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Generalized Impact-Parameter Method for Low-Energy Molecular Collisions

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A generalized impact-parameter method (not based upon perturbation theory) which is capable of describing the evolution of a collision system throughout the entire interaction region is developed. The method is then applied to the collision of a proton and a hydrogen atom at low (chemical) energies. The results obtained suggest that static calculations such as those using molecular potential-energy surfaces do not represent a very real picture of a dynamic process like a collision. Furthermore, the model does not assume linear trajectories for the atoms. This is shown from the calculations to be of importance in such low-energy collisions, the trajectories being far from linear. The model is capable of generalization to collisions in which more than two atoms are involved, such as the three-body reaction $A + BC \rightarrow AB + C$.

I. INTRODUCTION

A considerable amount of activity is currently evident in the theory of reactive molecular collisions.[1-3] Although interest in this field is ultimately aimed at the understanding of the physical "mechanism" of chemical reactions, much current work is more closely directed towards the interpretation of the results of molecular-beam studies.[4-7] Typical calculations of this sort include the following two main steps: (1) the assumption of some potential-energy surface describing the interaction between the colliding species; (2) some kind of trajectory calculation which is carried out to evaluate the angular distribution of products, differential cross sections, etc. Let us discuss what is involved in these two steps of calculation, beginning with the second.

In the first place, the whole idea of a trajectory implies a semiclassical model in which the atoms move along "classical" trajectories which are determined by some potential [step (1)]. Presuming that such a potential can be found, then step (2) requires the solution of the classical many-body problem, which is quite feasible by present-day computer techniques. Step (2), therefore, can be regarded as being possible, even if it does require substantial amounts of computer time to evaluate the large number of trajectories at different impact parameters necessary to calculate angular distributions, etc. Step (1), on the other hand, has not been properly treated. Common approaches to potentials are as follows: (a) If the system is sufficiently simple (for example, atom-atom colli-

sions) the potential surface may be taken, for thermal collisions, to be the static (velocity independent) ground-state potential-energy surface or some analytic approximation to it; (b) for more complicated cases, some model potential[8-12] (or even set of model potentials[5] may be assumed, the general characteristics of the process being described by this potential. At the present state of development of such calculations, it is perhaps unfair to criticize, but it would appear to us that one can achieve no more understanding of the details of a given process than one puts in by suitably "doctoring" the model potential which one employs. Even if one accepts the idea of a model potential, it must be admitted that the nonuniqueness of the results obtained by suitably choosing a variety of parameters is scarcely satisfactory. A further criticism, and undoubtedly a much more serious one, of this whole method of calculation, is that the validity of assuming a static potential-energy surface in the first place as an "interaction potential" is somewhat questionable. Certain of the results obtained in this paper cast some light on this problem.

The interest of the present authors in reactive molecular collisions derives from previous work in the theory of molecular processes in general[13,14] and a concurrent interest in techniques for describing the evolution of a quantum system in time.[15] Our interest in semiclassical calculations therefore relates to the model one might use to calculate a given trajectory, rather than the calculation of many trajectories to evaluate quantities of interest to molecular-beam specialists. Apart from the

previous shortcomings of existing techniques, one might add that there appears to be little in the way of a theory in existence which is capable of generalization to molecules possessing more than about two atoms.

In this paper we shall describe a semiclassical model for treating molecular collisions which we believe overcomes many of the previously mentioned criticisms and which is capable, at least in principle, of generalization. The characteristics of this model are as follows: (a) The nuclei are considered to be classical particles and the electrons are treated quantum mechanically. (b) Within this model the equations of evolution of the electrons and the nuclei are developed and solved without using crippling approximations such as perturbation theory. The major approximation is that common to all molecular quantum theory, namely, that the electrons are described by some truncated basis set. This model may be regarded as a highly generalized impact-parameter method which is applicable to systems of more than two particles, is not limited by the assumption of linear trajectories, and does not rest upon perturbation theory. The salient advantages of the model are as follows: (a) The model is entirely dynamic. (b) Interaction forces are treated explicitly so that no potential-energy surface need be assumed. As a result of the calculation it is possible to identify a dynamic potential-energy surface, the properties of which will be discussed. (c) The state of the system is described all the way through the interaction and not merely asymptotically. Thus a description within the interaction region is obtained.

The example which we have chosen to illustrate the techniques developed in this paper, namely, charge exchange in the proton-hydrogen atom system, deserves some mention at this point since a great amount of work has been carried out upon this system.

