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Kenneth Kulander

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WAVEPACKET THEORY OF COLLISIONAL DISSOCIATION IN MOLECULES[†]

Kenneth C. Kulander

University of California, Lawrence Livermore National Laboratory
Theoretical Atomic and Molecular Physics Group, Livermore, CA 94550

Abstract: An explicit integration scheme is used to solve the time dependent Schrodinger equation for wavepackets which model collisions in the collinear $H + H_2$ system. A realistic LEPS-type potential energy surface is used. Collision energies considered are above the dissociation threshold and probabilities for collision induced dissociation are reported. Also quantum mechanical state-to-state transition probabilities are generated. These results are compared to extensive classical trajectory calculations performed on this same system. We study the time evolution of the wavepacket densities to understand the dynamics of the collinear collisional dissociation process.

1. Introduction

Collisional dissociation of molecules plays an important part in the kinetics of high temperature systems such as in gas lasers and flames and in molecular beam and shock tube experiments. Traditional time independent methods of investigating chemically reactive systems fail when the collision energy exceeds the dissociation threshold. Solution of the time dependent Schrodinger equation,[‡]

$$i \frac{\partial}{\partial t} \Psi = H\Psi, \qquad (1)$$

using wavepacket methods, however, does provide a means of obtaining a detailed understanding of the collision-induced dissociation (CID) process. We have utilized this approach to study the collinear $H + H_2$ system for a range of collision energies which includes the dissociative continuum and for three different initial vibrational levels of the diatomic. The main advantage of the wavepacket approach is that the wavefunction remains localized in configuration space whether the products include states with three free particles or not. An additional benefit results from the fact that the wavepacket consists of a linear combination of energy states so that for a particular choice of initial states, it is possible to obtain state-to-state transition probabilities for a range of collision energies from a single wavepacket calculation. The major drawback of time dependent methods is that they require the solution of Eq. (1) for the evolution of the wavefunction over a period corresponding to the entire collision time. In general this is more expensive in computational effort than solving the time independent equations many times for the different energies required. However, for systems in which both reaction (rearrangement) and dissociation are possible the time dependent approach seems to be required. Finally the recent emergence of fast, large computers has made these calculations feasible.

In the next section the model collinear system is briefly described, the equations to be solved are derived and our method of integrating the Schrodinger equation is presented. The following section contains the results of our calculations which include probabilities for reaction and dissociation along with state-to-state vibrational transition probabilities. We also compare our results to quasiclassical probabilities generated from extensive trajectory calculations on this same system. Our concluding remarks regarding future efforts using these methods appear in the final section.

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[‡] Atomic units, $e = m_e = \hbar = 1$, are used unless otherwise noted.

2. Calculations

We have chosen the collinear, reactive H + H_2 system as a model for study of CID. This system has received the most attention of theoretical dynamicists as the test case for all new collision theories. Assuming the validity of the Born Oppenheimer approximation we calculate the wavefunctions only for the nuclear motion on a single adiabatic potential energy surface. The three nuclei, which we label A for the incident atom and B and C for the nuclei of the diatomic, are constrained to lie on a line which we identify as the x-axis. The positions of the three nuclei are given by x_A, x_B and x_C and their masses by m_A, m_B and m_C. Defining mass weighted internal coordinates

$$q_1 = x_A - (m_B x_B + m_C x_C)/(m_B + m_C) \tag{2a}$$

and

$$q_2 = [m_B m_C M/(m_B + m_C)^2 m_A]^{1/2} (x_B - x_C) \tag{2b}$$

and removing the center of mass motion, we can write the Hamiltonian in the convenient form

$$H = -\frac{1}{2\mu}\left[\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2}\right] + V(q_1, q_2) \tag{3}$$

where $\mu = m_A(m_B + m_C)/M$ and M is the total mass. The potential energy surface, V, given by a LEPS function with parameters chosen by Kellerhalls et. al[1]) is shown in fig. 1. Asymptotically the surface becomes a Morse diatomic interaction with a dissociation energy of 4.7466 eV. In the interaction region there is a saddle point whose height is approximately 0.4 eV. The initial arrangement is shown schematically in fig. 1 with an arrow indicating the collisional motion into the interaction region. The repulsive walls of the surface have been truncated at about 10 eV above the asymptotic limit.

