

Study of Collinear Collision in Impulsive Model

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Exact quantum solution of the collinear collision problem is found in the impulsive model. The transition probabilities compare well with those for real systems, except when multiple collisions become important.

I. INTRODUCTION

Various models are used when understanding the collision processes is required. Their role is to emphasize those features which are dominant in collisions and to neglect those which are not so important. There are various kind of models¹ e.g. the distorted wave Born approximation, the Infinite Order Sudden (IOS) approximation, collinear model, two dimensional model etc., but among them there is the one which needs particular attention. We call it the impulsive model, although different authors have different approach to describe it. Physically it is associated with the process whereby energy transfer between projectile and target happens in very short time intervals. Particular example of our interest is energy transfer due to the direct collision between atom and molecule, in contrast to orbiting which is not considered impulsive process. Most of energy transfer in such collisions occurs in the region of the short range repulsive wall of atom-molecule potential, and it takes very short time interval. Since the repulsive wall is very steep it is not a great error if it is replaced by an infinitely high barrier. We assume that the rest of the potential can be approximated by a spherically symmetric average of the potential. We shall call this model the impulsive model, although it is also known as the hard sphere or the hard wall model.²

In this paper we show how to find exact quantum solution of this model for a general collinear atom-molecule collision problem. The method of solution is general enough to be easily extended to more dimensions.³ By using this technique we investigate validity of the model on various systems. We also show how to find approximate solution for the model and discuss its relationship to the various other approximate solutions.

The proposed method of solution of the impulsive model is algebraic, meaning that the transition amplitude (S-matrix) is solution of a set of linear equations. However, there are various other approaches to find solution of the collinear collision problem, but they are all approximate. The technique of these solutions is based either on the time independent or time dependent approach. In the time independent approach the simplest solution is the distorted wave approximation,^{4,5} but it has limited use.⁶ Furthermore in the limit of the impulsive model it becomes meaningless because the coupling matrix in the diabatic multichannel equations is infinite.⁷ Perturbation technique can be formulated in the adiabatic basis,⁸ when coupling matrix is finite, but even then it is only restricted to systems where one can find simple basis. Even then the perturbation approach gives only accurate results for systems with small number of channels and very small energy transfer. Another possibility is to use the IOS approximation, which gives the S-matrix in a closed form,¹ but it is restricted to systems with small energy transfer. The approximation solution, however, was found in the momentum representation of the scattering amplitude.^{9,10} In this representation one obtains the transition amplitudes as expansion in powers of the potential but not in the way the Born expansion does. Each power of potential is also weighted by the similar power of the propagator for a free atom. This is interpreted as expansion of transition amplitude in multiple collisions events. Thus, for example, the lowest approximation is interpreted as contribution of the single collision event. In this respect the approximation is also called the impulsive. There are a few other ways of solving this problem,¹¹ within the time independent formalism, but they are very specific for the collinear collisions and therefore not useful if one has the aim of applying them to multidimensional problems. In the time-dependent approach approximate solution for the transition amplitudes is found in a closed form.¹²⁻¹⁵ We shall discuss it in the last section of the paper.

II. QUANTUM THEORY

Hamiltonian for a collinear system of an atom A and a diatomic molecule BC is in their centre of mass coordinates

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial y^2} + \frac{K}{2} (y - y_0)^2 + V(x,y) \quad (1)$$

where μ is the reduced mass of the system, μ_{BC} is the reduced mass of the molecule, while the coordinates x and y are defined in terms of the coordinates x_A , x_B and x_C of the three atoms as

$$x = x_A - \frac{x_B m_B + x_C m_C}{m_B + m_C} \quad (2)$$

$$y = x_B - x_C$$

where m_A , m_B and m_C are masses of the respective atoms. It was assumed that the molecule BC is harmonic oscillator and the atom-molecule potential is $V(x,y)$.

The potential $V(x,y)$ is assumed to be function of only the coordinate x , however, it is infinitely repulsive at certain separation between atoms A and B (atoms are assumed to be aligned in the order A-B-C). In other words the potential $V(x,y)$ has the form

$$V(x,y) = \begin{cases} U(x); & z > z_0 \\ \infty & ; z \leq z_0 \end{cases} \quad (3)$$

where z is the distance between atoms A and B and it is given by

$$z = x - \frac{m_C}{m_B + m_C} y \quad (4)$$

z_0 is the radius of the infinite repulsive core between atoms A and B. Solution of Schrödinger's equation for this potential one easily finds when $z > z_0$. A particular solution is

$$\Psi_n = \varphi_n(y) \omega_n(x) \quad (5)$$

where $\varphi_n(y)$ is the harmonic oscillator eigenfunction of the n -th state with the eigenenergy ε_n , and $\omega_n(x)$ is the wave function for potential $U(x)$ and energy $E - \varepsilon_n$. The harmonic oscillator eigenfunction are

$$\varphi_n(y) = \left(\frac{K^{1/4}}{\hbar^{1/2} \pi^{1/2} 2^n n!} \mu_{BC}^{1/4} \right)^{1/2} H_n(Q) e^{-Q^2/2} \quad (6)$$

where $H_n(Q)$ is the Hermite polynomial and

$$Q = \left(\frac{K}{\hbar^2} \mu_{BC} \right)^{1/2} (y - y_0) \quad (7)$$

where y_0 is the equilibrium separation of the harmonic oscillator. The energies ε_n are

$$\varepsilon_n = \hbar \omega (n + 1/2) = \hbar (K/\mu_{BC})^{1/2} (n + 1/2) \quad (8)$$

