Quantum mechanical effects in the three dimensional low energy
$D + H_2 \rightarrow HD + H$ reaction

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In this work possible quantum mechanical effects for the three dimensional reactive
$D + H_2 \rightarrow HD + H$ reaction are discussed. The study is carried out by comparing quantum
mechanical and quasiclassical backscattered differential cross sections as a function of collision
energy. A strong quantum effect is detected for the $u = 0 \rightarrow u' = 0$ transition in the energy
range around $E_{tr} = 13$ kcal/mol.

I. INTRODUCTION

One of the main motivations for carrying out an exact
quantum mechanical (QM) calculation for a reactive atom-diatomic system is the possibility of encountering a pro-
nounced nonclassical effect. The suitable systems most likely
to yield these effects are the hydrogenic systems, and an
obvious choice is the $D + H_2$ reaction. Usually, one distin-
xuishes between integral cross sections (ICS) and differ-
etial cross sections (DCS). For energy-dependent ICS, it
was known and has recently been reverified that, except
for slight threshold effects, the quasiclassical trajectory
(QCT) ICS are very similar to the QM ones. Regarding the
energy-dependent DCS, the ones most likely to exhibit unus-
ual effects are those for $\theta \sim 180^\circ$, which are the back-
scattered differential cross sections (BDCS). This is due to
the fact that only a relatively small number of $I$ values and a
short range of the angle $\gamma$ (the angle between the diatomic
axis and the vector from the diatom center of mass to the
atom) contribute to the formation of the BDCS. Conse-
quently, possible quantum effects detected for the collinear
arrangement may sustain the averaging processes leading to
those cross sections.

In a recent publication, Zhang and Miller (ZM) presented such energy-dependent BDCS for the process

$$D + H_2 (v = 0, j = 0) \rightarrow HD (v' = 1, \Sigma j') + H \quad (i)$$

and interpreted the observed oscillations as being an indica-
tion for QM effects.

In order to obtain a better understanding of this phe-
nomenon, we performed a quasiclassical trajectory study
solely devoted to the BDCS. Part of this study was presented
in a short communication, where it is shown that these osci-
llations can also be seen in the QCT treatment, which
means that they are due to effects not necessarily of quantum
mechanical origin.

In the present work we report on additional results re-
lated to the BDCS for the reactions

$$D + H_2 (v = 0, j = 0, 1) \rightarrow HD (v' = 0, 1, \Sigma j') + H \quad (ii)$$

The study of this subject is continued for two reasons:
(a) To establish our claims that the observed QCT oscillations
for reaction (ii) are not due to statistical fluctuations
related to the averaging calculation process. (b) To report

on a strong quantum effect which appears at the $(u = 0,
u' = 0)$ transition in the proximity of the translational en-

ergy $E_{tr} = 13$ kcal/mol.

The paper is organized in the following way: A few de-
tails concerning the QCT calculations are given in the next
section, the results are presented in the third, a discussion is
performed in the fourth and the conclusions are summarized
in the fifth section.

II. COMPUTATION PROCEDURE

The QCT computation procedure was the same as that
employed by us in earlier studies of backscattered partial
cross sections for the heavy + light heavy ($H + LH$) sys-
tems $O + HCl, Cl + HCl$, and $O + HBr$ (see also Ref. 6).
As before, the statistics of the calculations were improved
significantly by carrying out the calculations over limited
ranges of the impact parameter $b$ and of the initial azimuthal
orientation angle $\theta_i$, the angle between the axis of the $H_2$
molecule and the initial direction of the relative velocity vec-
tor. In regular QCT calculations $\theta_i$ is randomly selected
from the full possible range $0^\circ$ to $180^\circ$, to be
somewhat larger than the largest value of $\theta_i$ found to lead to
reactive collisions with the products scattered in the angular
range of interest $170^\circ$ to $180^\circ$. The partial cross sections $\sigma_R$
$(170^\circ$ to $180^\circ$) obtained from the calculations were multiplied
by a factor $f$ to derive the same partial cross section
$\sigma_R (170^\circ$ to $180^\circ$) that would be obtained if $\theta_i$ had been select-
ed from the full range $0^\circ$ to $90^\circ$.

$$\sigma (170^\circ$ to $180^\circ$) = $f \sigma_R (170^\circ$ to $180^\circ$), \quad (1)

$$f = 1 - \cos \theta_{r, \max}$$. \quad (2)

The connection between the differential cross section
$(d\sigma/d\Omega)$ and the partial cross section is given by

$$\sigma_R (170^\circ$ to $180^\circ$) = $2\pi \int_{170^\circ}^{180^\circ} d\theta \sin \theta \left( \frac{d\sigma}{d\Omega} \right), \quad (3)$$
Similarly, values of $b_{\text{max}}$ were also chosen to be somewhat larger than the largest impact parameter that leads to reactive collisions with the products scattered in the angular range of interest (170° to 180°).