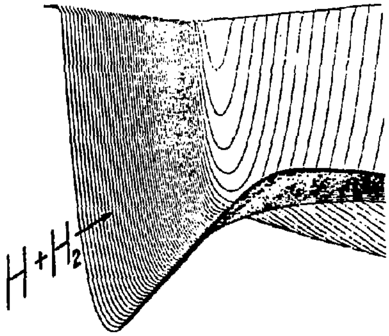


Fig. 1. Potential energy surface for collinear H + H_2

We solve eq. (1) by setting up an initial wavepacket which corresponds to a single vibrational state of the diatomic and a range of collision energies. The wavepacket is a product of a Morse oscillator in the coordinate q_2 and a Gaussian distribution centered in the asymptotic region in the scattering coordinate q_1. The wavepacket is given an initial relative momentum k_0 in the direction of the interaction region. The operation of the Hamiltonian on the wavefunction is evaluated using finite difference methods. The wavepacket is defined on a two dimensional grid with 100-200 points in each direction. The second derivatives are generated using a 5-point formula. Thus, knowing the right-hand-side of eq. (1), we have a (complex) first-order differential equation (in time) to solve. A fifth-order Adams-Bashforth predictor corrector (PC) is used to perform the time integration. Further details of this method can be found in ref. 2. A similar method was originally developed by McCullough and Wyatt[3]) to study this system but at much lower collision energies. The collision times are found to be 400-500 atomic time units (2.42×10^{-17} sec) and for the collision energies considered approximately 3000 integration steps were necessary.

Since the wavepacket is a linear combination of different momentum states, it tends to spread during evolution through a collision. It is necessary to have a sufficiently large grid that the wavepacket does not reach the boundary. After the wavepacket has returned to the asymptotic region, where the motion is separable, we can project onto final states to obtain probabilities for generating particular products. The wavefunction in the initial arrangement channel, for example becomes

$$\Psi(q_1\ q_2\ t) \rightarrow (2\pi)^{-1/2} \sum_n \int dk\ a_n(k)\ e^{ikq_1}\ \chi_n(q_2)\ e^{-iE_{nk}t} \tag{4}$$

where χ_n is a bound or scattering Morse wavefunction and $E_{nk} = \epsilon_n + k^2/2\mu$. The square of the expansion coefficient $a_n(k)$ gives the probability for that particular state in the final wavefunction. In the initial wavepacket, each total energy corresponds to a unique initial state. This is true only because the chosen molecular vibrational state is an eigenfunction. Knowing the probability of an energy component in the initial wavepacket and the probability of a final state of the same energy is sufficient to define the state-to-state transition probability. An expression similar to that in eq. (4) can be used in the rearrangement channel to obtain state-to-state reactive probabilities. If we project our final wavefunction onto all possible bound final states (there is only a finite number for a fixed total energy) we can obtain the dissociation probability from the formula