The most general solution is a linear combination of the particular solutions (5), which we write as

$$\Psi_n = \sum_m \varphi_n(y) [\omega_m^+(x) A_{mn} + \omega_m^-(x) B_{mn}] \quad (9)$$

where ω_m^+ and ω_m^- are the two irregular solution, defined with the boundary condition for $x \rightarrow \infty$

$$\omega_m^\pm(x) = e^{\pm i x k_m} \quad (10)$$

where the channel wave numbers k_m are

$$k_m = \sqrt{\frac{2\mu}{\hbar^2} (E - \varepsilon_m)} \quad (11)$$

The index n of the coefficients S_{mn} and B_{mn} designates the n -th linearly independent solution. These coefficients are determined by imposing two scattering process and b) it must be zero for $z = z_0$. the second condition gives

$$\sum_m \varphi_m(y) [\omega_m^+(z_0 + \frac{m_C}{m_B + m_C} y) A_{mn} + \omega_m^-(z_0 + \frac{m_C}{m_B + m_C} y) B_{mn}] = 0 \tag{12}$$

which must be satisfied for all y . If we write

$$\varphi_m(y) \omega_m^\pm(z_0 + \frac{m_C}{m_B + m_C} y) = \sum_1 \varphi_1(y) \langle 1 | \pm | m \rangle \tag{13}$$

where the coefficients are given by

$$\langle 1 | \pm | m \rangle = \int_{-\infty}^{\infty} dy \varphi_1(y) \omega_m^\pm(z_0 + \frac{m_C}{m_B + m_C} y) \varphi_m(y) \tag{14}$$

then the set of equations (12) is

$$\sum_{m1} \varphi_1(y) [\langle 1 | + | m \rangle A_{mn} + \langle 1 | - | m \rangle B_{mn}] = 0 \tag{15}$$

The solution is

$$A = \langle | + | \rangle^{-1} ; B = - \langle | - | \rangle^{-1} \tag{16}$$

where we have defined matrices $\langle | \pm | \rangle$ with the elements

$$\langle | \pm | \rangle_{mn} = \langle m | \pm | n \rangle \tag{17}$$

The scattering solution, if the incident wave propagates towards $x \rightarrow \infty$, has the asymptotic form

$$\Psi_n = \omega^+(x) \varphi_n(y) + \sum_m \omega_n^-(x) \varphi_m(y) S_{mn} \left(\frac{k_n}{k_m} \right)^{1/2} \tag{18}$$

where $|S_{mn}|^2$ are transition probabilities.

If (9) and (18) are compared then S_{mn} are

$$S_{mn} = - [\langle | - | \rangle^{-1} \langle | + | \rangle]_{mn} \left(\frac{k_m}{k_n} \right)^{1/2} \tag{19}$$

For the impulsive model this result is exact. It simplifies considerably if small energy transfer is assumed. The inverse of $\langle | - | \rangle$ is then approximately

$$[\langle | - | \rangle^{-1}]_{mn} \simeq \int_{-\infty}^{\infty} dy \varphi_m(y) (\omega_m^-)^{-1} \varphi_n(y) \tag{20}$$

which can be shown by calculating the product $\langle | - | \rangle^{-1} \langle | - | \rangle$, taking into account the completeness of the basis functions $\varphi_n(y)$ and the assumption of small energy transfer for which we can write $\omega_m \simeq \omega_n$. The elements S_{mn} are then

$$S_{mn} \simeq - \left(\frac{k_m}{k_n} \right)^{1/2} \int_{-\infty}^{\infty} dy \varphi_m \frac{\omega_n^+}{\omega_m^-} \varphi_n \tag{21}$$

which resembles very much the IOS approximation.¹

In our study we shall consider the case when $U(x)$ in (3) is zero. The two irregular solution $\omega_{\pm m}$ are then

$$\omega^{\pm} = e^{\pm i k_n y} \quad (22)$$

and the matrices $\langle \pm | \pm \rangle$ are

$$\langle m | \pm | n \rangle = \int_{-\infty}^{\infty} dy \varphi_m(y) e^{\pm i k_n (z_0 + m_C y / (m_B + m_C))} \varphi_n(y) \quad (23)$$

For the harmonic oscillator eigenfunction (6) the integral (23) can be evaluated analytically,¹⁶ and for $m \leq n$ it is given by $\langle m | \pm | n \rangle =$

$$\sqrt{\frac{m!}{2^{m-n} n!}} \left(\pm \frac{i k_n C}{2} \right)^{n-m} e^{\pm i k_n y_0 \eta \pm i k_n z_0 - k_n^2 C^2 / 4} L_m^{n-m}(k_n^2 C^2 / 2) \quad (24)$$

where

$$\eta = \frac{m_C}{m_B + m_C} ; C = \frac{\hbar^{1/2}}{K^{1/4} \mu_{BC}^{1/4}} \eta \quad (25)$$

and $L_m^{n-m}(z)$ is the Laguerre polynomial. For $m > n$ the indices m and n in (24) interchange, expect the index of k_n .