Two comments should be made with regard to the importance sampling procedure described above. (a) A limited range of $\theta$, was employed in the calculations for nonrotating reagents, $D + H_2(v = 0, j = 0)$, whereas the full range (0° to 90°) had to be used in the calculations for $D + H_2(v = 0, j = 1)$. (b) The value of $b_{\text{max}}$, to be used in the calculations was found to depend on the final vibrational state $HD(v')$. The values of $b_{\text{max}}$ for $v' = 1$ were found to be smaller than those for $v' = 0$, and this was especially significant for low collision energies. In most of our calculations (for $j = 0$), partial cross sections for the two final states $v' = 0$ and 1 were calculated simultaneously, and therefore the larger value of $b_{\text{max}}$ (corresponding to $v' = 0$) was employed. In the calculations for $j = 1$, we were especially interested in partial cross sections for $v' = 1$, and therefore employed the smaller value of $b_{\text{max}}$ (suitable for $v' = 1$, but too small for $v' = 0$). In this way we not only improved the statistics of the calculation but also compensated for the use of the full range of $\theta$. The values of $b_{\text{max}}$, used in the present study varied between 0.17 Å at $E_t = 6.5$ kcal/mol to 0.5 Å at $E_t = 30$ kcal/mol.

For each set of initial conditions (initial rotational state and collision energy $E_t$) usually 50 000 to 100 000 trajectories were calculated under the importance sampling conditions described above.

The potential energy surface employed throughout this study is the LSTH surface. In this study are discussed the QCT backscattered partial cross sections as calculated for the angular range 170° < $\theta$ < 180° and the QM differential cross sections as calculated at $\theta = 180°$. In what follows both will be termed as the backscattered differential cross section (BDCS).

### III. RESULTS

The results for the BDCS as a function of translation energy for the reaction

$$D + H_2(v = 0, j = 0, l) \rightarrow \text{HD}(v' = 0, l, j') + H$$

are given in Figs. 1 to 3. Figure 1 shows the results for $v = j = v' = 0$; Fig. 2 shows those for $v = j = 0, v' = 1$ and Fig. 3 those for $v = 0, j = 1, v' = 1$. In Figs. 1 and 2, the QCT results are compared with the corresponding QM results of ZM and of Zhao, Truhlar, Schwenke, and Kouri (ZTSK), and in Fig. 3 the QCT results are compared with the QM results of ZTSK. It should be noted that the QM results of ZTSK indicate that the DCS change only slightly in the angular range 170° to 180°, and therefore the results at 180° represent quite well the behavior in this angular range. The comparison between the QCT and the QM DCS is carried out employing normalization factors. In the vibrational adiabatic case ($v = 0 \rightarrow v' = 0$) the comparison is done between the QCT and each of the QM BDCS separately. Different normalization factors were used: 0.078 in the ZTSK case and 0.090 in the ZM case. In the vibrational nonadiabatic cases ($v = 0, j = 1 \rightarrow v' = 1$) presented in Figs. 2 and 3.

![Figure 1](image1.png)

**FIG. 1.** Backscattered differential cross sections (BDCS) as a function of translational energy; a comparison between quasiclassical and quantum mechanical results for the reaction $D + H_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 0, l, j') + H$. (O) quasiclassical results (units in Å²), range of scattering angles 170° to 180°, error bars indicate one standard deviation; (■) normalized quantum mechanical results of ZTSK (Ref. 2, scattering angle 180°, normalization factor 0.078); (△) normalized quantum mechanical results of ZM (Ref. 1(b), scattering angle 180°, normalization factor 0.090)

![Figure 2](image2.png)

**FIG. 2.** Same as Fig. 1 but for the reaction $D + H_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 1, l, j') + H$. (O) quasiclassical results; (■) quantum mechanical results of ZTSK (Ref. 2); (□) quantum mechanical results of ZM (Ref. 1(a)). The normalization factor for both QM treatments is 0.101.
FIG. 3. Same as Fig. 1 but for the reaction \( D + H_2(v = 0, j = 1) \rightarrow HD(v' = 1) + H \). (\( \sigma_R \)) quasiclassical results; (\( \bigtriangleup \)) quantum mechanical results of ZTSK (Ref. 2). The normalization factor is 0.101.