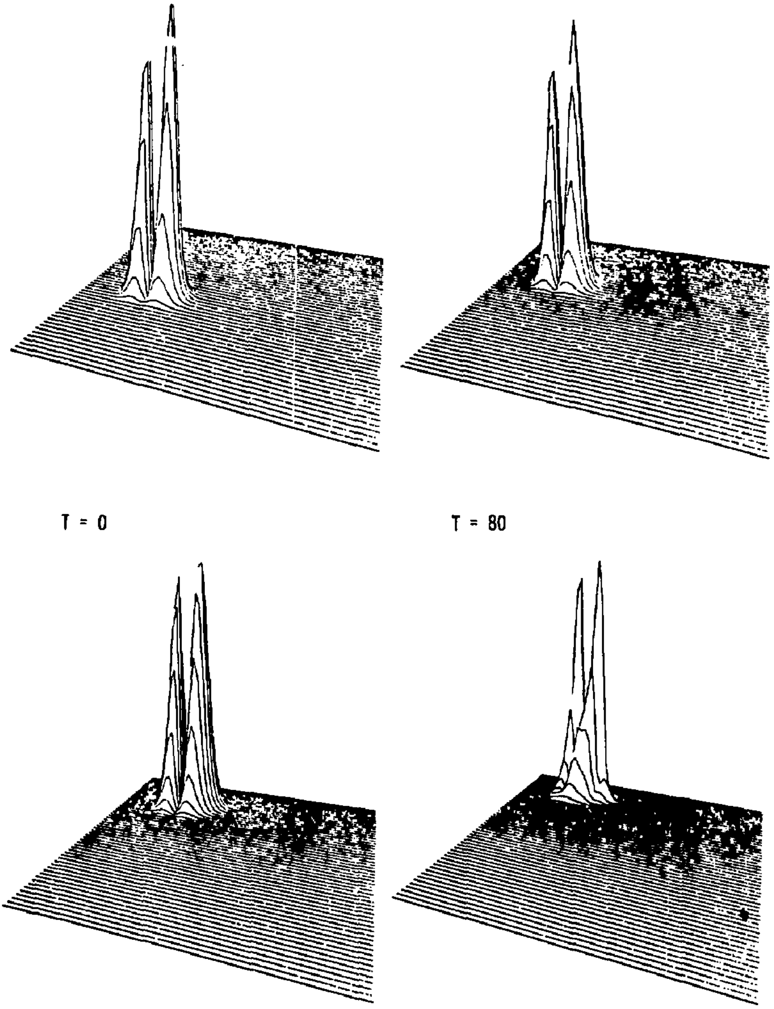
$$P^D(E) \;=\; 1 - \sum_n P_n^V(E) - \sum_n P_n^R(E) \tag{5}$$

where P_n^V and P_n^R are the probabilities of populating vibrational state n in the non-reactive and reactive arrangements respectively. In principle it would also be possible to calculate probabilities for specific dissociating states although we have not done so here. Therefore it is possible from a single calculation to obtain transition probabilities to all energetically accessible final states from a particular initial vibrational level of the diatomic for a range of collision energies.

A second sort of information is available from time dependent calculations. We can follow the evolution of the wavepacket through the collision and gain some insight into the dynamics of the CID process. We can see what regions of configuration space are explored by the wavepacket. Also it is possible to investigate systematically which features of the potential energy surface can cause the wavepacket to fragment or to spread rapidly or to behave unexpectedly. In the next section we present results of both kinds, wavepacket densities and transition probabilities for the H + H_2 system.

3. Results

We have studied the collision between an H atom and an H_2 molecule for a range of collision energies (4-12 eV) and for three different initial vibrational levels of the molecule v = 0, 1, 4. The three nuclei are constrained to lie on a line. In all cases we found that the wavepacket after collision returned to the region of configuration space corresponding to the initial arrangement. In figs. 2 we show snapshots of the wavepacket densities at different times during the evolution for a v = 1, $k_0 = 25a_0^{-1}$ case. The two peaks in the initial wavepacket result from the node in the vibrational wavefunction. In the final wavepacket the



