Comparison between Quantum Mechanical and Classical Treatment of a Hard-Sphere Model for Colinear Three-Body Rearrangement Collisions

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The three-dimensional model for exchange reactions previously presented by Baer and Aniel is now treated quantum mechanically in order to study quantum effects. To do this the three interacting particles are restricted to movement along a straight line. It was found that the assumed potential energy surface, in certain cases, yields a potential barrier when the computations are performed quantum mechanically. The characteristics of a potential barrier disappear when the problem is treated classically.

I. INTRODUCTION

Different models have been suggested in order to extract the reactive cross sections for exchange reactions of the form

$$ZY+X \rightarrow ZX+Y.$$

In all these models the particles $Z$, $Y$, and $X$ are assumed to be mass points moving in a given potential energy surface. Some of the models are three dimensional\(^{2-5}\) and others are one dimensional.\(^{6-16}\) Although the correct reactive cross sections are expected to be derived only from three-dimensional models, much attention has been given to one-dimensional models where the three particles are constrained to movement along a straight line. The reason for this is twofold:

1. In contrast to the three-dimensional model, the one-dimensional one can be solved classically as well as quantum mechanically. By comparing the results of both treatments, the different quantum effects and especially a tunneling effect can be studied.

2. It is believed that, at least in the low-energy region, i.e., in the vicinity of the threshold energy of the reaction, the linear model might yield, to a first approximation, the same results as the three-dimensional one.

The aim of the present work was to study quantum effects in a recently presented three-dimensional model.\(^{4,5}\) Reference is made to a one-dimensional model which was found to yield similar results to the three-dimensional one in the low-energy region. The study was performed twice, once quantum mechanically and once classically. The treatment is in general similar to other treatments performed previously but the main difference stems from the fact that a different potential is assumed in the interaction region. Instead of assuming the existence of a barrier of a certain height as was done by Tang, Kleinman, and Karplus\(^{18}\) (TKK) and by Kleinman and Tang\(^{14}\) (KT), the shape of the interaction region is changed to a more circular region. In this sense the model becomes close to the model of Hulbert and Hirschfelder,\(^7\) who treated the hyperbolic and elliptic channels.

II. THE MODEL

A. Quantum Mechanical Treatment

Let us consider the linear system given in Fig. 1. We start with a bound system $ZY$ vibrating in its ground state (or in any of its excited states) and a free particle $X$. After collision, either particle $X$ is reflected, or rearrangement occurs and a new bound system $ZX$ is formed and $Y$ becomes a free particle. The potential energy surface chosen is shown in Fig. 2 (see Refs. 4, 5 for details). The axes of the coordinate system are $r_x$ and $r_y$, where $r_x$ is the distance between $X$ and $Z$ and $r_y$ is the distance between $Y$ and $Z$.

If we perform the transformation

$$x = \frac{1}{2} \left[ \frac{m_y + m_z}{m_z} \right] S_1 r_x + \left[ \frac{m_y}{m_y + m_z} \right] r_y,$$

(II.1)

$$y = r_y,$$

where $S_1 = (m_x + 2m_y) \left( \frac{m_x}{m_x + m_y} \right)^{1/2}$, $m_z$, $m_y$, and $m_z$ are the masses of $X$, $Y$, and $Z$, respectively, and $M = m_z + m_y + m_z$, the potential energy surface is changed and takes on the well-known skewed form (see Fig. 3). This transformation makes the kinetic energy terms appearing in the Schrödinger equation separable in contrast to the case when they were present in terms of $r_x$ and $r_y$. The coordinate $x$ represents, except for the scaling factor in front of

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the parentheses, the distance between X and the center-of-mass system of Y and Z. These coordinates are convenient as long as the system is in region I. In order to describe the system if it moves into region II, another system of coordinates is required, i.e.,
\[
    u = \left[ (m_x + m_z)/(2m_x + m_z) \right] S_{11} \{ r_x + \left[ m_z/(m_x + m_z) \right] r_z \},
\]
\[
v = r_z,
\]
where \( S_{11} = (m_x + 2m_z)/(m_2/Mm_xm_z)^{1/2} \). Here \( u \) represents, except for the scaling factor in front of the parentheses, the distance between Y and the center-of-mass system of X and Z.

