Cumulative reaction probabilities for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ from a knowledge of the anharmonic force field

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In an earlier publication, the authors showed how knowledge of a quartic force field expanded about a transition state can be used to obtain transition state theory tunneling probabilities. Thus coupling between the reaction mode and other modes is included in this second-order perturbation theory approach. Here we study the very anharmonic reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ and show that even in this extreme case, there is reasonable agreement between the cumulative reaction probabilities calculated by this semiclassical approach, and full quantum calculations.

1. Introduction

In our first paper [1] (henceforth referred to as I), we considered an expansion of the potential energy surface V in normal coordinates Q_k ($k=1, 2, \dots, F$) about a transition state, through quartic terms, thus

$$V = V_0 + \frac{1}{2} \sum_k^F \omega_k^2 Q_k^2 + \frac{1}{6} \sum_{klm}^F f_{klm} Q_k Q_l Q_m + \frac{1}{24} \sum_{klmn}^F f_{klmn} Q_k Q_l Q_m Q_n + \dots, \quad (1)$$

where the summations are unrestricted, i.e. all terms are included. If mode F is the reaction coordinate, then the frequency ω_F is imaginary

$$\omega_F = i|\omega_F| \equiv i\tilde{\omega}_F. \quad (2)$$

We commented that if such an expansion was about a minimum, (i.e. all real frequencies) then use of standard second-order perturbation theory [2] led to the expression

$$E(n_1, n_2, \dots, n_F) = V_0 + E_0 + \sum_{k=1}^F \omega_k (n_k + \frac{1}{2}) + \sum_{k \leq l}^F x_{kl} (n_k + \frac{1}{2})(n_l + \frac{1}{2}), \quad (3)$$

for the vibrational energy levels. The term E_0 , which depends on the cubic and quartic force constants, was omitted from ref. [1] (see acknowledgement); it cancels in spectroscopy but enters into thermodynamic quantities. ω_k are the harmonic frequencies, and x_{kl} the anharmonic constants. $\{n_k + \frac{1}{2}\}$ are the quantum numbers, or, from the point of view of classical mechanics, they are the good action variables for these molecular vibrations. Using Miller's observation [3] that good action variables exist for a transition state, in I we noted that eq. (3) is also the expression for the energy (i.e. the classical Hamiltonian) in terms of the good action variables for a transition state, within the limits of second-order perturbation theory. The essential difference between a potential minimum and a transition state (i.e. a saddle point) is that in the former case one is interested in the energy as a function of the actions (quantum numbers), that is vibrational eigenvalues, while

in the latter case one seeks tunneling (or transmission) probabilities through the saddle point as a function of the energy.

In one dimension, for example, the semiclassical expression [4] for eigenvalues in a potential *well* is given implicitly by the Bohr-Sommerfeld quantization rule

$$(n + \frac{1}{2})\pi = \int dQ \sqrt{2[E - V(Q)]}, \quad (4)$$

which must be inverted to obtain $E(n)$. For a one-dimensional *barrier* the semi-classical tunneling probability is given by

$$P(E) = [1 + \exp(2\theta)]^{-1}, \quad (5)$$

where $\theta(E)$ is the action integral through the barrier (the transition state),

$$\theta(E) = \int dQ \sqrt{2[V(Q) - E]}. \quad (6)$$

From eqs. (4) and (6) one clearly sees the correspondence between the action variables for a well and a barrier,

$$n + \frac{1}{2} \rightarrow i\theta/\pi. \quad (7)$$

For a parabolic well (i.e. harmonic oscillator) or barrier, for example, eqs. (4) and (6) give

$$E(I) = V_0 + \omega I, \quad (8a)$$

where $I = n + \frac{1}{2}$ for the well and $I = i\theta/\pi$ for the barrier. In the latter case $\omega = i|\omega|$, so that eq. (6) reads

$$\theta(E) = \pi(V_0 - E)/|\omega|, \quad (8b)$$

which, when inserted into (5), gives the correct tunneling probability for energies E above or below the barrier height V_0 .