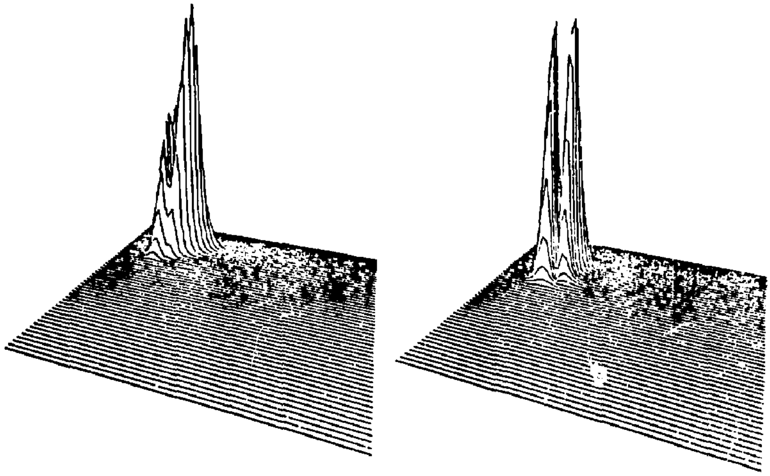
T = 0

T = 80

T = 160

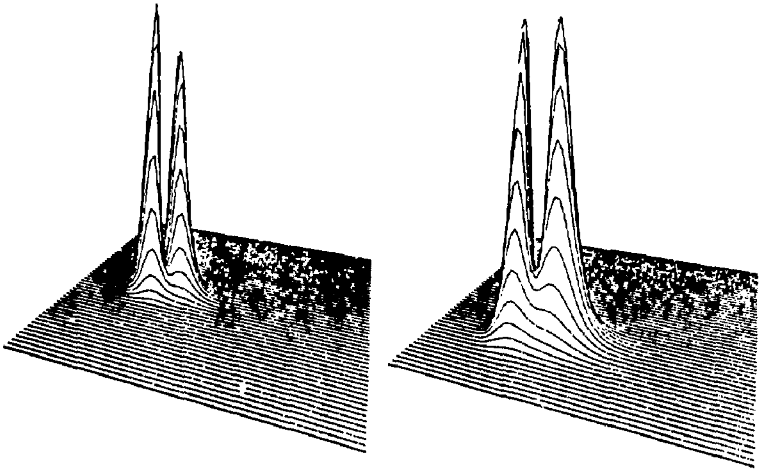
T = 240

Fig. 2. Time dependent densities for the $n_1 = 1$, $f_{k_0} = 25\ a_0^{-1}$ wavepacket.



T = 280

T = 320



T = 400

T = 480

Fig. 2. (continued).

two peaks are still evident indicating that there is a large elastic scattering component. An examination of the evolution shows that the wavepacket appears to reflect off the repulsive wall at the end of the entrance channel. This behavior is contrary to what one would expect from a classical, billiard ball picture in which the rearrangement process is most likely. It should be noted that only for this energy range are the non-reactive processes dominant. At lower energies, different parts of the surface determine the dynamics and the reactive probability becomes almost unity. Also for different mass combinations the skew angle of the surface will be different and the product distributions could be changed dramatically.

This sort of qualitative information can produce an understanding of the dynamics of particular CID processes, but as indicated above we obtain detailed quantitative results also. By projecting the final wavepacket onto separable asymptotic eigenfunctions we obtain state-to-state transition probabilities. The detailed results from these calculations will be reported elsewhere4). We present some of these results here to illustrate both the behavior of the results and the sort of information which is available from these calculations.

Since this system is only a model our results cannot be compared directly to experimental measurement. The collision energy is high enough, however, that classical mechanics can be expected to be approximately valid. In order to test our results and to assess the extent to which quantal effects are important for this system, extensive classical trajectory calculations have been performed4) and those results will be presented along with the quantum results.

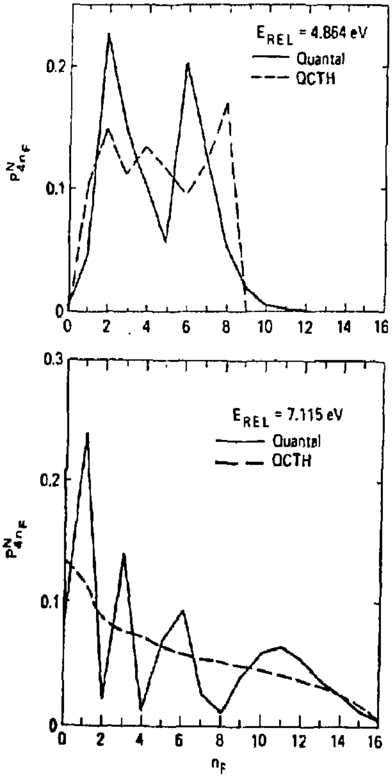


Fig. 3. Normalized final vibrational state distributions for $n_I = 4$ for two different collision energies, E_{rel}.