The approximation (21) has also a simple expression. The wave number k_n in the integral (23) is replaced by $k_n + k_m$ and the formula (24), which this change, gives the approximate value of the S-matrix (21). In this approximation the probability for transition $m \rightarrow n$ is

$$P_{mn} = \frac{m!}{n!} e^{-z} z^{n-m} \left(L_m^{n-m}(z) \right)^2 ; n \geq m \quad (26)$$

where

$$z = \frac{\hbar}{2} \left(\frac{m_C}{m_B + m_C} \right)^2 \left(\frac{1}{K \mu_{BC}} \right)^{1/2} (k_n + k_m)^2 \quad (27)$$

III. CLASSICAL THEORY

In this section we give a review of the classical theory for the collinear atom-diatom molecule collisions^{17,18} because we shall compare quantum and classical results. Classical equations of motion for the collinear atom-diatom system (molecule is treated as harmonic oscillator), which was described in the previous section, is in their centre of mass coordinates

$$\mu \frac{d^2 x}{dt^2} = - \frac{\partial V}{\partial x} ; \mu_{BC} \frac{d^2 y}{dt^2} = - K (y - y_0) - \frac{\partial V}{\partial y} \quad (28)$$

where the parameters are the same as in the previous section. It is convenient to transform x and y into a new set of coordinates which explicitly exhibit the observables. The new canonical variables are x, n, p_x and Φ , where n plays the role of the vibrational quantum number, which is defined as

$$E_{\text{osc}} = \hbar \omega n = \frac{p_y^2}{2\mu_{\text{BC}}} + \frac{K}{2}(y-y_0)^2 \quad (29)$$

where E_{osc} is the oscillator energy. Φ is the phase of oscillator and it is defined by

$$\Phi = \tan^{-1}\left(\frac{K(y-y_0)}{\omega p_y}\right) \quad (30)$$

In this set of coordinates the equations of motion are

$$\begin{aligned} \frac{dn}{dt} &= -\left(\frac{2n}{\hbar \omega \mu_{\text{BC}}}\right)^{1/2} \frac{\partial V}{\partial y} \cos \Phi \\ \frac{d\varphi}{dt} &= \omega + \left(\frac{1}{2\omega \hbar n \mu_{\text{BC}}}\right)^{1/2} \frac{\partial V}{\partial y} \sin \Phi \end{aligned} \quad (31)$$

$$\frac{d}{dt} p_x = -\frac{\partial V}{\partial x}; \quad \frac{dx}{dt} = \frac{1}{\mu} p_x$$

and the initial conditions are chosen according to the following recipe. For the coordinate x one takes a fixed value which is large enough so that the potential $V(x,y)$ is small. The velocity v_x is determined from the conservation of total energy and n is given the value of the initial state n_i of the molecule. The condition on the phase Φ_i is that after collision the molecule is in the chosen final state n_f . In practice one calculates the function $n_f(\Phi_i)$ in the interval $0 \leq \Phi_i < 2\pi$ and then the proper value for Φ_i is chosen by interpolation.

Transition probability from the initial state n_i to the final n_f is given by ¹

$$P_{n_i \rightarrow n_f} = \frac{1}{2\pi} \sum_{\Phi_i} \left| \frac{dn_f}{d\Phi_i} \right| \quad (32)$$

where the sum extends over all phases Φ_i which satisfy the previous condition. The derivative in (32) can be calculated numerically. This means that once Φ_i is found then n_f is calculated for the values $\Phi_i \pm \Delta$, which gives the approximate derivative

$$\frac{dn_f}{d\Phi_i} \simeq \frac{n_f(\Phi_i + \Delta) - n_f(\Phi_i - \Delta)}{2\Delta} \quad (33)$$