For a multi-dimensional transition state one proceeds analogously, by making the replacement indicated by eq. (7) for mode F (the reaction coordinate), so that eq. (3) reads

$$E = E(n_1, n_2, \dots, n_{F-1}, \theta), \quad (9)$$

and then inverting this expression to obtain $\theta(n_1, n_2, \dots, n_{F-1}, E)$; that is, θ is given in terms of the quanta in the vibrational modes at the transition state, and the total energy E . Eq. (9) will be a quadratic equation for θ in this case, and the solution is,

$$\theta(\underline{n}, E) = \frac{\pi \Delta E}{\Omega_F} \frac{2}{1 + (1 + 4x_{FF} \Delta E / \Omega_F^2)^{1/2}}, \quad (10)$$

where

$$\Delta E = V_0 + \bar{E}_0 - E + \sum_k^{F-1} \omega_k(n_k + \frac{1}{2}) + \sum_{k \leq l}^{F-1} x_{kl}(n_k + \frac{1}{2})(n_l + \frac{1}{2}), \quad (11)$$

$$\Omega_F = \bar{\omega}_F - \sum_{k=1}^{F-1} \bar{x}_{kF}(n_k + \frac{1}{2}), \quad (12)$$

and we have defined real anharmonic constants $\bar{x}$ as

$$\bar{x}_{kF} = i x_{kF}. \quad (13)$$

Thus the transition state theory tunneling probability for state $\underline{n} = (n_1, n_2, \dots, n_{F-1})$ of the activated complex is

$$P_n(E) = (1 + \exp[2\theta(n, E)])^{-1}. \quad (14)$$

The cumulative reaction probability (CRP) is then given as

$$N(E) = \sum_n P_n(E). \quad (15)$$

All of the above was discussed in greater detail in I and Seideman and Miller [5] have further shown how this semiclassical theory relates to a full quantum mechanical theory. (In this completely quantum theory the energy as a function of the good action variables at a transition state become Siegert eigenvalues [6].) Expressions for x_{kk} , x_{kl} , x_{kF} and x_{FF} were given in terms of ω , f_{klm} and f_{klmn} for the case of a non-linear transition state. $\bar{E}_0$, in (11), is equivalent to the constant E_0 in eq. (2) except that it is modified for a potential barrier. Quantum-chemistry calculations were performed at the transition state for the unimolecular decomposition of formaldehyde $D_2CO \rightarrow D_2 + CO$, to determine quadratic, cubic and quartic force constants. In that case, where there is a high barrier (94.7 kcal/mol), the anharmonic constants were small and their effect on the tunneling probabilities was not very significant.

It is therefore of interest to study, using this theory, a case where anharmonicity is known to be significant, to see whether this second-order perturbation theory approach can give results which are in agreement with full quantal calculations. Needless to say, the cost of these studies is negligible compared with those full calculations. The obvious problem is $H + H_2 \rightarrow H_2 + H$, which has the symmetric linear transition state. In section 2 we give the necessary formulae for such a transition state, and in section 3 we apply this theory using the double many body expansion (DMBE) surface of Varandas, Brown, Mead, Truhlar and Blais [7].

2. Anharmonic constants for a linear transition state

The corresponding expression to (2) for the vibrational levels of a linear molecule is [2]

$$E(n_1, n_2, \dots, n_F) = V_0 + E_0 + \sum_k \omega_k(n_k + \frac{1}{2}) + \sum_s \omega_s(n_s + 1) + \sum_{k \leq l} x_{kl}(n_k + \frac{1}{2})(n_l + \frac{1}{2}) \\ + \sum_{s \leq t} x_{st}(n_s + 1)(n_t + 1) + \sum_{k,s} x_{ks}(n_k + \frac{1}{2})(n_s + 1) + \sum_{s \leq t} g_{st} l_s l_t, \quad (16)$$

where k, l are non-degenerate modes and s, t are doubly degenerate. l_s is the vibrational angular momentum of mode s . For the case (such as $H + H_2 \rightarrow H_2 + H$) where the reaction mode F is non-degenerate, the corresponding formulae for $E(n_1, n_2, \dots, n_{F-1}, \theta)$, using (8) for $(n_F + \frac{1}{2})$, and also (13), is