The closest approach to the method which we have developed in this paper is the type of close-coupled calculation originally performed for p-H by Gallaher and Wilets[16] and subsequently improved upon, notably by Cheshire and co-workers.[17] Alternative approaches have been provided by a variety of researchers, notably Bates and Williams[18] and Thorson.[19] Such approaches in general involve improvements upon the adiabatic approximation.

The majority of papers upon the p-H system are aimed at an explanation of the experimental results of Everhardt and Lockwood[20]; that is, they are aimed at scattering at energies greater than 1 keV. On the other hand, the present paper is concerned with collisions at energies less than about 10 eV. At such low energies the electronic translational energy is negligible in comparison to electronic internal energy, and for this reason low- and high-

energy calculations are not really comparable. Treatment of the p-H system at high energies (>1 keV) has been successfully carried out and will be presented elsewhere.

Before proceeding to the development of our equations we shall briefly discuss the basic ideas involved in the adiabatic approximation which lead to the static potential-energy surface.

II. ADIABATIC APPROXIMATION AND POTENTIAL-ENERGY SYSTEM

Consider the process[21,22]

$$A + B^+ \to A^+ + B$$
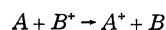
for which the coordinate system is shown in Fig. 1. Suppose that the relative velocity $\vec{v}$ between A and B^+ is much less than the orbital velocities of the electrons but that the relative kinetic energy is much greater than the energy of excitation of either of the atoms. Then energy transfers to excitation are considered to be small compared with the relative kinetic energy and their effect on the classical trajectory is neglected. Since $\vec{v}$ is small relative to the orbital velocities of the electrons, the starting point of the adiabatic approximation is an expansion of the wave function for the collision in terms of molecular wave functions.

Excluding center-of-mass motion, the time-independent Schrödinger equation for the collision is

$$\left(-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 - \frac{\hbar^2}{2M} \nabla_R^2 + V(\vec{r}_i, R) - E \right) \Psi = 0 , \quad (2.1)$$

where M is the reduced mass of the nuclei, and the total potential energy $V(\vec{r}_i, R)$ can be written as

$$V(\vec{r}_i, R) = V_e(\vec{r}_i, R) + Z_A Z_B e^2 / R . \quad (2.2)$$

Now if the electrons are regarded as moving in the combined field of the nuclei of A and B^+ (both being spatially fixed), the equation

$$H_e(\vec{r}_i, R)\phi_j(\vec{r}_i, R) = \left(-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V_e(\vec{r}_i, R) \right) \phi_j(\vec{r}_i, R)$$

$$= E_j(R)\phi_j(\vec{r}_i, R) \quad (2.3)$$

generates the complete set of molecular electronic eigenfunctions and corresponding eigenvalues for this combined potential field felt by the electrons. The wave function Ψ describing the relative motion of the nuclei and the electronic motion is then expanded as
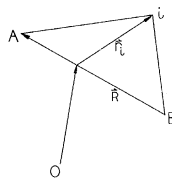

FIG. 1. Coordinate system appropriate to discussion of adiabatic approximation.

$$\Psi = \sum_j F_j(\vec{R})\phi_j(\vec{r}_i, R) \qquad (2.4)$$

and substitution of this expansion into (2.1) followed by multiplication from the left by ϕ_j^* and integration over the electron coordinates yields the set of equations

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2 + \frac{Z_A Z_B e^2}{R} + E_j(R) - E\right)F_j(\vec{R})$$

$$= \frac{\hbar^2}{2M}\sum_k \left(2[\nabla_R F_k(\vec{R})] \cdot \int d\vec{r}_i \phi_j^* \nabla_R \phi_k\right)$$

$$+ F_k(\vec{R})\int d\vec{r}_i \phi_j^* \nabla_R^2 \phi_k\right). \qquad (2.5)$$

Now all the coupling terms on the right-hand side are neglected, the argument being that at low relative velocities most of the scattering takes place at internuclear distances which are large compared with the extent of the atomic electrons. This results in the wave equation in the adiabatic approximation, which we may write as

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2 + \frac{Z_A Z_B e^2}{R} + E_j(R)\right.$$

$$\left. - E_j(\infty) - [E - E_j(\infty)]\right)F_j(\vec{R}) = 0. \qquad (2.6)$$

The effective central field given by

$$V_j(R) = Z_A Z_B e^2/R + E_j(R) - E_j(\infty) \qquad (2.7)$$

is known as the potential-energy surface of the diatomic molecule AB^+.