Another way is to calculate this derivative directly. Let us assume that one knows the solution of the set of equations (31) for particular initial conditions. If Φ_i is slightly changed the set x, p_x, n and Φ also changes by a small value (we consider only the cases without catastrophes i.e. the cases when the final value of solution of (31) is continuous function of the initial conditions). If all the initial conditions are kept constant, except Φ_i is slightly changed, then at any instant of time the solution of (31) is approximately

$$q_\nu(t, \Phi_i + \delta\Phi_i) \sim q_\nu(t, \Phi_i) + \Delta q_\nu \quad (34)$$

where q represents one of the variables x , n , p_x , or Φ . The time derivative of Δq is

$$\frac{d}{dt} \Delta q_\nu = \sum_{\mu=1}^4 \frac{\partial f_\nu}{\partial q_\mu} \Delta q_\mu = \sum_{\mu=1}^4 \frac{\partial f_\nu}{\partial q_\mu} \frac{\partial q_\mu}{\partial \Phi_i} \delta\Phi_i \quad (35)$$

where f are the functions on the right of equations (31). If we take the limit $\delta\Phi_i \rightarrow 0$ then

$$\frac{d}{dt} \frac{\partial q_\nu}{\partial \Phi_i} = \sum_{\mu=1}^4 \frac{\partial f_\nu}{\partial q_\mu} \frac{\partial q_\mu}{\partial \Phi_i} \quad (36)$$

The set of equations (36) should be solved together with (31) in order to obtain $dn/d\Phi_i$, which has now the exact value in contrast to (33) which is approximate. The initial conditions for (36) are $\partial n/\partial \Phi_i = \partial x/\partial \Phi_i = \partial v_x/\partial \Phi_i = 0$ and $\partial \Phi/\partial \Phi_i = 1$.

Within the classical theory one can also study the impulsive model. In the simplest case, when the potential $V(x,y)$ is zero except at the hard core, the model is known as the hard sphere model. Under the assumption of single impact between A and B this model gives for the energy transfer from the incoming atom into the molecule (e.g. ref (9))

$$\Delta E = r E_{CM} \left(1 - \sqrt{\frac{E_{OSC}}{E_{CM}}} s \cos \Phi \right) \left(1 + \sqrt{\frac{E_{OSC}}{s E_{CM}}} \cos \Phi \right) \quad (37)$$

where

$$s = \frac{m_A m_C}{m_B (m_A + m_B + m_C)}; \quad r = \frac{4 m_A m_B m_C (m_A + m_B + m_C)}{(m_A + m_B)^2 (m_C + m_B)^2} \quad (38)$$

The energy transfer ΔE is defined as the difference between the final and the initial vibrational energy of the molecule. E_{CM} is the initial kinetic energy of the system and E_{OSC} is the initial vibrational energy of the molecule. If the potential $V(x,y)$ is not zero, but is defined as in (3), we can also use (37) for the energy transfer, except that the initial relative translational energy should be lowered by the value $U(x)$ at the hard core.

When multiple collisions between A and B are considered the formula (37) is no longer applicable. Energy transfer is obtained by considering various possibilities of multiple collisions between all partners A , B and C , and the result is not as straightforward as (37).

IV. APPLICATION

We have made a study of energy transfer in a collinear He-CO collision, and compared the accuracy of the impulsive model against the exact calculations. It was assumed that He atom hits oxygen atom of CO molecule, which was assumed to be harmonic oscillator with the force constant $K=1900 \text{ Nm}^{-1}$. For the interaction between He and CO we have taken exponential repulsion of the form

$$V(x,y) = V_0 e^{-\alpha(z-z_0)} \quad (39)$$

where $V_0 = 1.6 \cdot 10^{-21}$ J (0.01 eV), $\alpha = 20 \cdot 10^{10} \text{ m}^{-1}$ (20 \AA^{-1}) and $z_0 = 3 \cdot 10^{-10}$ m (3 \AA), while in the impulsive model it had the form (3) with $U(x)=0$. The potential of the impulsive model is obviously the limit of (39) when $\alpha \rightarrow \infty$.

In Figure 1. we show the two dimensional plot of the entire potential for the system with $K=900 \text{ Nm}^{-1}$ (this system will be also discussed). The solid line represents the impulsive potential. The broken line is the intermediate case when $\alpha = 50 \cdot 10^{10} \text{ m}^{-1}$ (50 \AA^{-1}).