The Schrödinger equation can be written in the following form in region I:
\[
    (\partial^2/\partial u^2 + \partial^2/\partial v^2 + \alpha_1^2) \psi_1 = 0,
\]
and in region II:
\[
    (\partial^2/\partial u^2 + \partial^2/\partial v^2 + \alpha_1^2) \psi_{11} = 0,
\]
where
\[
    \alpha_1^2 = (2\mu_1/k^2) E; \quad \alpha_1^2 = (2\mu_1/k^2) E;
\]
\[
    \mu_1 = m_xm_y/(m_x + m_y); \quad \mu_{11} = m_xm_z/(m_x + m_z).
\]

In what follows we assume \( m_x = m_y \). The relationship between \((u,v)\) and \((x,y)\) is given by
\[
    \begin{pmatrix}
        u \\
        v
    \end{pmatrix} = \begin{pmatrix}
        m_x/(m_x + m_z) & m_z/(m_x + m_z) \\
        m_z/(m_x + m_z) & m_z/(m_x + m_z) 
    \end{pmatrix} \begin{pmatrix}
        x \\
        y
    \end{pmatrix},
\]
where \( S = S_1 = S_{11} = (M/m_x)^{1/2} \) and is equal to \([\tan(\frac{1}{2}\theta)]^{-1}\) (cf. Fig. 3). If initially ZY is vibrating in state I, the wavefunction \( \psi_1 \), which is the solution of the Schrödinger equation subject to unit incident flux, has the form in region I:
\[
    \psi_1 = (2/l)^{1/2} \exp(-ik_x x) \sin[(n\pi/l)y] + (2/l)^{1/2} \sum_{n=1}^{\infty} R_n \exp(ik_n x) \sin[(n\pi/l)y],
\]
and in region II:
\[
    \psi_{11} = (2/l)^{1/2} \sum_{n=1}^{\infty} T_n \exp(ik_n x) \sin[(n\pi/l)y],
\]
where \( k^2 + (n\pi/l)^2 = \alpha_1^2 \) and \( k_n^2 = k_n \).

The first term in (II.5) represents particle X impinging on the system ZY which is vibrating in state I, and the sum represents reflection of particle X with the system left vibrating in any of the energetically possible states. The sum in (II.6) represents the repelled particle Y with the new system ZX left vibrating in any of the possible states. \( R_n \) and \( T_n \) are the reflection and the transmission coefficients and are closely related to the transition probabilities \( P_{I \rightarrow m}(R) \) and \( P_{I \rightarrow m}(T) \) through the equations
\[
    P_{I \rightarrow m}(R) = (k_m/k_l) | R_m |^2,
\]
\[
    P_{I \rightarrow m}(T) = (k_m/k_l) | T_m |^2.
\]

In order to solve for \( T_n \) and \( R_n \) we must know the solution in region III.

In order to see what influence the skewed line AB has on the rearrangement scattering we chose to define this line by the equation
\[
    y = -S(x - S_l)
\]
so that region III is bounded by three lines:
\[
    x = S_l, \quad u = S_l, \quad y = -S(x - S_l).
\]

For region III the following solution was chosen:
\[
    \psi_{III} = (2/l)^{1/2} \sum_{n=1}^{\infty} \left[ A_n \exp(+ik_n x) + B_n \exp(-ik_n x) \right] \sin[(n\pi/l)y - \eta] + c, \quad (\text{II.10})
\]
where \( \xi \) and \( \eta \) are related to \( x \) and \( y \) by the formulas
\[
    \xi = (x - S_y)/(1 + S^2)^{1/2},
\]
\[
    \eta = (S_x + y)/(1 + S^2)^{1/2}, \quad (\text{II.11})
\]
and \( t \) is given by
\[
    t = [S^2/((1 + S^2)^{1/2})]. \quad (\text{II.12})
\]

The coefficients \( A_n \) and \( B_n \) are constants to be determined. A solution of this form was chosen because it fulfills the boundary condition along the line AB, namely \( \psi_{III} = 0 \) for \( \eta = t \). Having done this, we are now in a position to solve the problem. The continuity conditions require at \( x = S_l \)
\[
    \psi_1 = \psi_{III}, \quad \partial \psi_{III}/\partial x = \partial \psi_{III}/\partial x \quad (\text{II.13})
\]
and at $u = SL$

$$\psi_{11} = \psi_{111}, \quad \partial \psi_{11}/\partial u = \partial \psi_{111}/\partial u. \quad (II.13')$$