Figs. 3 show vibrational state distributions, $P^{N}_{n_I n_F}$, for the non-reactive arrangement channel for two different collision energies and the initial vibrational quantum number, n_I, being four. The superscript N indicates these probabilities are normalized such that $\sum_{n} P^{N}_{n'n} = 1$. The diatomic potential in the asymptotic region supports 17 bound states ($0 \leq n \leq 16$). The final vibrational state of a classical trajectory is assigned using the standard quasi-classical trajectory histogram method (QCTH)5). Two conclusions can be drawn from figs. 3. First, the quantum distributions can have a considerable amount of structure and second, the classical results reproduce the quantum behavior only in an average sense, not in detail. The dependence of these normalized probabilities on collision energy (E_{rel}) is shown in fig. 4. Again the classical results agree on the average with the quantum which show an interesting oscillatory structure. We found less structure in the cases when the initial vibrational level was less excited. An assessment of the accuracy of the calculations can be gained by determining whether the probabilities satisfy detailed balance. Probabilities $P_{nn'}$ are compared to $P_{n'n}$ for n,n' = 0,1, and 4 from the quantum calculation in fig. 5a and from the classical results in fig. 5b. We find excellent agreement quantum mechanically but not classically. It is well known that the QCTH method is not the best way to extract "quantum" results from classical calculations. Better methods6) make use of the lower moments of the final state distributions and information theory to quantize the trajectory results. We have tested whether the quantum moments can be generated classically. In fig. 6 the second (root mean squared) moments are compared for the different initial states. We found in general that the lower classical and quantum moments agree quite well but that the higher moments can disagree significantly.

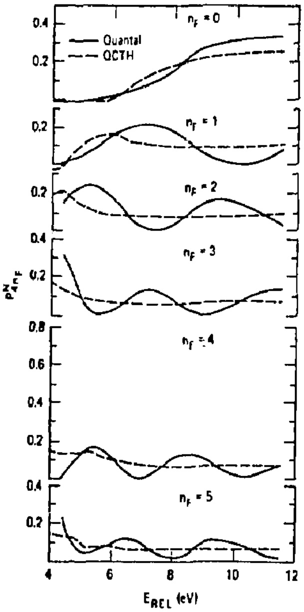


Fig. 4. Normalized state-to-state transition probabilities for select final states as a function of collision energy, E_{rel}.

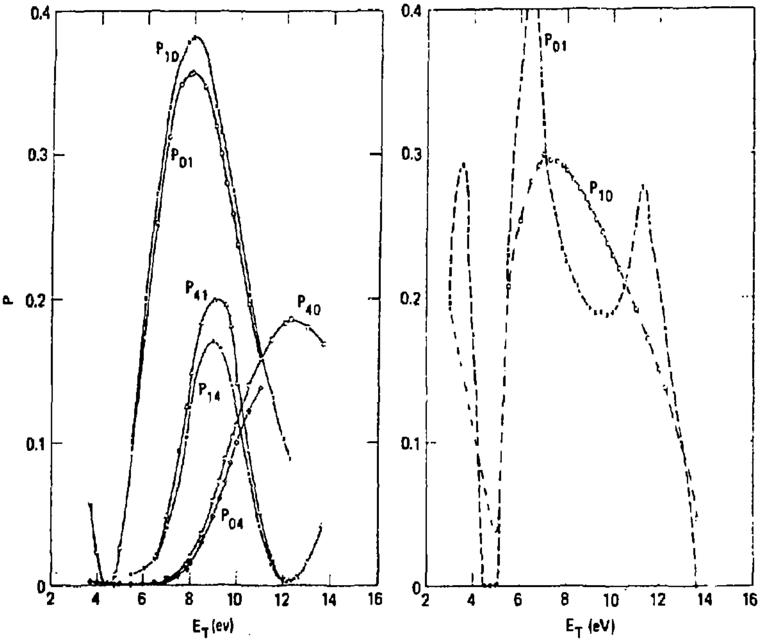


Fig. 5. Detailed balance. Probabilities for forward and reverse transitions as a function of total energy, E_T, from (a) quantum and (b) classical calculations.