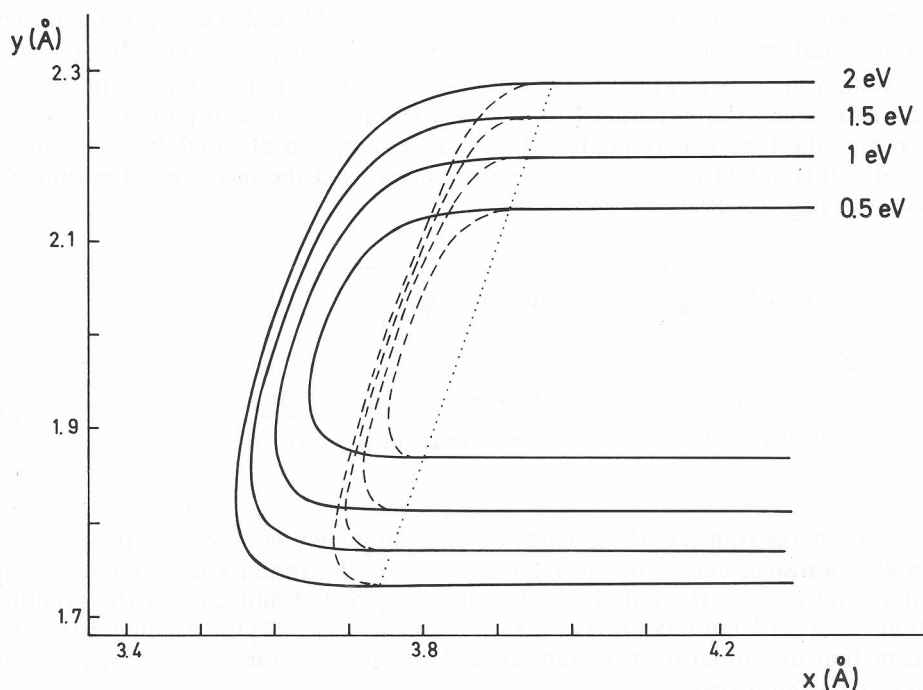


Figure 1. Potential energy contours for the system atom-diatomic molecule. The molecule is assumed to be harmonic oscillator and atom-molecule potential is (39). Solid line is for $\alpha=20 \text{ \AA}^{-1}$ while the dotted line is for impulsive model potential. The broken line is the intermediate case $\alpha=50 \text{ \AA}^{-1}$.

We have made study of this system at collision energy $E=3.2$ J (2eV). At this energy there are 7 open channels ($n=6$ is the last open channel), which is sufficient number of channels to observe reasonable resolved structure of transition probabilities. Furthermore, with this number of open channels we are in the regime of the semiclassical limit, where it is expected that classical mechanics is adequate description of collisions.

Figure 2. shows results of four different calculations for the transition probabilities $0 \rightarrow n$: exact quantum (solid line), impulsive quantum (broken line), approximate impulsive quantum based on (26) (dotted line) and classical (broken-dotted line). Classical transition probabilities were obtained by integrating the set of equations (31) and (36). Exact quantum transition probabilities were obtained by integrating the appropriate set of multichannel equations, using the log-derivative method (the term exact is perhaps too strong but we shall use it in order to distinguish it from the other calculations).

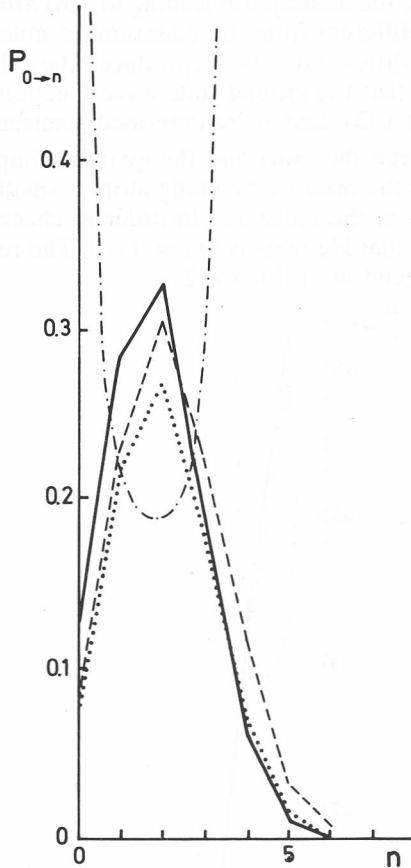


Figure 2. Transition probabilities for He-CO collision at 2 eV collision energy from exact quantum (solid line), impulsive model (broken line), approximation (26) (dotted line) and classical (broken-dotted line) calculations. Initially CO is in the ground state.

Impulsive model results are in reasonable good agreement with the exact ones. Since the qualitative features of transition probabilities are reproduced well it is clear that hard collisions (impulsive) are an important factor which determines energy transfer in atom-molecule collisions. Deviation between the two results can be attributed to the simple choice of the potential in the impulsive model. If instead of the choice $U(x)=0$ in (3) we had assumed that the potential has some average value

of the true potential $V(x,y)$, the agreement could be improved. The result would be lowering the kinetic energy of collisions prior to the impact with the hard core, and hence transition probabilities for large energy transfer would be lowered. Likewise the low energy transfer probabilities would be enhanced, which is just the deviation in Figure 2.

Transition probabilities based on the formula (26) are not in such a good agreement with the exact results, although they are not entirely meaningless. The reason for this is that the energy transfer is relatively large compared with the number of open channels, and hence the assumption leading to (26) are not satisfied. The classical results are entirely different from the quantum, so much so that even the averaged quantum probabilities do not reproduce the classical ones. This is manifestation of the fact that the ground state wave function of the harmonic oscillator (the initial state of CO) cannot be described semiclassically.

The agreement between the exact and the quantum impulsive transition probabilities is much better if the mass of incoming atom is small compared to the mass of the atom which it hits in the molecule. In order to check this we have analyzed energy transfer assuming that He mass is $m_A = 1$ a.u. The results are shown in Figure 3, with the same legend as in Figure 2.