$$E(n_1, n_2, \dots, n_{F-1}, \theta) = V_0 + \bar{E}_0 + \sum_k \omega_k(n_k + \frac{1}{2}) + \sum_s \omega_s(n_s + 1) - \bar{\omega}_F \frac{\theta}{\pi} + \sum_{k \leq l} x_{kl}(n_k + \frac{1}{2})(n_l + \frac{1}{2}) \\ + \sum_{s \leq t} x_{st}(n_s + 1)(n_t + 1) + \sum_{k,s} x_{ks}(n_k + \frac{1}{2})(n_s + 1) + \sum_{s \leq t} g_{st} l_s l_t + \sum_k \bar{x}_{kF}(n_k + \frac{1}{2}) \frac{\theta}{\pi} \\ + \sum_s \bar{x}_{sF}(n_s + 1) \frac{\theta}{\pi} - x_{FF} \frac{\theta^2}{\pi^2}, \quad (17)$$

where here and below all summations exclude mode F , the reaction coordinate. The expressions for x , $\bar{x}$ and g may be straightforwardly derived from the corresponding expressions for vibrations, which may be found in ref. [2]. In the following, the f are normal coordinate force constants (they are related to the dimensionless normal coordinate force constants k by $f_{klm} = k_{klm} \sqrt{\omega_k \omega_l \omega_m}$ and $f_{klF} = \bar{k}_{klF} \sqrt{\omega_k \omega_l \omega_F}$)