Equation (2.6) is just the eigenvalue equation for the $F_j(\vec{R})$, and the neglect of the coupling terms on the right-hand side of Eq. (2.5) implies that the functions $\phi_j(\vec{r}_i, R)$ used as an expansion set for the collision are velocity independent. Obviously any calculation based on a potential-energy surface of this type is a completely static representation of a dynamic process.

The calculations described in this paper do not depend upon a static potential-energy surface, nor do they result from the assumption of linear trajectories. The results indicate that these are significant improvements in such low-energy calculations.

III. DEVELOPMENT OF THE EQUATIONS

In our approach to the problem we do not assume a static potential-energy surface. We consider the atoms to follow the classical trajectory determined by the interatomic potential which is a dynamical variable in that it depends on the internal states of the atoms, these states having an implicit dependence on the velocities of the classical nuclei through their explicit dependence on the time-dependent interatomic separation $R(t)$. The interac-

tion between the atoms in this trajectory provides a time-dependent perturbation which can lead to excitation and exchange processes. Thus all changes within the system are coupled in that a change in the internal states of the atoms results in a corresponding change in the interatomic potential and the trajectory.

In this first application of our method to low-energy atomic collisions we have chosen the simple system consisting of a proton scattering from hydrogen atom.

A. Quantum-Mechanical Equations

To develop the quantum-mechanical equations we choose a molecular coordinate system fixed on the nuclei. The problem reduces to two dimensions because of the cylindrical symmetry about the internuclear line, and to one dimension for the zero-impact-parameter collision. The coordinate system used is shown in Fig. 2. The derivation is carried out in atomic units, in which the values of the electronic charge, the electron mass, and $\hbar$ are unity.

We wish to solve the time-dependent Schrödinger equation

$$i\partial_t \left| \Psi(R, t) \right\rangle = H \left| \Psi(R, t) \right\rangle \qquad (3.1)$$

for the collision. For the proton-hydrogen atom system the Hamiltonian H may be resolved as $H = H_0 + V$ (where H_0 is the Hamiltonian for the hydrogen atom) in two physically meaningful ways, corresponding to the two channels available to the reaction. In the initial or nonrearrangement channel (which we shall call channel α), the electron remains bound to proton A and we have

$$H = H_0^\alpha + V^\alpha , \qquad (3.2a)$$

$$H_0^\alpha = -\tfrac{1}{2}\nabla^2 - 1/r_a , \qquad (3.2b)$$

$$V^\alpha = 1/R - 1/r_b , \qquad (3.2c)$$

while in the rearrangement channel (channel β)

$$H = H_0^\beta + V^\beta , \qquad (3.3a)$$

$$H_0^\beta = -\tfrac{1}{2}\nabla^2 - 1/r_b , \qquad (3.3b)$$

$$V^\beta = 1/R - 1/r_a . \qquad (3.3c)$$

For either channel the set of eigenfunctions for the asymptotic channel Hamiltonian is the set of eigenfunctions for the hydrogen atom, and we use this set as a basis on which to project the collision.
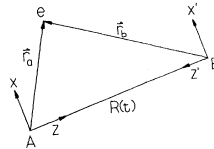
FIG. 2. Molecular coordinate system used in derivation of quantum-mechanical equations.

The wave function for the collision is expanded as

$$|\Psi(R,t)\rangle = \overline{N}(R,t)\sum_c\sum_j a_j^c(t)|\phi_j^c(t)\rangle , \qquad (3.4)$$

where the summation over j is over states and that over c is over the channels:

$$|\phi_j^c(t)\rangle = |\Phi_j^c\rangle e^{-iE_j^c t} , \qquad (3.5)$$

$$H_0^{\alpha,\beta}|\Phi_j^{\alpha,\beta}\rangle = E_j^{\alpha,\beta}|\Phi_j^{\alpha,\beta}\rangle . \qquad (3.6)$$

From the normalization requirement, we have

$$\langle\Psi(R,t)|\Psi(R,t)\rangle = 1 = \overline{N}^2\sum_{c',c}\sum_{i,j} a_i^{c'*}(t)$$

$$\times\langle\phi_i^{c'}(t)|\phi_j^c(t)\rangle a_j^c(t) \qquad (3.7)$$

and denoting $\langle\phi_i^{c'}(t)|\phi_j^c(t)\rangle$ by $N_{ij}^{c'c}(R,t)$ this becomes

$$1 = \overline{N}^2\sum_{c',c}\sum_{i,j} a_i^{c'*}(t)N_{ij}^{c'c}(R,t)a_j^c(t) \qquad (3.8)$$

or, in matrix terms,

$$1 = \overline{N}^2\underline{a}^*(t)\underline{N}(R,t)\underline{a}(t) . \qquad (3.9)$$