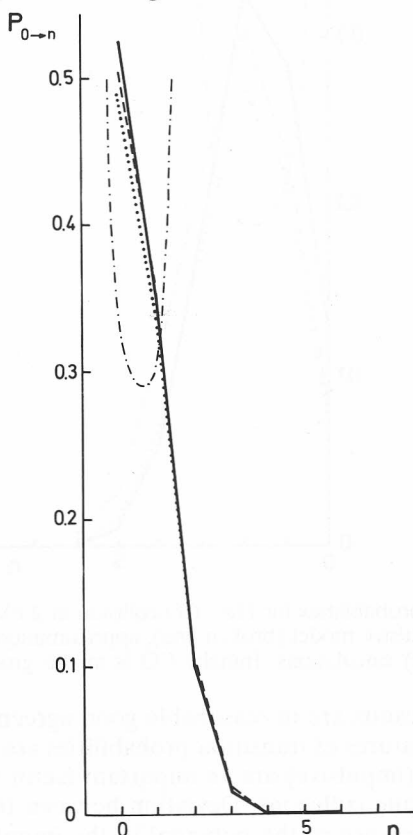


Figure 3. Transition probabilities as in Figure 2. expect the mass of He atom is $m_A=1$ a.u.

We notice that the impulsive model transition probabilities and the exact ones are almost equal. The same is true with the approximate impulsive model results, which is result of the smaller overall energy transfer into the molecule due to the lighter incoming atom.

Energy transfer depends also on the force constant K of the harmonic oscillator. For the case with $m_A=1$ a.u. we have case of relatively loosely bound atoms, more like a Van der Waals dimer than a molecule. Because of smaller K it is expected that there will be more open channels. Figure 4. shows results for this system. All three quantum calculations give nearly the same result, similar to that in Figure 3. There is deviation for the elastic channel, but for the rest of the channels the difference is practically negligible. We have also done calculations for the same system but with $m_A=4$ a.u. The comparison is more or less the same as in Figure 2. and therefore we conclude that for the working of the impulsive model, and especially its approximation, the mass of the incoming atom is more critical than the force constant of the molecule.

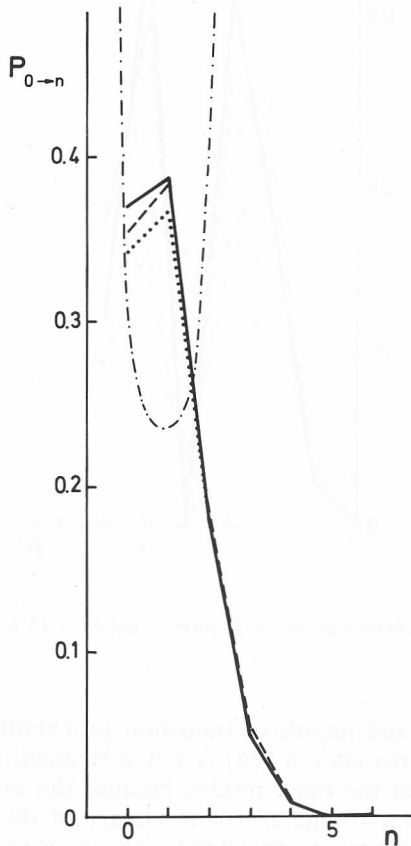


Figure 4. Transition probabilities as in Figure 2. except the mass of He atom is $m_A=1$ a.u. and $K=900 \text{ nm}^{-1}$.

So far we have only analyzed energy transfer if initially the molecule is in its ground state. Next we have assumed that the oscillator is initially in the $n=4$ state. For the mass $m_A=1$ a.u. and $K=1900$ Nm^{-1} the results are shown in Figure 5.

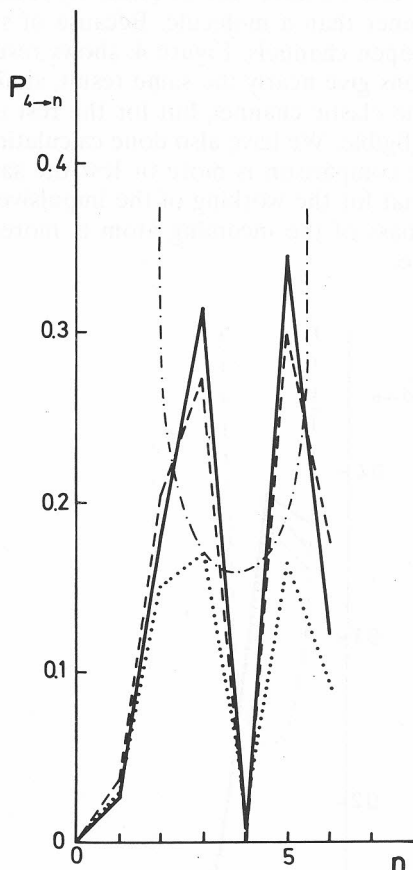


Figure 5. Transition probabilities as in Figure 3. expect CO is initially in $n=4$ state.