IV. ANALYSIS AND DISCUSSION

A. The absolute backscattered differential cross sections

It is noticed that the QCT and the QM(ZM) BDCS curves are both quite oscillatory for the case where the initial rotational state is \( j = 0 \) (the reason that the QM ZTSK BDCSs seem to be smooth is probably because only five of them are given in each case). These oscillations exist for both the adiabatic transitions \( (v = 0 \rightarrow v' = 0) \) and the nonadiabatic transitions \( (v = 0 \rightarrow v' = 1) \). However, once the initial rotational state becomes \( j = 1 \), the oscillations almost disappear and the corresponding curve becomes much smoother. That rotations tend to wash out any structure related to the dynamics of the exchange process was already known from our studies on heavy + light-heavy (H + LH) systems\(^6(b)\)\(^\dagger\)\(^6(c)\)\(^\dagger\)\(^6(c)\) and was, to a certain extent, expected. The fact that the QCT curves are oscillatory for \( j = 0 \) and smooth for \( j = 1 \), while both were obtained from calculations with similar statistical accuracy, strongly supports the deduction that the observed oscillations for \( j = 0 \) are real (like the QM ones) and not a result of statistical fluctuations connected with the averaging process which leads to the BDCS.

In order to gain more insight into the oscillatory behavior, we carried out additional calculations for specific values of the initial orientation angle \( \theta_1 \), defined in Sec. II. Previous calculations for H + LH systems\(^7(c)\)\(^\dagger\) indicated that the oscillatory behavior is significantly affected by the initial value of \( \theta_1 \) [Ref. 7(c), Figs. 6 and 7], and that for the specific values of \( \theta_1 \) used, the oscillations were more pronounced than for random distributions. Results for three values of \( \theta_1 \) (20°, 40°, and 50°) are presented in Fig. 5. Here \( \sigma_R (170°-180°) \) values are shown for \( v' = 1 \), as well as the ratios of partial cross sections \( f(v' = 1)/f(v' = 0) \), as a function of the collision energy \( E_\text{tr} \).

The dependence of \( \sigma_R (170°-180°) \) on \( E_\text{tr} \) obtained from our calculations with a random distribution of \( \theta_1 \) (results in Figs. 1 and 2) are actually the sum of contributions due to a variety of initial specific values of \( \theta_1 \) (weighted by \( \cos \theta_1 \)), three of which are presented in Fig. 5. Thus the oscillatory behavior as encountered in Figs. 1 and 2 seems to be due to the strong dependence of those partial cross sections on \( \theta_1 \). The dependence on \( \theta_1 \) becomes almost meaningless for \( j \neq 0 \), because the final \( \theta_f \) dependent cross sections will probably vary with the initial translational distance. And indeed, the oscillations disappear once \( j = 1 \), as can be seen from Fig. 3.

FIG. 4. The ratio of BDCS for products formed in the vibrational state \( v' = 1 \) and \( 0 \) \( f(v' = 1)/f(v' = 0) \), see Eq. (4), as a function of translational energy (here the comparison is presented without a normalization),

\[
\frac{f(v' = 1)}{f(v' = 0)} = \frac{\text{d} \sigma}{\text{d} \Omega} (v' = 1) \int \text{d} \theta \quad \text{and} \quad \frac{\text{d} \sigma}{\text{d} \Omega} (v' = 0) \int \text{d} \theta - \Pi .
\]

(4)

The dependence of \( \sigma_R (170°-180°) \) on \( E_\text{tr} \) obtained from our calculations with a random distribution of \( \theta_1 \) (results in Figs. 1 and 2) are actually the sum of contributions due to a variety of initial specific values of \( \theta_1 \) (weighted by \( \cos \theta_1 \)), three of which are presented in Fig. 5. Thus the oscillatory behavior as encountered in Figs. 1 and 2 seems to be due to the strong dependence of those partial cross sections on \( \theta_1 \). The dependence on \( \theta_1 \) becomes almost meaningless for \( j \neq 0 \), because the final \( \theta_f \) dependent cross sections will probably vary with the initial translational distance. And indeed, the oscillations disappear once \( j = 1 \), as can be seen from Fig. 3.