$$\begin{aligned}
x_{kk} &= \frac{1}{16\omega_k^2} \left(f_{kkkk} - \sum_l \frac{f_{kkl}^2 (8\omega_k^2 - 3\omega_l^2)}{\omega_l^2 (4\omega_k^2 - \omega_l^2)} \right) + \frac{f_{kkF}^2 (8\omega_k^2 + 3\bar{\omega}_F^2)}{16\omega_k^2 \bar{\omega}_F^2 (4\omega_k^2 + \bar{\omega}_F^2)}, \\
x_{kl} &= \frac{1}{4\omega_k \omega_l} \left(f_{kkll} - \sum_m \frac{f_{kkm} f_{llm}}{\omega_m^2} + \sum_m \frac{2f_{klm} (-\omega_m^2 + \omega_k^2 + \omega_l^2)}{[(\omega_k + \omega_l)^2 - \omega_m^2][(\omega_k - \omega_l)^2 - \omega_m^2]} \right) \\
&\quad + B_z (\zeta_{kl}^z)^2 \left(\frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k} \right) + \frac{f_{kkF} f_{llF}}{4\omega_k \omega_l \bar{\omega}_F^2} + \frac{f_{klF}^2 (\omega_k^2 + \omega_l^2 + \bar{\omega}_F^2)}{2\omega_k \omega_l [(\omega_k + \omega_l)^2 + \bar{\omega}_F^2][(\omega_k - \omega_l)^2 + \bar{\omega}_F^2]}, \\
x_{st} &= \frac{1}{8\omega_s \omega_t} \left(f_{sasata} + f_{sasatbtb} - 2 \sum_k \frac{f_{kss} f_{ktu}}{\omega_k^2} + 2 \sum_k \frac{f_{kst}^2 (-\omega_k^2 + \omega_s^2 + \omega_t^2)}{[(\omega_k + \omega_t)^2 - \omega_s^2][(\omega_k - \omega_t)^2 - \omega_s^2]} \right. \\
&\quad + 4 \sum_u \frac{f_{stu}^2 (-\omega_u^2 + \omega_s^2 + \omega_t^2)}{[(\omega_s + \omega_t)^2 - \omega_u^2][(\omega_s - \omega_t)^2 - \omega_u^2]} \left. + [\frac{1}{2} B_z (\zeta_{st}^z)^2 + B_x (\zeta_{st}^x)^2] \left(\frac{\omega_s}{\omega_t} + \frac{\omega_t}{\omega_s} \right) \right. \\
&\quad \left. + \frac{1}{8\omega_s \omega_t} \left(\frac{2f_{Fss} f_{Ftt}}{\bar{\omega}_F^2} + \frac{2f_{Fst}^2 (\omega_s^2 + \omega_t^2 + \bar{\omega}_F^2)}{[(\omega_s + \omega_t)^2 + \bar{\omega}_F^2][(\omega_s - \omega_t)^2 + \bar{\omega}_F^2]} \right) \right), \\
x_{ss} &= \frac{1}{16\omega_s^2} \left(f_{ssss} - \sum_k \frac{f_{kss}^2 (8\omega_s^2 - 3\omega_k^2)}{\omega_k^2 (4\omega_s^2 - \omega_k^2)} - \sum_t \frac{f_{sst}^2 (8\omega_s^2 - 3\omega_t^2)}{\omega_t^2 (4\omega_s^2 - \omega_t^2)} \right) + \frac{f_{Fss}^2 (8\omega_s^2 + \bar{\omega}_F^2)}{16\omega_s^2 \bar{\omega}_F^2 (4\omega_s^2 + \bar{\omega}_F^2)}, \\
x_{ks} &= \frac{1}{4\omega_k \omega_s} \left(f_{kkss} - \sum_l \frac{f_{kkl} f_{lss}}{\omega_l^2} + \sum_l \frac{2f_{kst}^2 (-\omega_l^2 + \omega_k^2 + \omega_s^2)}{[(\omega_k + \omega_s)^2 - \omega_l^2][(\omega_k - \omega_s)^2 - \omega_l^2]} \right) \\
&\quad + B_x [(\zeta_{ks}^x)^2 + (\zeta_{ks}^y)^2] \left(\frac{\omega_k}{\omega_s} + \frac{\omega_s}{\omega_k} \right) + \frac{f_{kkF} f_{Fss}}{4\bar{\omega}_F^2 \omega_k \omega_s}, \\
x_{FF} &= \frac{1}{16\bar{\omega}_F^2} \left(-f_{FFFF} + \sum_k \frac{f_{FFk}^2 (8\bar{\omega}_F^2 + 3\omega_k^2)}{\omega_k^2 (4\bar{\omega}_F^2 + \omega_k^2)} - \frac{5}{3} \frac{f_{FFF}^2}{\bar{\omega}_F^2} \right), \\
\bar{x}_{Fk} &= \frac{1}{4\omega_k \bar{\omega}_F} \left(f_{kkFF} + \frac{f_{FFF} f_{kkF}}{\bar{\omega}_F^2} + \frac{2f_{FFk}^2}{(4\bar{\omega}_F^2 + \omega_k^2)} - \sum_l \frac{f_{FFl} f_{kkl}}{\omega_l^2} \right. \\
&\quad \left. + \sum_l \frac{2f_{kFl}^2 (-\bar{\omega}_F^2 + \omega_k^2 - \omega_l^2)}{[(\omega_k + \omega_l)^2 + \bar{\omega}_F^2][(\omega_k - \omega_l)^2 + \bar{\omega}_F^2]} \right) + B_z (\zeta_{kF}^z)^2 \left(\frac{\omega_k}{\bar{\omega}_F} - \frac{\bar{\omega}_F}{\omega_k} \right), \\
\bar{x}_{Fs} &= \frac{1}{4\omega_s \bar{\omega}_F} \left(f_{ssFF} + \frac{f_{FFF} f_{ssF}}{\bar{\omega}_F^2} + \sum_t \frac{2f_{sFt}^2 (-\bar{\omega}_F^2 + \omega_s^2 - \omega_t^2)}{[(\omega_s + \omega_t)^2 + \bar{\omega}_F^2][(\omega_s - \omega_t)^2 + \bar{\omega}_F^2]} - \sum_k \frac{f_{FFk} f_{kss}}{\omega_k^2} \right) \\
&\quad + B_x [(\zeta_{Fs}^x)^2 + (\zeta_{Fs}^y)^2] \left(\frac{\omega_s}{\bar{\omega}_F} - \frac{\bar{\omega}_F}{\omega_s} \right), \\
g_{ss} &= -\frac{1}{48\omega_s^2} \left(f_{ssss} + 3 \sum_k \frac{f_{kss}^2}{(4\omega_s^2 - \omega_k^2)} - 3 \sum_t \frac{f_{sst}^2 (8\omega_s^2 - \omega_t^2)}{\omega_t^2 (4\omega_s^2 - \omega_t^2)} \right) + B_z (\zeta_{ss}^z)^2 - \frac{3f_{Fss}^2}{48\omega_s^2 (4\omega_s^2 + \bar{\omega}_F^2)}, \\
g_{st} &= \frac{1}{2} \sum_k \frac{f_{kst}^2}{[(\omega_k + \omega_s)^2 - \omega_t^2][(\omega_k - \omega_s)^2 - \omega_t^2]} - \sum_u \frac{f_{stu}^2}{[(\omega_s + \omega_t)^2 - \omega_u^2][(\omega_s - \omega_t)^2 - \omega_u^2]} \\
&\quad - 2B_x (\zeta_{st}^x)^2 + B_z (\zeta_{st}^z)^2 + 2B_z \zeta_{st}^x \zeta_{ss}^z + \frac{f_{Fst}^2}{2[(\omega_s + \omega_t)^2 + \bar{\omega}_F^2][(\omega_s - \omega_t)^2 + \bar{\omega}_F^2]},
\end{aligned}$$