The exact quantum and impulsive transition probabilities are in good agreement. However, the approximation (26) is not very good, although it reproduces the qualitative features of the exact results, because the initial state $n=4$ is close to the last open channel $n=6$ and therefore change of the channel wave number k_n with the vibrational energy is nonnegligible. This is just the opposite to the condition under which the formula (26) was derived suggesting that this approximation may not be so good.

Much better agreement between the approximation (26) and the exact results is obtained for $m=1$ a.u. and $K=900 \text{ Nm}^{-1}$, as shown in Figure 6. In this case the last open channel is $n=10$ and the wave numbers around the initial state $n=4$ are less sensitive to the variations in the vibrational energy. Furthermore, energy transfer is not sufficiently effective so that only up to $n=7$ state is classically populated, as it can be seen from Figure 6. Therefore the condition for the approximation (26) is much better satisfied than in the previous case, resulting in a better agreement between these two calculations. Even so the approximation (26) is not perfect, but it reproduces all the qualitative features of the exact transition probabilities.

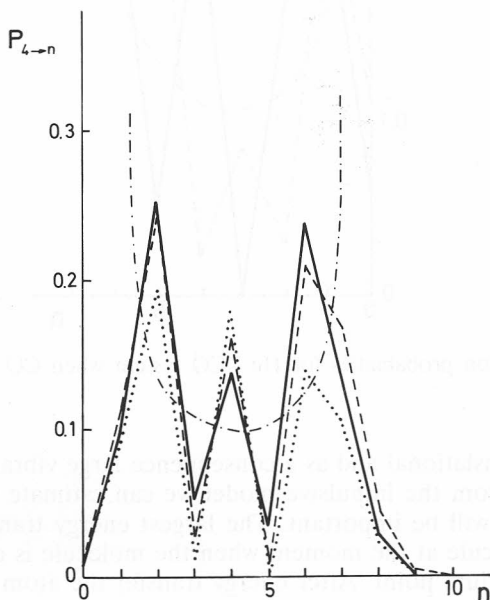


Figure 6. Transition probabilities as in Figure 4. expect CO is initially in $n=4$ state.

So far analysis showed that the impulsive model of collisions gives very good description of energy transfer. In fact one can say that deviation from the true results can be treated as perturbation. However, this is not always the case, as shown in Figure 7., where transition probabilities are calculated for $m_A=4$ a.u. and $K=1900 \text{ Nm}^{-1}$. The impulsive model is totally out of accord with the exact results, and the approximation (26) is not even shown.

The reason for this deviation one finds in the occurrence of multiple collisions. Multiple collisions sets in when all, or most, of the initial translational energy of atom and molecule is transferred into the vibrational energy of molecule. When this happens then after the impact between atom and molecule they do not separate fast enough so that second collision between atom A and atom B may occur, which we call multiple collisions. On the second impact the molecule releases its vibrational

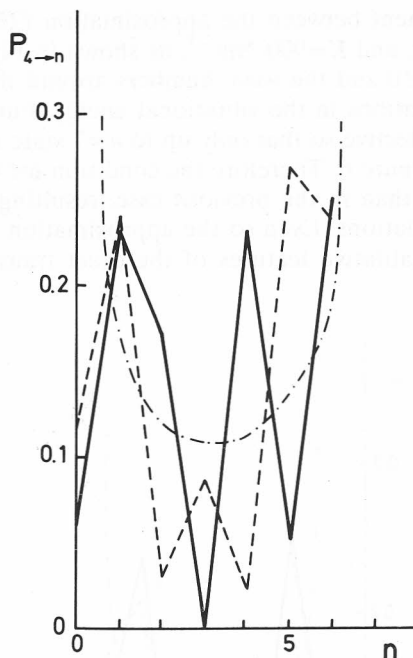


Figure 7. Transition probabilities for He-CO system when CO is initially in $n=4$ state.

energy into the translational and as a consequence large vibrational transitions will be first affected. From the impulsive model we can estimate when it is likely that multiple collisions will be important. The largest energy transfer occurs when the atom hits the molecule at the moment when the molecule is contracting and going through its equilibrium point. After energy transfer the atom must get beyond the amplitude of the oscillator before the molecule makes $3/4$ of its oscillation period. If it does not then the molecule will hit the atom, thus producing multiple collision effect. From this condition we obtain inequality

$$\frac{E_{\text{OSC}}^0/E_{\text{CM}} + 1}{E_{\text{OSC}}^0/E_{\text{CM}} + \Delta E/E_{\text{CM}}} < 1 + \frac{4\mu}{9\pi^2\mu_{\text{BC}}} \quad (40)$$

where E_{OSC}^0 is the initial energy of oscillator and ΔE is given by (37) for the phase $\Phi=0$. If the inequality (40) is satisfied then there will be multiple collisions. In our case this inequality is $1.007 < 1.023$ and indeed multiple collisions are expected. However, since this condition is marginally satisfied, it is doubtful whether the real system will show multiple collisions. If we look in Figure 7. we notice that the classical transition probability is slightly asymmetric with respect to the left and right of its minimum (in the absence of multiple collisions it is strictly symmetric) which indicates multiple collisions, but not very pronounced. On the other hand, in the impulsive model this effect is much more pronounced (which we confirmed but it is not shown) and therefore its affect on the transition probabilities is more dramatic. There have been studies of multiple collisions¹⁹ and the condition for their onset

has been given. However, that condition is much cruder and for our system it gives that it is far from being in the regime of multiple collisions.