Experimental measurements to test the predictions of Figs. 1 and 4 are conceivable, using molecular beams of state-selected reagents and measuring the backscattered
products in selected vibrational states. However, no detailed results of such measurements, as a function of collision energy, have been reported so far. Experiments to test the behavior presented in Fig. 5 are not conceivable at present. Such experiments would involve the orientation of a beam of H$_2$ molecules. This is impossible with the available techniques, which are limited mainly to reactions involving symmetric-top or paramagnetic molecules.

Overall, the fit between the QCT and the two QM results is unexpectedly very good. This applies to most of the energy interval for the \((v = j = 0, v' = 0)\) curve, to large portions of the energy interval for the \((v = j = 0, v' = 1)\) curve and again along most of the energy interval for the \((v = j = 1, v' = 1)\) curve. That the fit for \((v = 0, j = 1, v' = 1)\) is somewhat better than that for \((v = 0, j = 0, v' = 1)\) is an indication that the initial rotationally excited reagents tend to smear out quantum effects or at least make them weaker. The main discrepancies are obtained for the \((v = j = 0, v' = 1)\) transition at the low and high energy regions, for the \((v = j = v' = 0)\) transition at an intermediate regime \((E_{\text{tr}} = 13 \text{ kcal/mol})\), and for the \((v = 0, j = 1, v' = 1)\) transition at the low energy region.

As for the discrepancy at low energy region for the vibrational nonadiabatic transitions \((v = j = 0, v' = 1)\) and \((v = 0, j = 1, v' = 1)\), this could be attributable mainly to the way the quantization of the final vibrational states is done within the QCT calculations.

The discrepancy for the \((v = j = 0, v' = 1)\) at the high energy region is to a certain extent a surprise, and it seems that more QM calculations are needed in order to determine what is happening there.

Although our next subject is beyond the scope of this study, it has to be mentioned. We found that the two QM treatments yielded rather different BDCS (the difference is sometimes more than 25%) for the \((v = j = v' = 0)\) case. This is well noticed in Fig. 1 where we had to apply two different normalization factors (0.090 vs 0.078) in order to compare our QCT results with the QM ones. It could be that the source for the difference is due to the fact that the ZM calculations were carried out for the LSTH surface and the ZTSK calculations were carried out for the double many-body expansion (DMBE) potential.

Probably one of the most interesting findings obtained in this study is the large deviation (-20%) between the QCT and QM results for \((v = j = v' = 0)\) in the vicinity of \(E_{\text{tr}} = 13 \text{ kcal/mol}\). This subject will be discussed in a separate section.

### B. The ratio of backscattered differential cross sections \(f(v' = 1)/f(v' = 0)\)

The ratios of vibrational nonadiabatic to adiabatic BDCSS, \(f(v' = 1)/f(v' = 0)\) are presented in Fig. 4. It is important to emphasize that the comparisons in this figure are made on an absolute scale without using any normalization factors. The main points to be noted are as follows:

(a) The ratios are seen to be oscillatory, to about the same extent as the nonadiabatic BDCS curves.

(b) The overall fit between the QCT and QM ratios is reasonably good. However, the QM ratios are somewhat lower than the QCT ratios, indicating that the QCT treatment tends to emphasize the nonadiabatic transition (this could again be a result of the quasiclassical quantization process of the final vibrational states).

Quasiclassical trajectory calculations for backscattered products in the angular range 160°-180°, for the reaction \(D + H_2(v = 0, j = 1)\), employing the LSTH potential energy surface, have been reported by Blais and Truhlar. They carried out calculations at four collision energies. Although their calculations were performed for a wider range of scattering angles than in the present study, and their initial rotational state was \(j = 1\), rather than \(j = 0\), the values of \(f(v' = 1)/f(v' = 0)\) calculated from their results agree quite well with our results, except for their lowest collision energy. The values obtained by them in comparison with our results (given in parentheses) are as follows: 0.18 (0.12) for...
$E_{tr} = 16.1 \text{ kcal/mol}; 0.16 (0.16)$ for $E_{tr} = 19.6 \text{ kcal/mol}; 0.20 (0.19)$ for $E_{tr} = 21.9 \text{ kcal/mol}, and 0.27 (0.24)$ for $E_{tr} = 24.2 \text{ kcal/mol}$.