$$\begin{aligned}
\bar{E}_0 = & \frac{1}{64} \sum_k \frac{f_{kkkk}}{\omega_k^2} - \frac{7}{576} \sum_k \frac{f_{kkk}^2}{\omega_k^4} + \frac{3}{64} \sum_{k \neq l} \frac{f_{kll}^2}{(4\omega_l^2 - \omega_k^2)\omega_l^2} - \frac{1}{4} \sum_{k < l < m} \frac{f_{klm}^2}{[(\omega_k + \omega_l)^2 - \omega_m^2][(\omega_k - \omega_l)^2 - \omega_m^2]} \\
& + \frac{1}{48} \sum_s \frac{f_{ssss}}{\omega_s^2} + \frac{11}{144} \sum_s \frac{f_{sss}^2}{\omega_s^4} - \frac{1}{2} \sum_{s < t} \sum_k \frac{f_{kst}^2}{[(\omega_s + \omega_t)^2 - \omega_k^2][(\omega_s - \omega_t)^2 - \omega_k^2]} + \frac{1}{16} \sum_k \sum_s \frac{f_{kss}^2}{(4\omega_s^2 - \omega_k^2)\omega_s^2} \\
& + \frac{1}{16} \sum_{s \neq t} \frac{f_{sst}^2(8\omega_s^2 + \omega_t^2)}{\omega_t^2 \omega_s^2 (4\omega_s^2 - \omega_t^2)} - \sum_{s < t < u} \frac{2f_{stu}^2}{[(\omega_s + \omega_t)^2 - \omega_u^2][(\omega_s - \omega_t)^2 - \omega_u^2]} - \frac{f_{FFFF}}{64\bar{\omega}_F^2} - \frac{7f_{FFF}^2}{576\bar{\omega}_F^4} \\
& + \frac{3}{64} \sum_k \frac{f_{kkF}^2}{(4\bar{\omega}_F^2 + \omega_k^2)\bar{\omega}_F^2} + \frac{3}{64} \sum_k \frac{f_{kkF}^2}{(4\omega_k^2 + \bar{\omega}_F^2)\omega_k^2} - \frac{1}{4} \sum_{k < l} \frac{f_{klF}^2}{[(\omega_k + \omega_l)^2 + \bar{\omega}_F^2][(\omega_k - \omega_l)^2 + \bar{\omega}_F^2]} \\
& + \frac{1}{16} \sum_s \frac{f_{Fss}^2}{(4\omega_s^2 + \bar{\omega}_F^2)\omega_s^2} - \frac{1}{2} \sum_{s < t} \frac{f_{Fst}^2}{[(\omega_s + \omega_t)^2 + \bar{\omega}_F^2][(\omega_s - \omega_t)^2 + \bar{\omega}_F^2]}. \quad (18)
\end{aligned}$$

Once these expressions are programmed, tunneling probabilities and CRPs are obtained. At this stage we will comment on the expression, in particular paying attention to the problem of resonances. We note that there will be no resonance involving the reaction mode F , because the term $+\bar{\omega}_F^2$ always arises in the denominators. However, Fermi resonances amongst the vibrational modes may and will arise, for example the classic $2\omega_s \approx \omega_k$ resonance affects x_{ss} , x_{ks} and g_{ss} . We shall see that such a resonance is important in our interpretation of $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$.

As in the study of vibrations, the resonant term is removed from the perturbative expansion and treated directly at zeroth order. The diagonal terms are obtained using the expression for ΔE (eq. (12)), with the x modified to exclude the resonant partial fraction. While there are now off diagonal terms, the only non-trivial ones are the matrix elements of the resonance operator between the states of a given polyad. The energies of these states are obtained by diagonalizing the corresponding block of the Hamiltonian. In the same way amended vibrational energy levels at the transition state, $E(n_1, n_2, \dots, n_{F-1})$, can be obtained and used to calculate tunneling probabilities. Note that there is no danger of a resonance developing between the reaction mode and perpendicular modes as the reaction frequency is imaginary.