Expanding $\psi_{11}$ and its derivative in terms of Fourier series, we get, at $x = SL$,

$$\psi_{11} = (2/l)^{1/2} \sum_{n,m}^{\infty} \left( A_n \alpha_{nm} + B_n \beta_{nm} \right) \sin[(m\pi/l)y] \quad (II.14)$$

and

$$\partial \psi_{11}/\partial x = (2/l)^{1/2} (1+S_r)^{-1/2} \sum_{n,m}^{\infty} \left\{ [i k_n \alpha_{nm} + (n\pi/l) S \alpha_{nm}'] A_n 
- [i k_n \beta_{nm} - (n\pi/l) S \beta_{nm}'] B_n \right\} \sin[(m\pi/l)y],$$

where

$$\alpha_{nm} = \frac{2}{l} \int_{0}^{l} \exp(i \frac{k_n}{1+S_r} S) \sin[(m\pi/l)y] dy,$$

$$\beta_{nm} = \frac{2}{l} \int_{0}^{l} \exp(-i \frac{k_n}{1+S_r} S) \sin[(m\pi/l)y] dy,$$

$$\alpha_{nm}' = \frac{2}{l} \int_{0}^{l} \exp(i \frac{k_n}{1+S_r} S) \cos[(m\pi/l)y] dy,$$

$$\beta_{nm}' = \frac{2}{l} \int_{0}^{l} \exp(-i \frac{k_n}{1+S_r} S) \cos[(m\pi/l)y] dy,$$

and

$$\psi_{111} = (2/l)^{1/2} \sum_{n,m}^{\infty} \left( A_n \beta_{nm} + B_n \alpha_{nm} \right) \sin[(m\pi/l)y]. \quad (II.16')$$

Finally we obtain the following equations:

$$\delta_{m,1} \exp(-ik_1 S_l) + R \exp(ik_m S_l) = \sum_{n} \left( A_n \alpha_{nm} + B_n \beta_{nm} \right),$$

$$T_m \exp(ik_m S_l) = \sum_{n} A_n \beta_{nm} + B_n \alpha_{nm},$$

$$\delta_{m,1} \left( 1+S_r \right)^{-1/2} \sum_{n} \left\{ [i k_n \alpha_{nm} + (n\pi/l) S \alpha_{nm}'] A_n 
- [i k_n \beta_{nm} - (n\pi/l) S \beta_{nm}'] B_n \right\},$$

Equations (II.17) provide a system of simultaneous linear equations of infinite order in the unknowns $R_m$, $T_m$, $A_n$, and $B_n$. Termination of all of the series at $u = N$ yields a finite system of $4N$ equations as an approximation to the infinite one.

**B. Classical Treatment**

The same transformations that diagonalized the kinetic energy in the quantum mechanical treatment will do so also in the classical treatment. Consequently the kinetic energy may be written in the form

$$T = \frac{1}{2} \mu \left( \dot{x}^2 + \dot{y}^2 \right), \quad (II.18)$$

where the dots stand for $d/dt$. The collinear system of the three particles can be replaced by one particle—the configuration particle—moving in a plane. The Hamiltonian takes the form

$$H = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2) + V(x, y).$$

The potential field is shown in Fig. 3(b). Using this potential field the trajectory of the configuration particle can be traced rather easily. The particle is assumed to be initially in region I and the aim is to compute the probability that its trajectory ends in region II. The angle of collision $\phi$ between the directed line segments AA' or CC' and the trajectory of the configuration particle [Fig. 3(b)] is determined from the relation $\tan \phi = \dot{y}/\dot{x}$. If $E_0$ is the vibrational energy of ZY and $E$ is the total energy, then

$$\tan \phi = [E / (E - E_0)]^{1/2}. \quad (II.19')$$

If $d$ is some point along the segment AC and if the last collision of the configuration particle, before entering region III, happens to be with the line segment AA', then in order to get a rearrangement $d$ has to fulfill the condition