Thus, we have

$$\overline{N} = [\underline{a}^*(t)\underline{N}(R,t)\underline{a}(t)]^{-1/2} = \overline{N}(R,t) . \qquad (3.10)$$

To keep the notation as simple as possible, we shall incorporate the normalization $\overline{N}(R,t)$ into the coefficients $a_j^c(t)$, and write

$$|\Psi(R,t)\rangle = \sum_c\sum_j \overline{N}(R,t)a_j^c(t)|\phi_j^c(t)\rangle$$

$$= \sum_c\sum_j b_j^c(R,t)|\phi_j^c(t)\rangle . \qquad (3.11)$$

The normalization requirement now becomes

$$\underline{b}^*(R,t)\underline{N}(R,t)\underline{b}(R,t) = 1 . \qquad (3.12)$$

We now proceed to the development of the quantum mechanical equations. Substitution of the expansion (3.11) into the time-dependent Schrödinger equation yields

$$i\partial_t\sum_c\sum_j b_j^c(R,t)|\phi_j^c(t)\rangle = H\sum_c\sum_j b_j^c(R,t)|\phi_j^c(t)\rangle , \qquad (3.13a)$$

$$i\sum_c\sum_j[\partial_t b_j^c(R,t)]|\phi_j^c(t)\rangle + i\sum_c\sum_j b_j^c(R,t)\partial_t|\phi_j^c(t)\rangle$$

$$= \sum_c\sum_j b_j^c(R,t)H|\phi_j^c(t)\rangle , \qquad (3.13b)$$

$$i\sum_c\sum_j[\partial_t b_j^c(R,t)]|\phi_j^c(t)\rangle$$

$$= \sum_c\sum_j b_j^c(R,t)(H - i\partial_t)|\phi_j^c(t)\rangle$$

$$= \sum_c\sum_j b_j^c(R,t)(H - E_j^c)|\phi_j^c(t)\rangle . \qquad (3.13c)$$

Multiplying across from the left by the bra $\langle\phi_i^{c'}(t)|$, we obtain

$$i\sum_c\sum_j\langle\phi_i^{c'}(t)|\phi_j^c(t)\rangle[\partial_t b_j^c(R,t)]$$

$$= \sum_c\sum_j\langle\phi_i^{c'}(t)|H - E_j^c|\phi_j^c(t)\rangle b_j^c(R,t) . \qquad (3.14)$$

Defining the matrix $\underline{H}(R,t)$ by

$$H_{ij}^{c'c}(R,t) = \langle\phi_i^{c'}(t)|H|\phi_j^c(t)\rangle , \qquad (3.15)$$

the set of coupled equations (3.14) becomes

$$i\underline{N}(R,t)[\partial_t\underline{b}(R,t)] = [\underline{H}(R,t) - \underline{N}(R,t)\underline{E}]\underline{b}(R,t) \qquad (3.16)$$

or

$$\partial_t\underline{b}(R,t) = -i\underline{N}^{-1}(R,t)[\underline{H}(R,t) - \underline{N}(R,t)\underline{E}]\underline{b}(R,t) . \qquad (3.17)$$

The matrix $\underline{E}$ is diagonal, with its elements being the eigenvalues of the asymptotic channel Hamiltonian.

Recalling the two possible resolutions of H, we can write

$$\underline{H}(R,t) = \underline{N}(R,t)\underline{E} + \underline{V}(R,t) , \qquad (3.18)$$

where

$$\underline{V} = \begin{bmatrix} \underline{V}^{\alpha\alpha} & \underline{V}^{\alpha\beta} \\ \underline{V}^{\beta\alpha} & \underline{V}^{\beta\beta} \end{bmatrix} .$$

The general elements of these components of $\underline{V}$ are given below:

$$V_{ij}^{\alpha\alpha}(R,t) = \langle\phi_i^\alpha(t)|V^\alpha|\phi_j^\alpha(t)\rangle , \qquad (3.19a)$$

$$V_{ij}^{\beta\beta}(R,t) = \langle\phi_i^\beta(t)|V^\beta|\phi_j^\beta(t)\rangle , \qquad (3.19b)$$

$$V_{ij}^{\alpha\beta}(R,t) = \langle\phi_i^\alpha(t)|V^\beta|\phi_j^\beta(t)\rangle , \qquad (3.19c)$$

$$V_{ij}^{\beta\alpha}(R,t) = \langle\phi_i^\beta(t)|V^\alpha|\phi_j^\alpha(t)\rangle . \qquad (3.19d)$$