Although (19) includes multiple collisions, deviations between our results and those for exact potential are due to different reason. Any small change in potential (we have assumed $U(x)$ in (3) to be zero) is likely to cause large distortions of the transition probabilities since with multiple collisions the exponentially separating trajectories will be very important. In general, therefore, it is expected that the impulsive model will become inadequate for describing collisions with large energy transfer, but on the other hand the question is how accurate the potential should be in order to reproduce proper transition probabilities? Nothing, but the most accurate potential and good comparison with experiment but loses the beauty of simple models.

V. DISCUSSION

The solution (19) for the S -matrix in the impulsive model is exact and (21) is its approximation, which is valid for small energy transfer. These formulae are valid for a general potential (3) and they are not restricted to harmonic oscillator of the diatomic molecule. In the simplest case when atoms are treated as hard spheres and diatomic molecule is harmonic oscillator, the integrals which enter (21) and (26) can be evaluated analytically. In particular, the transition probabilities based on the approximation (21) are given by (26). Since we discussed in Introduction various other approaches to the collinear collision problem, it would be of interest to compare those results with our approximation (26). Basically we distinguish among them three (we do not consider the distorted wave approximation) solutions: a) from the time dependent approach, b) from the momentum representation and c) from the IOS approximation. The first one gives for the transition probability $P_{m \rightarrow n}$

$$P_{m \rightarrow n} = n!m! \epsilon^{m+n} e^{-\epsilon} \left| \sum_{l=0}^{\min(n,m)} \frac{(-1)^l \epsilon^{-l}}{l! (m-l)! (n-l)!} \right|^2 \quad (42)$$

where ϵ is the classical energy transfer into an initially nonvibrating molecule. For the harmonic oscillator ϵ is given by

$$\epsilon = \frac{1}{2\mu_{BC} \omega \hbar} \left| \int_{-\infty}^{\infty} dt' F(t') e^{i\omega t'} \right|^2 \quad (43)$$

where $F(t)$ is an effective force which acts on the molecule. The formula (41) should be compared with (26). It is relatively easy to show that the sum in (41) can be transformed into the Laguerre polynomial L_m^{n-m} , therefore, both formulae are formally equal, except for the normalization k_m/k_n . However, the major difference is in the argument, which in the case of (41) is essentially the final energy of oscillator

while in (26) it is essentially the momentum transfer squared. Our result is much closer to the transition probability obtained from the momentum representation.⁹ The probability is exactly the same as (26), including the form of argument, except that instead of the prefactor k_m/k_n there is $(1+M)^2(k_m+k_n)^2/(4k_mk_n)$, where $M=m_c m_A / [m_B (m_A+m_B+m_C)]$. We have investigated this approximation for the examples which discussed in the previous section. In general, this approximation is not qualitatively better than ours, in fact sometimes it gives better results and sometimes worse. The IOS approximation is the same as (26) except that $k_m=k_n$.

This was a brief account of the results of various approaches to the impulsive model. The question, however, is not how much do they differ one from the other but to what degree the impulsive model describes reality. We have seen that in most cases the model is quite adequate and one would need a small correction to take it more accurate. The exception is when multiple collisions sets in, but then more fundamental questions are raised, as discussed in previous section. One correction to the model is to assume that $U(x)$ in (3) is not zero, but has a form $V_0 \exp(-\alpha x)$, where the parameters α and V_0 have some effective value. In such a case the irregular solutions (22) would generalize to

$$\omega_{\pm} = J_{\pm 2} \frac{k}{i\alpha} \left(2i \frac{\sqrt{z}}{\alpha} \right) \quad (44)$$

where $z=V_0 \exp(-\alpha x)$. With these solution one could evaluate the integrals (14) and obtain correction to the model. Even then, however, the transition probabilities are not expected to be accurately reproducing the exact results, but this solution may be the starting point for the perturbation expansion in the powers of the difference between $U(x)$ and $V(x,y)$. This would appear quite a straightforward procedure but this is not the case. The source of the problems can be traced to the unperturbed solutions, which cannot be easily obtained for the potential with a hard core.

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SAŽETAK

Impulsivni model u kolinearnom sudaru

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Prikazano točno kvantnomehaničko rješenje impulsivnog modela i primijenjeno na kolinearni problem. Vjerojatnosti prijelaza dobro se slažu s onima za realni sistem, osim u slučajevima kada se višestruki sudari ne mogu zanemariti.