Finally we have obtained reaction and dissociation probabilities for the states studied. We found that within the accuracy of the calculations, the reaction probabilities in this energy range are zero. The classical calculations$^{4)}$ also found anti-thresholds for collision energies between 3 or 4 eV and zero probabilities above. The dissociation probabilities are plotted in fig. 7.

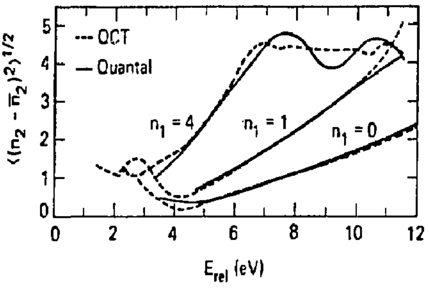


Fig. 6. Second (root mean squared) moments of the quantum and classical final vibrational state distributions as a function of collision energy, E_{rel}.

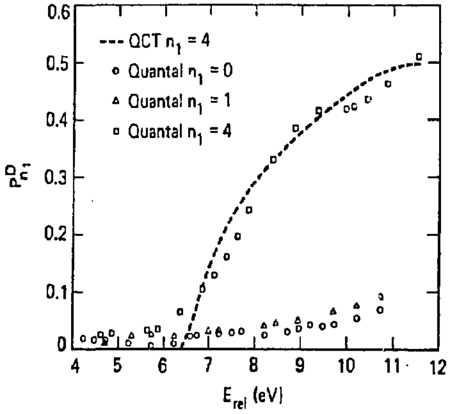


Fig. 7. Quantal and classical dissociation probabilities as a function of collision energy, E_{rel}.

We observe that dissociation thresholds in the collinear system are displaced from the energy thresholds which are 4.48, 3.96 and 2.61 eV for n_1 = 0, 1 and 4 respectively. Only in the case n_1 = 4 is there an appreciable probability of dissociation in the energy range considered. This is due to the more diffuse nature of the initial wavepacket in this state so that much more of the potential energy surface including parts of the repulsive wall which do not reflect back into the entrance channel bound states is involved in the collision. For n_1 = 0 and 1 the classical calculations show no dissociation while the quantum results rise to around ten percent.

These calculations provide insight into the process of molecular dissociation in the collinear world. In three dimensions the stripping mechanism which cannot occur in a collinear arrangement has been found to be very important. Future calculations which will involve relaxation of the geometric constraints will produce a more complete understanding of the dissociation process.

4. Conclusions

We have investigated the collinear H + H_2 system for collision energies above the dissociation threshold by integrating the time dependent Schrodinger equation. Reaction, dissociation and vibrational transition probabilities have been obtained and compared to classical trajectory calculations on the same system. We found that in the energy regime where classical mechanics can be expected to be valid the classical and quantum results agreed on the average but not in detail. The time evolution of the wavepacket densities provided insight into the dynamics of the collisional dissociation process. The wavepacket was reflected back into the initial arrangement channel and no reaction or rearrangement was found to occur.

We are presently adapting these methods to treat more complicated processes. Wavepacket methods are best suited for higher energy collision processes in which the normal spreading during the propagation is minimal. At higher energies in real systems additional electronic states will be accessible. Therefore we are generalizing these methods to study scattering on two interacting surfaces whether they are coupled by the nuclear motion (Born Oppenheimer coupling) or by a strong radiation field in case of laser induced chemical reactions. Secondly we have been using wavepacket methods to investigate the photodissociation of triatomic molecules. In this process a photon is absorbed by the molecule which changes the electronic state from an attractive, bound surface to one which is repulsive. It is necessary to determine the evolution of a wavepacket on the dissociative surface in order to calculate the cross section for the process. It has been shown7) that the total cross section is determined by the short time behavior of the wavepacket but that by following the propagation into the asymptotic region, it is possible to completely characterize the product state distributions8). From a single wavepacket calculation the total and partial cross sections can be calculated for all photon energies. Systems which dissociate to three-body final states have been studied using wavepacket methods8). It would be difficult if not impossible to treat these processes using time independent methods.

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