Now using (3.18), Eq. (3.17) becomes

$$\partial_t\underline{b}(R,t) = -i\underline{N}^{-1}(R,t)[\underline{N}(R,t)\underline{E} + \underline{V}(R,t)$$

$$-\underline{N}(R,t)\underline{E}]\underline{b}(R,t)$$

$$= -i\underline{N}^{-1}(R,t)\underline{V}(R,t)\underline{b}(R,t) . \qquad (3.20)$$

The total time derivative of $\underline{b}(R,t)$ is easily obtained as follows:

$$\frac{d\underline{b}}{dt} = \frac{\partial\underline{b}}{\partial t} + \frac{\partial\underline{b}}{\partial R}\frac{dR}{\partial t} , \qquad (3.21)$$

$$\frac{\partial\underline{b}}{\partial R} = \partial_R[\overline{N}(R,t)\underline{a}(t)] = [\partial_R\overline{N}(R,t)]\underline{a}(t)$$

$$= \{\partial_R[\underline{a}^*(t)\underline{N}(R,t)\underline{a}(t)]^{-1/2}\}\underline{a}(t)$$

$$= -\tfrac{1}{2}[\underline{a}^*\underline{N}\,\underline{a}]^{-3/2}[\underline{a}^*(\partial_R\underline{N})\underline{a}]\underline{a}(t)$$

$$= -\tfrac{1}{2}[\underline{b}^*(\partial_R\underline{N})\underline{b}]\underline{b} . \qquad (3.22)$$

$\partial_R\underline{N}$ can be obtained analytically from the matrix

elements of $\underline{N}$, and dR/dt is simply related to the velocities of the classical particles (the nuclei).

B. Classical Equations of Motion

We derive the classical equations of motion for the nuclei in the lab frame in which their coordinates are (x_1, y_1, z_1) and (x_2, y_2, z_2).

To obtain the classical equations we use Hamilton's canonical equations,[23]

$$\dot{q}_k = \frac{\partial \mathcal{H}}{\partial p_k} , \qquad (3.23a)$$

$$\dot{p}_k = \frac{-\partial \mathcal{H}}{\partial q_k} , \qquad (3.23b)$$

where p_k and q_k are the generalized momentum and coordinate for the kth particle, and $\mathcal{H}$ is the total Hamiltonian function for the system. $\mathcal{H}$ is defined as

$$\mathcal{H} = \sum_{j=1} \frac{p_j^2}{2m_j} + \overline{E}(R, t) . \qquad (3.24)$$

$\overline{E}(R, t)$ is the mean quantum-mechanical energy, given by

$$\overline{E}(R, t) = \langle \Psi(R, t) | H | \Psi(R, t) \rangle$$
$$= \underline{b}^*(R, t) \underline{H}(R, t) \underline{b}(R, t) , \qquad (3.25)$$

and we assume that its fluctuations are small. Thus Hamilton's equations become

$$\dot{q}_j = p_j/m_j , \qquad (3.26a)$$

$$\dot{p}_j = - \partial \overline{E}/\partial q_j . \qquad (3.26b)$$

Consequently, the mean quantum-mechanical energy $\overline{E}(R, t)$ is the interatomic potential energy which determines the trajectories of the nuclei. It is readily apparent that $\overline{E}$ is a dynamic variable since, through its dependence on the coefficients $b_j^c(R, t)$, it has an implicit dependence on the velocities of the classical particles.

Now we have to solve the set of equations consisting of

$$\frac{d\underline{b}(R, t)}{dt} = \frac{\partial \underline{b}(R, t)}{\partial t} + \frac{\partial \underline{b}(R, t)}{\partial R} \frac{dR}{dt} , \qquad (3.21)$$

$$\dot{q}_j = p_j/m_j , \qquad (3.26a)$$

$$\dot{p}_j = - \partial \overline{E}/\partial q_j . \qquad (3.26b)$$

IV. METHOD OF SOLUTION OF THE EQUATIONS

To solve the set of equations (3.21), (3.26a), and (3.26b) we use Gill's adaptation of the Runge-Kutta method (19).[24] This generates a fourth-order solution to a total differential equation. The computer program was written to solve the equations simultaneously, with momentum and total energy (classical plus quantum-mechanical) conservation. Unitarity of the solutions was ensured by normaliz-

ing after each cycle of the Runge-Kutta process. Thus, from the initial positions, momenta, and state of the system $\underline{b}(R, t)$ (for all the calculations reported here the electron was initially in the $1s$ level of the atom) we obtain the initial potential and kinetic (and, therefore, the total) energy; using this potential energy we may solve for the new positions, momenta, and the coefficient matrix $\underline{b}(R, t)$ at a time Δt later, this information then defining a new potential and kinetic energy. Proceeding in this iterative fashion, we thus obtain all these quantities throughout the interaction region.