$$1 - d/l > \max \{0, 1 - 2[1 + S \tan \phi]/(1 + S_r)\}. \quad (II.20)$$

If, on the other hand, the last collision happens to be with the line CC', then $d$ has to fulfill the condition

$$1 - d/l > 1 - 2[1 - S \tan \phi]/(1 + S_r). \quad (II.21)$$

Defining $E^*$ as

$$E^* = (8\mu P/l^2) E$$

and assuming the molecule ZY to be in its ground state, one finds that $E^* = 1$ and

$$\tan \phi = (E^* - 1)^{-1/2}. \quad (II.19')$$

**Table I.** Numerical data used in the calculations.

<table>
<thead>
<tr>
<th>$m_x$</th>
<th>$m_y$</th>
<th>$\theta$</th>
<th>$S$</th>
<th>$\rho_{xy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>90</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>60</td>
<td>$\sqrt{3}$</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>$\sqrt{2} - 1$</td>
<td>45</td>
<td>1/($\sqrt{2} - 1$)</td>
<td>0.3414</td>
</tr>
</tbody>
</table>
Applying Eqs. (II.20), (II.21), and (II.19'), the probability for rearrangement can be determined. However, we have to distinguish between two cases depending on the value of $S$:

**Case 1:** $S < \sqrt{3}$

$$P = \frac{1}{2}$$

$$E^* < 1 + S^2,$$

$$= \frac{1}{2} (1 + 2 \{1 - \frac{S}{(E^* - 1)}\} (1 + S^2)^{-1});$$

$$1 + S^2 < E^* < 1 + \frac{2S}{(S^2 - 1)},$$

$$= \frac{2}{(1 + S^2)};$$

$$E^* > 1 + \frac{2S}{(S^2 - 1)}. \quad \text{(II.22)}$$

**Case 2:** $S > \sqrt{3}$

$$P = \frac{1}{2};$$

$$E^* < 1 + \frac{2S}{(S^2 - 1)},$$

$$= \frac{1}{2} \{S^2/(E^* - 1)\} (1 + S^2)^{-1};$$

$$1 + \frac{2S}{(S^2 - 1)} < E^* < 1 + S^2,$$

$$= \frac{2}{(1 + S^2)};$$

$$E^* > 1 + S^2. \quad \text{(II.23)}$$

For $S=3$ we obtain $P = \frac{1}{2}$ for any $E^*>1$.

**III. RESULTS AND DISCUSSION**

We have studied three cases; in the first the mass $m_z$ of the scattering center is infinitely heavy compared to the masses of $X$ and $Y$ ($\theta = 90^\circ$), in the second the mass of the scattering center is equal to the masses of $X$ and $Y$ ($\theta = 60^\circ$), and in the third the masses of $X$ and $Y$ are heavier than the mass of $Z$ ($\theta = 45^\circ$). Since it is assumed for each case that $m_z = m = 1$ $mu$ one obtains $m_z = \infty$ for the first case, $m_z = 1$ $mu$ for the second, and $m_z = (\sqrt{2} - 1)$ $mu$ for the third case.

The line $AB$ (cf. Fig. 3) originates due to the assumed direct interaction of $X$ and $Y$ and is closely connected with the radius of the billiard ball potential assumed to exist between $X$ and $Y.\text{[4,5]}$ If $\rho_{xy}$ is defined as the radius of the billiard ball potential, then the equation of the line $AB$ in the $(r_x, r_y)$ coordinate system is given by

$$r_x + r_y = \rho_{xy}. \quad \text{(III.1)}$$

In general the value of $\rho_{xy}$ is assumed to be energy dependent. However, in this study we assumed it to be constant, and its value was chosen so that, after performing transformation (II.1), the line $r_x + r_y = \rho_{xy}$ transforms to $y = -S(x - S)$. This value of $\rho_{xy}$ is

$$\rho_{xy} = 2[S^2/(1 + S^2)]. \quad \text{(III.2)}$$

Actually, there is no physical reason to write $\rho_{xy}$ in this way, but by so doing the quantum mechanical as well as the classical treatments are both simplified. From (III.2) $\rho_{xy}$ is seen to vary with $S$ but since $S$ varies as a function of $m_z$, different values of $\rho_{xy}$ can be obtained by varying the mass of the scattering center. The maximal value of $\rho_{xy}$ for which rearrangement is still possible is $2S$. The values of $\rho_{xy}$ used in the calculations for $l = 0.2$ Å are listed in Table I. For $m_z = \sqrt{2} - 1$, $\rho_{xy}$ is equal to 0.3414 Å which is rather close to the maximum (0.4 Å).