3. Studies of the hydrogen exchange reaction

As we have said we shall use the DMBE [7] surface, which is analytic and is agreed to be close to the exact surface. We obtained a subroutine^{#1} which evaluated this potential for any value of the internal coordinates for this ABC system, with $R_1 = |AB|$, $R_2 = |BC|$ and $\theta = |ABC|$. By optimization we found that at equilibrium $R_1 = R_2 = 1.754635 a_0$ and that the barrier height was 9.65 kcal/mol.

After an attempt to use an algebra program (REDUCE) to evaluate all the first, second, third and fourth derivatives analytically, which failed due to algebraic complexity, we proceeded to obtain the required derivatives through finite displacements based upon

$$\partial V / \partial x = [f(x + \epsilon) - f(x - \epsilon)] / 2\epsilon, \quad (19)$$

$$\partial^2 V / \partial x^2 = [f(x + \epsilon) + f(x - \epsilon) - 2f(x)] / \epsilon^2. \quad (20)$$

Use of quadruple precision allowed a reliable evaluation of the necessary derivatives which are given in table 1. The normal coordinate force constants were obtained from the curvilinear force constants by nonlinear transformations using the computer program SPECTRO [8]. The harmonic frequencies thus determined were $\omega_1 = 2066.9$ (symmetric stretch) $\omega_2 = 899.5$ (degenerate bend) and $\bar{\omega}_4 = 1493.1$ (the imaginary reaction mode),

^{#1} Kindly obtained with permission of Professor D.G. Truhlar.

Table 1

Potential surface constants of $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ at the transition state, for the DMBE surface [5], using the notation $\partial V / \partial A \partial B \partial C \dots \equiv [ABC \dots]$ with units in $\text{bohr}^{-1} \text{rad}^{-1}$

$[R_1 R_1] = 1.048$	$[R_1 R_1 R_1 R_1] = 79.23$
$[\theta \theta] = 0.069$	$[\theta \theta R_1 R_1] = -0.178$
$[R_1 R_2] = 1.489$	$[\theta \theta \theta \theta] = 0.401$
$[R_1 R_1 R_1] = -11.807$	$[R_1 R_1 R_2 R_2] = 9.40$
$[R_1 R_1 R_2] = -0.754$	$[\theta \theta R_1 R_2] = 0.129$
$[\theta \theta R_1] = -0.045$	$[R_1 R_1 R_1 R_2] = -9.783$

Table 2

Values for harmonic ω and anharmonic constants x , $\bar{x}$, g at the transition state for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$, (i) including the near resonance $\omega_1 \approx 2\omega_2$ (ii) excluding the resonance. All values are in cm^{-1}

	(i)	(ii)
ω_1	2066.9	2066.9
ω_2	899.5	899.5
$\bar{\omega}_4$	1493.1	1493.1
x_{11}	-25.4	-25.4
x_{12}	455.3	-120.7
$\bar{x}_{14}$	699.1	699.1
x_{22}	-80.8	60.7
$\bar{x}_{24}$	-107.7	-107.6
x_{44}	-246.2	-246.2
g	74.7	-38.2
$\bar{E}_0$	-279.84	-138.32

Fig. 1. Cumulative reaction probabilities for collinear H_3 . The points correspond to the exact quantum calculations of Bondi and Connor [9]. The solid curve is obtained by including the anharmonic terms in the semiclassical model. The dashed curve is obtained by including only the harmonic terms.

in cm^{-1} . In table 2 the first column of values gives the anharmonic constants, derived using the formulae (18)–(26), in cm^{-1} .

One sees that the anharmonic constants are very large, an order of magnitude larger than those reported in 1 for $\text{D}_2\text{CO} \rightarrow \text{D}_2 + \text{CO}$. Questions of reliability of this theory immediately arise. As a first test, we consider the *collinear* version of this reaction, which involves only modes 1 and 4. In this case there is no question of Fermi resonance, only the anharmonicity in the barrier and the coupling between the two modes (reaction path curvature). Fig. 1 shows the CRP in the low energy tunneling regime, as given by our full semiclassical theory, compared to the exact quantum results^{#2} [9] and also to the harmonic limit of the theory. One sees that the

^{#2} Kindly provided by Professor J.N.L. Connor.

present perturbative anharmonic theory does well quite far into the deep tunneling regime. At high energies, the contribution to the CRP from transition states with quanta in the perpendicular mode fails because the large anharmonicity in the perpendicular mode causes the argument of the square root in eq. (10) to be negative. However, in a system with more degrees of freedom, it seems plausible that the breakdown in the perturbation could be mitigated by a cancellation of the anharmonicities in the various perpendicular modes.