The accuracy of the calculation was controlled by using a variable step size Δt such that the total energy at a given iteration was equal to the total energy at the previous iteration by an amount not less than $E_T^0 \times 10^{-5}$ nor greater than $E_T^0 \times 10^{-7}$, where E_T^0 is the initial asymptotic total energy. This resulted in the over-all energy conservation being to three significant figures.

We should mention here that (3.26b) presents no problem since, for example,

$$\dot{p}_{x_1} = \frac{-\partial \overline{E}}{\partial x_1}$$

can be written as

$$\dot{p}_{x_1} = \frac{\partial \overline{E}}{\partial R} \frac{\partial R}{\partial x_1}$$

and

$$\frac{\partial \overline{E}}{\partial R} = \partial_R(\underline{b}^* \underline{H} \underline{b}) = \underline{b}^*(\partial_R \underline{H})\underline{b} + [\underline{b}^* \underline{H}(\partial_R \underline{b}) + (\partial_R \underline{b}^*)\underline{H} \underline{b}] ,$$
$$(4.1)$$

where $\partial_R \underline{H}$ can be obtained analytically from the matrix elements of $\underline{H}$, and the gradients of $\underline{b}$ with respect to R are obtained numerically within the computer program. Since

$$R = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2} , \qquad (4.2)$$

we have $\partial R/\partial x_1$ and, therefore, $\dot{p}_{x_1}$.

V. RESULTS FOR THE PROTON-HYDROGEN ATOM COLLISION

Since our present interest is in collisions at low energies ($\lesssim 10$ eV) and since the time of computation rises markedly with increase in the dimension of the basis set employed to describe the electrons, we considered the hydrogenic orbitals $\{1s, 2s, 2p_z\}$ on each center to be a sufficiently large set for our purposes. The orbitals $2p_x$ and $2p_y$ on each center may be omitted by symmetry considerations.

It is well known from the general theory of scattering that the Schrödinger equation (or the corresponding integral equation) describing the scattering process may have several solutions depending upon how one chooses the asymptotic boundary conditions. This is borne out by test calculations

which we carried out largely to check the computer program. Thus if, for example, the initial asymptotic state is chosen to be the antisymmetric molecular function $(1\sigma_u{}^*)$

$$\Psi(\infty) = 2^{-1/2}\left[\phi_A(1s) - \phi_B(1s)\right] \qquad (5.1)$$

and the atoms are directed towards each other with relative incident energy corresponding to 4 eV, it is found that the wave function $\Psi(R)$ always maintains the antisymmetric character with which it started. The calculated dynamic potential-energy surface for the collision turns out to be the same (to within numerical accuracy) as the static potential-energy surface of the $1\sigma_u{}^*$ molecular state. This is easily understood in terms of the static molecular potential-energy surfaces. Since only antisymmetric states can contribute, it follows that the only potential-energy surfaces which could influence that due to the $1\sigma_u{}^*$ state would be those due to the other antisymmetric states, all of which lie at sufficiently high energy to make a negligible contribution.

Similar results were obtained by starting out with a symmetric asymptotic molecular state

$$\Psi(\infty) = 2^{-1/2}\left[\phi_A(1s) + \phi_B(1s)\right] . \qquad (5.2)$$

In this case $\Psi(R)$ retains its symmetric character, the dynamic potential-energy surface correlating exactly with the static $1\sigma_g$ molecular potential-energy surface, this being expected on grounds analogous to those applied to the antisymmetric collision. It is worth noting that these symmetric and antisymmetric collisions are not entirely unphysical, the photodecomposition of the $H_2{}^+$ molecule from the $1\sigma_u{}^*$ state corresponding closely to the reverse of the antisymmetric collision described above.

