)]\,, \tag{10a}$$

[†] Ref. [15] describes a phase integral justification.

[‡] These forms were prompted by those used in refs. [14] and [2], respectively, which were developed for a simpler case, one for which (10a) had a more rigorous derivation than (10b). Now, however, neither is rigorous.

and

$$S_{n_1 m} = \sum_{\text{branches}} e^{iA} [(p_1^{1/2} + p_2^{1/2}) \zeta^{1/2} \,\mathrm{Ai}(-\zeta)$$

$$+ i(p_1^{1/2} - p_2^{1/2}) \zeta^{1/2} \,\mathrm{Bi}(-\zeta)] \,, \qquad (10b)$$

where Ai and Bi denote Airy functions and the prime denotes derivative [17]. A and ζ are given by

$$A = \tfrac{1}{2}(\Delta_2^u + \Delta_1^u) \,, \qquad \zeta = \{\tfrac{3}{4}(\Delta_2^u - \Delta_1^u)\}^{2/3}$$

and

$$\Delta_1^u = \Delta_1^c - \tfrac{1}{2}\pi \,, \qquad \Delta_2^u = \Delta_2^c \,. \qquad (11)$$

where Δ_1^u should approach Δ_2^u as a $\overline{w}_i$ approaches the point of jacobian sign change, at any given energy. To decide which of the two Δ^c's determined from eqs. (4) and (7) is Δ_1^c, one notes that subtraction in eq. (11) of $-\pi/2$ from the wrong Δ^c yields a Δ^u which does not have this property of continuity.

5. Numerical calculations and results

The zeroth, first and second order stationary phase trajectories (14 reactive and 14 nonreactive) were found for $n_i = 0$ and $m = 0$ at a particular energy. Higher orders were neglected, since typically the classical probabilities became smaller as the order increased, by somewhat less than an order of magnitude each time, with some overlapping of the successive orders. The trajectories had initial and final conditions as discussed in section 2, and the phase Φ was calculated using eqs. (3) and (4). All trajectories were real-valued. The classical probabilities p in eq. (7) were calculated from n_f versus $\overline{w}_i$ data, using a quadratic differentiation formula with $\delta \overline{w}_i$ chosen sufficiently small that p remained constant if $\delta \overline{w}_i$ was halved. The N in eq. (7) was calculated using three adjacent trajectories (one on either side of the stationary phase trajectory) with $\delta \overline{w}_i$ equal to the value used in the differentiation. N is equal to the number of sign changes of the thus calculated determinant in eq. (8).

The detailed calculation of Δ^c using eqs. (4) and (7), and then using eq. (11) and continuity of Δ^u to determine Δ_1^u and Δ_2^u, was necessary only for a single energy. For any other energy it then sufficed to use the following expression for φ [7]

$$\varphi = \int_{t_1}^{t_2} [P^I \dot{R}^I + p^I \dot{r}^I] \,dt + f_2(r_i^I, n_i) + P_i^I R_i^I$$

$$- f_2(r_f^\gamma, n_f) - P_f^\gamma R_f^\gamma \,, \qquad (12)$$

where $f_2(r, n)$ is the generating function for the Morse oscillator [7], and then add or subtract multiples of π so as to make Δ_1^u and Δ_2^u continuous functions of the energy. This method was checked by comparing the resulting value with an independent detailed calculation which we made of Δ_1^u and Δ_2^u at another energy. The results agreed.

The phases Δ^u and classical probabilities p were found for the zeroth, first, and second order trajectories at 13 equi-spaced energies in the range 16 to 29 kcal/mole. The transition probability is simply given by

$$P_{n_i m} = |S_{n_i m}|^2 \,. \qquad (12)$$

Figs. 2 and 3 show the reactive probabilities as a function of total energy, for the two uniform approximations. The exact quantum mechanical values of Truhlar and Kuppermann [12] are also given, as is the semiclassical result for the zeroth order trajectory. Only the latter was used in earlier applications of semiclassical theory to this problem [8, 9].

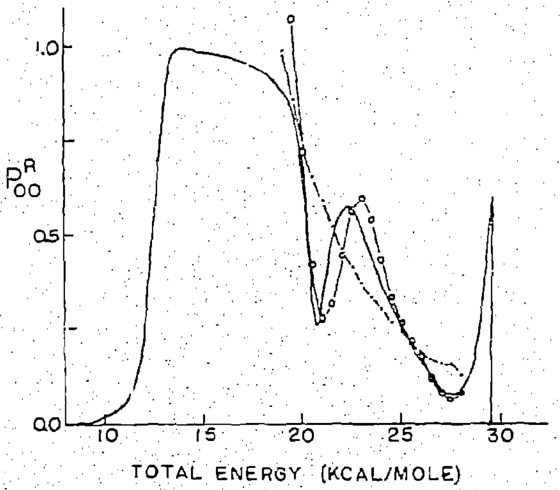

Fig. 2. Comparison of exact quantum reactive transition probabilities P_{00}^R of Truhlar and Kuppermann [12] (—), those calculated using eq. (10a) where the sum includes zero, first and second order branches (o–o–o), and those calculated varying only the zero order branch (.–.–.).

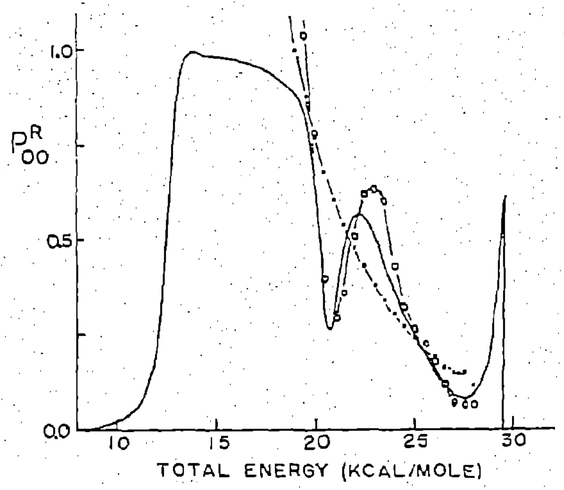

Fig. 3. Same as fig. 2 except eq. (10b) is used in place of eq. (10a).

6. Conclusion

In the present paper attention has been focused on the broad resonance occurring in quantum mechanical calculations for the collinear $H + H_2$ reaction‡. It has been shown that introduction of the trajectories which arise from multiple collisions within a collision complex (i.e., which arise from short-lived collision complexes), interfere with the direct collision trajectories and yield a semiclassical interpretation of the resonance.

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‡ We do not consider here, for example, the behavior at lower energies, namely outside this resonance region but above the tunneling region. In that region the quantum transition probability is close to unity but any simple semiclassical value yields a result greater than unity, even when a Bessel uniform approximation [5] is used. The structure of the semiclassical wavefunction in that region is too complicated – there are too many regions of jacobian sign change, for example – to permit any *simple* uniform approximation. In this case, an expedient which we have adopted in other analogous problems might be employed, namely setting the semiclassical probability equal to unity whenever the calculated uniform approximation value exceeds unity.