We now address the 3-dimensional version of the reaction. One of the largest x is $x_{12}=455\text{ cm}^{-1}$ and upon examination it is seen that there is a substantial resonance effect arising from the fact that (i) $\omega_1-2\omega_2=286\text{ cm}^{-1}$ and (ii) the associated force constant $k_{122}=1101\text{ cm}^{-1}$ is very large. Thus although $\omega_1-2\omega_2$ might not be considered a case of significant Fermi resonance, after the magnitude of k_{122} is taken into account, it has a real effect. The second column of table 2 gives the amended values for x_{12} , x_{22} and g after removal of this resonance. We observe that x_{12} has changed by 576 cm^{-1} . The constant $\bar{x}_{14}$ is large because the force constant $\bar{k}_{1144}$ is very large. The values of all reduced normal coordinate force constants are given in table 3.

Chatfield et al. [10] determined a density $\rho(E)$ of reactive states from the differential of the CRP derived from full quantum calculations. For $J=0$, there are five peaks in $\rho(E)$, in the energy range considered here, which they correlate with quantized transition states. These peaks are labelled by v_1, v_2 quantum numbers for the symmetric stretch and bending vibrations. By fitting these peaks to a two-dimensional expansion in v_1, v_2 of the form (2), Chatfield et al. [10] determined values for $\omega_1=2331$, $\omega_2=1008$, $x_{11}=222$, $x_{22}=-12$ and $x_{12}=-81$, in cm^{-1} . These are totally different to our values for x presented in table 2. We are surprised at the smallness of the Chatfield values, given the very anharmonic nature of the potential.

At the transition state values may be determined for vibrational energy levels $E(n_1, n_2)$ using the values of ω_1, ω_2 and x_{11}, x_{12}, x_{22} in table 2. We use the value of x after the removal of resonance. The energies of the (1,0) and (2,0) levels are found by 2×2 matrix diagonalization. For a potential well the term E_0 gives a positive contribution to the zero point energy. Therefore, in this transition state theory, E_0 contributes to a lowering of the potential barrier and being large, -138 cm^{-1} , causes a significant increase in the reaction rates. In table 4 we also give the values for the peaks of $\rho(E)$ determined by Chatfield et al. [10] together with their assignments. We see good agreement between our values for the vibrational energies of these states and Chatfield's values, but a disagreement in the assignments. Of course in our approach we included the effects of resonance, but in ref. [10] a direct fit of the form (2) is made to the peaks. It seems that the quantum number assignment for these states of the activated complex is not a simple procedure.

We give our values for the Boltzmann weighted BWCRP, $\exp(-E/kT)N(E)$, in fig. 2, for the temperatures $T=200, 600$ and 1000 K and compare them with values obtained from the purely harmonic potential and with the BWCRP obtained by Chatfield, Truhlar and Schwenke [11] with their full quantum calculations. We used our values of x after the removal of resonance, including the contributions of (1,0) and (0,2) to the sum in (15) as described in section 2. In (15) we used values of n : $0\leq n_1\leq 5, 0\leq n_2\leq 5$. When we used the values of x before the resonance was removed, the BWCRP were too small in comparison with both those obtained after

Table 3

Normal coordinate force constants f_{lmn} and f_{lmnp} and dimensionless normal coordinate force constants $k_{lmn}, k_{lmnp}, \bar{k}_{lmF}, \bar{k}_{lmnF}$ etc. for $\text{H}+\text{H}_2\rightarrow\text{H}_2+\text{H}$, evaluated at the transition state, in cm^{-1} , using the DMBE potential [5]

lmn	k_{lmn}	f_{lmn}	$lmnp$	k_{lmnp}	f_{lmnp}
111	-1031.17	-9.69×10^7	1111	450.34	1.92×10^9
122	1101.49	4.50×10^7	1122	-875.31	-1.63×10^9
144	-3364.59	-2.28×10^8	2233	767.50	6.21×10^8
			2222	2302.00	1.86×10^9
			1144	1912.13	5.90×10^9
			2244	-2182.58	-2.93×10^9
			4444	16666.43	3.72×10^{10}