The collision of a proton with a hydrogen atom corresponds to an asymmetric asymptotic state and therefore one might expect "conservation" of asymmetry in the process. In particular, since the asymptotic atomic state, ϕ_A say, can be regarded as a linear combination of symmetric (5.2) and antisymmetric (5.1) molecular states

$$\phi_A = \tfrac{1}{2}\left[1\sigma_g(R=\infty) + 1\sigma_u{}^*(R=\infty)\right] , \qquad (5.3)$$

we should expect static potential-energy surfaces due to both $1\sigma_g$ and $1\sigma_u{}^*$ to contribute. Equation (5.3) also suggests that we be extremely careful in choosing the initial state $(R_0 = \text{finite})$ for numerical calculations, since even small errors in this choice would cause the system initially to "shoot" along an erroneous potential-energy surface. In practice, this difficulty was overcome by repeating the calculation using increasing values of the initial distance R_0 until the dynamic potential-energy surface became independent of R_0. For the collision $H + H^+$, the leading terms in the interaction depend

upon R^{-2} and it was found that a suitable R was in the range of 150–200 a.u. Confidence in the validity of the results obtained in calculations was also reinforced by verifying the invariance of the calculations to time reversal. In this respect, the accuracy of the calculations proved to be remarkable in view of the extremely complicated behavior of the electronic wave function which we shall shortly discuss.

The contribution of both states $1\sigma_g$ and $1\sigma_u{}^*$ to the scattering process is borne out by our calculations. Figure 3 portrays the dynamic potential-energy surfaces for a variety of zero-impact-parameter calculations. As the incident energy decreases, the dynamic potential-energy surface correlates more closely with the $1\sigma_g$ state. Note, however, that even for thermal (0.02 eV) and subthermal collisions, the dynamic potential-energy surface is still significantly different from the static $1\sigma_g$ surface, as indeed one might expect from the above symmetry conservation arguments. These differences are even more obvious in the wave functions, or, more conveniently, in the electron densities. In the symmetric and antisymmetric collisions the electron density in one channel is the same as that in the other at any instant of time. On the other hand, the density for the $H^+ + H$ collision oscillates rapidly in the interaction region (resonant charge exchange) as depicted in Fig. 4. The region in the vicinity of the turning point of the trajectory has been omitted in this diagram since it is rather complex. This type of exchange behavior could in no way be accounted for by perturbation theory techniques since the "initial value" of the wave function is drastically altered in the course of the process.[15]

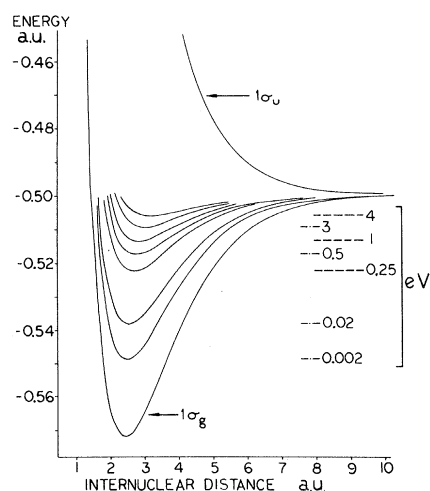A variety of calculations were carried out for

FIG. 3. Dynamic potential-energy surfaces for zero-impact-parameter collisions. (Figures on the right refer to the asymptotic proton kinetic energies.)
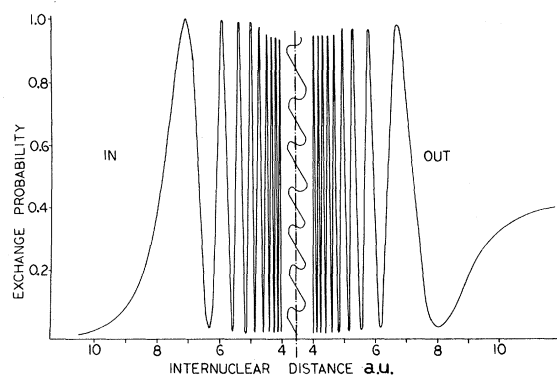
FIG. 4. Electron exchange probability as a function of internuclear distance. (Left side of the diagram refers to the approach to the turning point; right side, to retreat from turning point.)