C. Quantum effects apparent in the backscattered differential cross sections

In a previous section we mentioned the fact that relatively large deviations between the QCT and QM BDCS for $(\nu = j = \nu' = 0)$ in the vicinity of $E_{tr} = 13 \text{ kcal/mol}$ were observed. It turns out that this energy value is in proximity to the collinear resonance energy for the $(0-0)$ reactive transition \(^{1}\) (see Fig. 6). That a collinear quantum effect is at all discernible in a 3D calculation is to a large extent a surprise. Most of the three-dimensional magnitudes, whether integral or differential, total or state to state, follow a summation of many partial waves. It has been shown in various reactive infinite order sudden approximation (RIOSA) calculations \(^{3,15}\) (which can be considered at least as an intermediate type of treatment between the collinear and the exact 3D calculations) that collinear effects tend to disappear very fast once the summation over $I$ values and integration over the IOSA angle $\gamma$ are carried out. (Recently, a similar behavior was observed in exact three dimensional treatments \(^{1(b),16}\). The fact that only a small number of $I$ values (or $J$ values, for that matter) contribute to these BDCS and the fact that the angular cone of acceptance for these BDCS is very small are probably the reasons that this quantum effect still sustained.

It has to be mentioned that the existence of resonance effects in this system was already an important issue in previous publications following the exact three dimensional quantum mechanical treatments \(^{1(a),2,16}\). However, in all these studies the analysis of the resonance was performed with respect to fixed-$J$ probability of $S$-matrix elements [see in particular the detailed analysis given in Ref. 16(b)]. It was also claimed by Valentini and co-workers that resonance behavior of integral cross sections was observed experimentally \(^{17}\), but this was not observed in more recent experiments of Zare and co-workers \(^{18}\). From these theoretical studies it was established that the resonance energy is in the vicinity of $E_{tr} \sim 15 \text{ kcal/mol}$ (which corresponds to $E_{ion} \sim 0.92 \text{ eV}$).

It seems to us that this large discrepancy between the QM and the QCT BDCS could be traced back to the collinear resonance. To show that this is really the case, the collinear reactive QCT and QM probabilities \(^{3}\) are presented as a function of the translational energy in Fig. 6. The main feature to be observed is the QM shoulder around $E_{tr} = 11 \text{ kcal/mol}$. In the vicinity of this energy the QM reactive probabilities are about 30% larger than the QCT ones. The main difference between the collinear and the 3D case is the fact that the 3D cross section decreases once the energy becomes smaller than the “shoulder” energy, whereas the collinear probability function is stable. However, it can be verified that this decrease is mainly due to the cutoff of the reactive cross section caused by the orbital angular momentum potential barrier.

The other difference is with respect to the position of the shoulder. It is noticed that the collinear shoulder appears at $11 \text{ kcal/mol}$ whereas the present 3D one appears at $13 \text{ kcal/mol}$. Both values differ significantly from the well established 3D resonance energy which is, as was mentioned earlier, at $E_{tr} \sim 15 \text{ kcal/mol}$. The fact that the collinear and 3D resonance energies differ so significantly is not new (a similar situation was encountered for the $H + H_2$ system) \(^{3,15}\), but the fact that the large discrepancy between the QM and the QCT BDCS is at an energy range which does not seem to contain the 3D resonance energy is somewhat puzzling. This fact seems to indicate that the individual $J$-dependent-state-to-state $S$ matrix elements may not yield a complete description of the behavior of the interacting particles. It seems that the dependence on the angle $\gamma$ which is smeared out in the way the exact QM treatment is carried out is also important. Some support to this statement can be found in the RIOSA study \(^3\) where it is shown how the position of the resonance changes not only with $l$ but also with $\gamma$.

V. SUMMARY

In this study energy dependent QM and QCT BDCS are compared for reactions (2i) with the aim of detecting quantum mechanical effects. We have shown that oscillations in the energy dependent $(\nu = 0 \rightarrow \nu' = 1)$ BDCS previously claimed to be of a quantum mechanical nature may not necessarily be such (similar oscillations were encountered for the QCT BDCS) but then a strong quantum effect was uncovered for the adiabatic $(\nu = 0 \rightarrow \nu' = 0)$ transition. We have established that the QM and the QCT BDCS differ significantly in an energy range around $E_{tr} = 13 \text{ kcal/mol}$. The energy range does not seem to contain the previous established 3D resonance energy at $E_{tr} \sim 15 \text{ kcal/mol}$. This fact seems to indicate that orientation effects (steric factor) which can not be directly exposed in terms of the $J$-dependent $S$-matrix elements could play a significant role in producing this difference.

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