Table 4

Vibrational energy levels $E(n_1, n_2)$ in eV at the transition state of $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$

This calculation		From ref. [6]	
assignment	$E(n_1, n_2)$	assignment	$E(n_1, n_2)$
(0, 0)	0.658	(0, 0)	0.645
$0.813(1, 0) + 0.581(0, 2)$	0.858	(0, 2)	0.871
$0.581(1, 0) + 0.813(0, 2)$	0.961	(1, 0)	0.978
$0.681(2, 0) + 0.732(1, 2)$	1.058	(0, 4)	1.093
$0.732(2, 0) + 0.681(1, 2)$	1.194	(1, 2)	1.186

removal of the resonance and the results of Chatfield et al. [11]. One reason for this was that the argument of the square root in (11) was negative for many values of n , and was not admissible in this theory (see comments above regarding the collinear case).

A detailed comparison of these BWCRP shows that the harmonic approximation gives results that are poor. Values for small E and large E are too large, with the result that the peaks are too broad. On the other hand the introduction of anharmonic effects brings much better agreement with the calculations of Chatfield et al. [11]. At $T=200$ K the peak is at 4.1×10^{-16} instead of 1.9×10^{-16} , at $T=600$ K the peak is at 4.2×10^{-6} instead of 3.9×10^{-6} and at $T=1000$ K the peak is at 6.7×10^{-4} instead of 6.5×10^{-4} . The remaining features are in good agreement. In particular the shoulder at $E \approx 1.0$ eV at $T=1000$ K is reproduced.

The thermal reaction rate constant for zero total angular momentum can be written

$$k^{J=0}(T) = \frac{1}{h\Phi^R} \int_0^\infty dE \exp(-E/kT) N^{J=0}(E), \quad (21)$$

where the H_2 partition function is

$$\Phi^R = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2} \sum_{v,j} (2j+1) \exp(-\epsilon_{v,j}/kT). \quad (22)$$

The integral in eq. (21) was evaluated using a four point finite difference quadrature scheme [12] with 400 quadrature points. In table 5 we present values of the thermal rate constants at the temperatures $T=200$, 600 and 1000 K, using both the harmonic and anharmonic constants, the values are given in comparison with the results of Chatfield et al. [11]. The rate constants calculated from the purely harmonic field are overall significantly different from those of Chatfield et al., particularly at low temperatures where anharmonic effects are most important. By contrast the anharmonic rate constants are in much closer agreement, particularly at high temperatures and this is a pleasing aspect of this theory.

4. Discussion and conclusions

In this paper, we have determined properties of the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction from a knowledge of a quartic expansion of the potential surface expanded around the transition state. No other knowledge has been put into the calculations, except for the barrier height which was used in the Boltzmann weighting factor. It may at first seem remarkable that this limited knowledge gives such good agreement with the quantum mechanical studies of Chatfield et al. [10,11], for both the vibrational energy and the reaction probabilities. But we observe that a knowledge of a quartic force field expanded about a minimum is very often used to study vibrational levels 10000 cm^{-1} or more above the zero point level.

We recognize that often transition states will be very anharmonic, but this is likely to be the extreme case.

Fig. 2. Graphs of the Boltzmann weighted cumulative reaction probability (BWCRP) versus energy in eV at temperatures $T=200$, 600 and 1000 K. Column (a) uses the harmonic terms only, (b) are from the calculations described in this paper and (c) is taken from the full quantum mechanical calculations of Chatfield et al. [10].

Table 5

Rate constants in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$T(\text{K})$	$k(T)$ harmonic	$k(T)$ anharmonic	$k(T)$ ref. [10]
200	6.808×10^{-15}	6.588×10^{-20}	6.428×10^{-20}
600	2.032×10^{-15}	1.944×10^{-15}	1.988×10^{-15}
1000	1.817×10^{-14}	1.864×10^{-14}	1.578×10^{-14}

The fact that reasonable results were obtained here suggests that studies using this method will be valuable when more atoms are involved; in those cases full quantum calculations will be impossible. Recall also that this approach requires only the quadratic, cubic and quartic force constants, and not an analytic representation of the whole surface. Therefore the modern gradient theory of quantum chemistry may be directly used.

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