nonzero impact parameters. The dynamic potential-energy surfaces for these collisions were similar to those for zero impact parameters. The trajectories for these calculations are of interest, however, since they illustrate the ability of the method to handle trajectories which are very far from the usual linear trajectory approximation normally employed in an impact-parameter treatment. A typical trajectory is shown in Fig. 5 corresponding to an impact parameter of 1 a.u. and incident energy of 0.5 eV. The coordinates refer to the laboratory frame. It can be seen how the initial and final interactions are attractive (corresponding to the outer region of the dynamic potential-energy surface), the intermediate interaction being repulsive (corresponding to the inner region of the potential-energy surface).
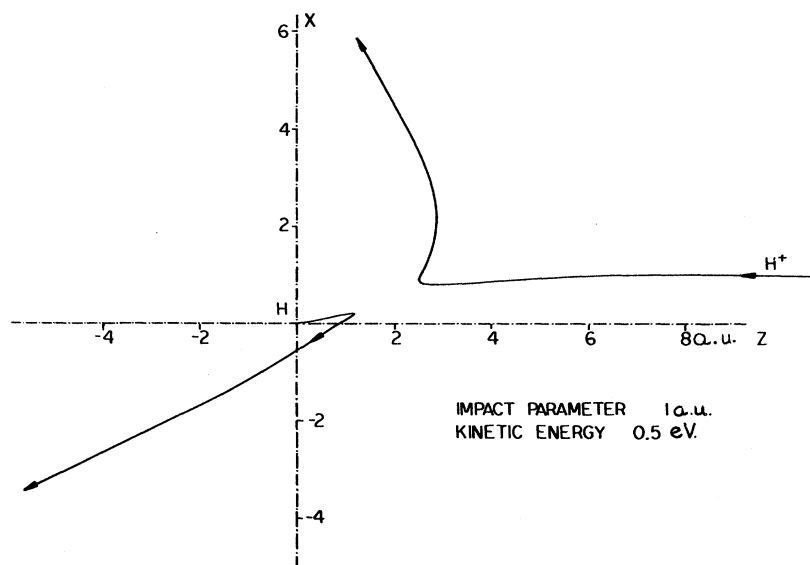
VI. DISCUSSION OF SEMICLASSICAL MODEL

The type of calculation which we have described in this paper would at this stage seem to have a considerable number of virtues, a few of which are as follows: (a) It appears capable of extension to many-electron systems, the only difficulties anticipated being those of molecular quantum theory, which, in some approximation, are not insuperable. (b) It is capable of extension to systems with more than two nuclei, e.g., to the exchange reaction

$$A + BC \rightarrow AB + C .$$

Work in this direction is proceeding at present. (c) The method provides a detailed step-by-step description of the evolution of the reacting system and should therefore yield information as to how and why a reactive collision proceeds in the manner which is predicted. It is difficult to see how alternative procedures, such as the S-matrix, which are concerned only with the calculation of asymptotic probabilities, could provide such information.

The limitations of the model do not appear to be in any way insuperable. Although the techniques employed in this paper describe a semiclassical model, conversion to an entirely quantum-mechanical model would require no more than a suitable way for handling continuum states in addition to discrete states. Avenues of approach to this problem are currently being explored.

ACKNOWLEDGMENTS

FIG. 5. Typical trajectory in the laboratory frame.

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m_J Mixing in Oriented $4\,^2P_{3/2}$ Potassium Atoms Induced by Collisions with Inert Gases*

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The cross sections for the decay of circular and of linear polarization in oriented $4\,^2P_{3/2}$ potassium atoms, induced in collision with inert-gas atoms, were determined in a series of fluorescence experiments. A modified Zeeman scanning method was used to populate selectively the m_J sublevels of the $^2P_{3/2}$ potassium atoms mixed with inert gases and placed in a strong magnetic field. Measurements of depolarization of the fluorescence, in relation to gas pressures, yielded the following depolarization cross sections: σ_1 (disorientation): K-He, 86 Å^2; K-Ne, 86 Å^2; K-Ar, 164 Å^2; K-Kr, 248 Å^2; K-Xe, 251 Å. σ_2 (disalignment): K-He, 127 Å; K-Ne, 120 Å^2; K-Ar, 240 Å^2, K-Kr, 301 Å^2, K-Xe, 336 Å^2. The experimental values are in satisfactory agreement with the calculations of Nikitin and Ovchinnikova.

I. INTRODUCTION

The depolarization of alkali atoms in their $^2P_{1/2}$ and $^2P_{3/2}$ resonance states, induced in collisions with inert-gas atoms, has been the subject of several recent studies, both theoretical and experimental. The general theoretical problem of collisional relaxation of excited atoms has been treated by Dyakonov and Perel,[1] and by Omont.[2] Franz and Franz[3] proposed two models for the description of the depolarization in the particular case of alkali atoms, of which one involved a random reorientation of the total electronic angular momentum J, while the second assumed the existence of selection rules according to which $\Delta m_J = 0, \pm 2$. Elbel and Naumann[4] suggested that the mixing of the Zeeman sublevels is due to collisional phase shifts between the molecular σ and π substates, into which the atomic ^2P state is split during a collision, and obtained the selection rule $m_J \not= -m_J$ for mixing within a J multiplet state. A similar result was derived by Franz, Leutert, and Shuey.[5] Mandelberg,[6] using an impact-parameter method, calculated the cross sections for m_J mixing in alkali atoms, induced in collisions with the inert gases. His results did