The rearrangement probabilities for the quantum mechanical and the classical systems are presented in Figs. 4–6.

**A. Quantum Mechanical Results**

(i) Comparing the quantum mechanical results with those of TKK and KT derived assuming the existence of a potential barrier, we notice that the shapes of the functions in the low-energy region are rather similar (except at $\theta = 90^\circ$). The line $AB$ apparently produces a potential energy barrier and the closer the line is to the corner $C$ (cf. Fig. 3), the larger the corresponding height of the effective barrier. This situation is similar to the one discussed by Hulbert and Hirschfelder\text{[8]} when considering the hyperbolic and elliptic channel. They found “that though the height of the energy surface is perfectly constant a system moving in a curved path encounters an effective potential energy barrier which is partially due to the change in the zero point vibration as the channel narrows and partially due to the curvature of the
path.” The conclusions of Hulburt and Hirschfelder are confirmed in our case although we could not separate the contribution of each of the factors that lead to the creation of the effective potential barrier. It seems that the more important factor is the curvature of the path because in our model a channel of well-defined width in the interaction region does not exist.

(ii) Although the quantum mechanical probabilities are oscillating functions of the energy, the violent oscillations found by TKK and KT are not observed here. Actually, along the energy range studied, only one peak is observed, always in the very close vicinity of the same \( E^* \) value, i.e., \( E^*=4 \), which is a resonance energy. The peaks themselves are not sharp in the first two cases \( \theta = 90^\circ, 60^\circ \) (cf. Figs. 4, 5) and only in the third case \( \theta = 45^\circ \) (cf. Fig. 6) is the peak sharp enough to indicate the possibility of the formation of an activated complex of a relatively long mean life. It was also found that the functions never decrease to zero indicating that the transmission probability \( P_{\text{class}}(T) \) differs from zero along the entire reactive zone.

(iii) Comparing \( P_{\text{class}}(T) \) with \( P_{\text{eq}}(T) \) we notice that the former is much more sensitive to the value of \( \rho_{\text{eq}} \) than the latter. As \( \rho_{\text{eq}} \) increases the value of the integral \( \int P_{\text{class}}(T) dE^* \) decreases sharply, whereas the value of \( \int P_{\text{eq}}(T) dE^* \) initially increases (cf. Figs. 4 and 5) and then remains approximately constant (cf. Figs. 5 and 6).

**B. Comparison Between the Quantum Mechanical and the Classical Treatment**

The classical transmission probabilities are also presented in Figs. 4–6. The functions are seen to behave more smoothly here than in the case of KT. The striking difference is, however, that in each case the transmission probability starts at \( P = \frac{1}{2} \). As the energy increases, for \( m_z = \infty \) the transmission probability increases, for \( m_z = 1 \) it remains constant, and for \( m_z = \sqrt{2} - 1 \) it decreases. The main reason for this behavior is that upon going from the heavier to the lighter mass the value of \( \rho_{\text{eq}} \) increases, thus constraining the passage from region I to region II.

Comparing the quantum mechanical transmission probabilities with the classical ones, it was found that for \( m_z = \infty \) the quantum mechanical treatment yields much larger transmission probabilities; for \( m_z = 1 \) both treatments yield similar results (with regard to areas) and for \( m_z = \sqrt{2} - 1 \) the classical treatment yields larger probabilities. In general, the constriction of the passage appears to influence the classical as well as the quantum mechanical probabilities in a similar way. However, a closer look indicates that increased shrinking of the passage affects the two probabilities differently. The classical probability decreases in a continuous way without additional significant effects. On the other hand, the quantum mechanical probability decreases sharply (in the low-energy region) indicating clearly the existence of a potential barrier. We may therefore conclude that a potential barrier in the “classical sense” exists only in the quantum mechanical picture whereas it is absent in the classical one.

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