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Concept of Intermolecular Forces in Collisions*

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For polar or electronically excited molecules the concept of intermolecular forces requires clarification. To calculate the equation of state or equilibrium properties, it suffices to use intermolecular forces which are averaged over the magnetic quantum numbers, but for nonequilibrium or transport properties it is necessary to know the intermolecular energy for each separate quantum state. There are many different representations of intermolecular forces, depending on which degrees of freedom are treated quantum mechanically and which classically. The whole concept of intermolecular force becomes nebulous when a large fraction of the collisions are not adiabatic.

A semiclassical treatment is developed for describing the trajectories of nonadiabatic collisions in which transitions occur infrequently. For grazing collisions, the colliding molecules are loosely coupled and best represented in terms of space fixed coordinates, but when the molecules approach each other more closely the internal degrees of freedom become tightly coupled, and then the intermolecular forces are best calculated in terms of a body fixed representation. The collisions with tight coupling are especially important for determining the kinetic theory properties of gases.

I. INTRODUCTION

FOR atoms in their ground states colliding with thermal velocities, the concept of intermolecular forces is clear. Using quantum mechanics to predict the functional form and experimental data to evaluate constants, one can obtain expressions for the interaction energy of two such systems which are correct to a high degree of accuracy.[1,2] For polyatomic molecules or molecules in excited electronic states, the concept of intermolecular forces is not entirely clear. As long as the large proportion of collisions are adiabatic in the sense that the quantum numbers defining the state of internal coordinates remain unchanged during a collision, the concept of intermolecular force is meaningful; when this is no longer the case, the concept becomes nebulous. The present paper is a discussion of the conceptual difficulties of describing molecular collisions, and our attempts to overcome them.

To characterize a molecular collision completely, one must give the simultaneous behavior of the four groups of coordinates which describe the translations, rotations, vibrations, and electronic motions of the two molecules during the encounter. The quantized nature of these degrees of freedom varies widely, ranging from the translational motion which is very nearly classical, to the electronic motions which are quantized with energy spacings which are generally much larger than kT. Pure vibrations are usually strongly quantized, and pure rotations are very frequently almost classical. Twisting and bending vibrations, as well as rotations of hydrogen containing diatomic molecules represent a critical intermediate case, since they frequently have energy spacings which are just of the order of kT.

When nonadiabatic collisions are frequent, so that the concept of intermolecular forces is not useful, it is always possible to treat the collision process from a purely quantum mechanical standpoint. In this treatment each collision process is characterized by a set of differential scattering cross sections[3] which are a measure of the composite probability that the collision results in a particular angular deflection and that this is accompanied by a particular set of initial and final quantum numbers defining the internal state of the molecules. All of the macroscopic properties of a gas can be expressed in terms of these differential scattering cross sections[4] and thus, from a formal standpoint, a knowledge of them would be equally as satisfactory as a knowledge of the intermolecular forces. In point of fact, the differential scattering cross sections are very difficult to calculate, so that to date a full set of them has not been obtained for even a single case. Furthermore, it is difficult to develop the sort of intuitive feeling for the cross sections which would make it possible to estimate their behavior under a wide variety of conditions. It is on these accounts that we shall try to push the intermolecular force concept until we are forced from practical considerations to abandon it.

A semiclassical treatment implies that the coordinates be separated into two groups, those which are treated classically and those which are treated quantum mechanically. The approximate methods necessary for such a procedure are similar to those of the Born-Oppenheimer separation of electronic and nuclear coordinates. One first regards the group of classical coordinates as fixed, thus obtaining a set of clamped energy levels which represent the motion of the quan-

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[1] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

[2] The nonadditivity of pair potentials is being investigated both theoretically and experimentally. A comparison between the potentials determined from crystal structure and those determined from the properties of a dilute gas would, for example, provide an empirical determination of the nonadditive forces.

[3] Reference 1, p. 672.

[4] deBoer, Uhlenbeck, and Wang Chang, Physica (to be published).

tized coordinates. It is these clamped energy levels which give rise to the notions of intermolecular forces between polyatomic molecules. Since a complete semiclassical theory provides trajectories for both elastic and inelastic collisions and assigns a relative probability to each such trajectory, it is clear that, when this is desirable, one can always use the semiclassical results to evaluate the differential scattering cross sections.

There seem to be three sorts of semiclassical descriptions which we might consider, each leading to a different concept of intermolecular force:

(a) Only the electronic states are treated quantum mechanically. In this case we obtain a set of Eyring-type potential energy surfaces in a space of a large number of variables. A point in this space corresponds to a value of the energy for a particular instantaneous configuration of all of the nuclei of the molecules participating in the collision. There are an infinite number of these potential energy surfaces stacked as sheets one above the other, corresponding to all of the possible electronic states of the system thought of as a super-molecule. The motion of all except the electronic coordinates may be interpreted in terms of the motion of a particle on one of these potential energy surfaces, providing the coordinate axes are skewed in order that the kinetic energy appear in diagonal form and in order that the same effective mass be associated with each coordinate.[5]

(b) Electronic and vibrational degrees of freedom are treated quantum mechanically while translations and rotations are treated classically. This leads to a set of potential energy surfaces with somewhat fewer degrees of freedom. Such a treatment has considerable merit.

(c) Only translations are treated classically, while all other degrees of freedom are quantum mechanical. This leads to a set of potential energy curves. Let us examine the separation and the meaning of intermolecular force in considerable detail for this case.

First, regard the colliding molecules a and b as a single quantum mechanical system. Let $\mathbf{r}_a$ represent all coordinates necessary for specifying the configuration of molecule a relative to its mass center, and $\mathbf{r}_b$ all coordinates for specifying the configuration of molecule b relative to its mass center. The location of molecule b relative to molecule a is given by $\mathbf{R}$. The motion of the center of mass of the whole system may always be separated out, and the Schrödinger equation in the relative coordinates may be written[6]

$$\left[H_a(\mathbf{r}_a)+H_b(\mathbf{r}_b)-\frac{\hbar^2}{2\mu}\nabla_R{}^2+\Phi(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})\right]\Theta_k(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})$$

$$=E_k{}^{\text{tot}}\Theta_k(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R}). \quad (1)$$

Here H_a and H_b represent the Hamiltonian operators of the isolated molecules, $\Phi(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})$ is the potential energy of interaction, E^{tot} is the total energy of the system relative to its mass center, and $\mu=m_am_b/(m_a+m_b)$. As far as the translational degrees of freedom are concerned, Eq. (1) corresponds to holding molecule a fixed at the origin of the relative coordinate axes and letting molecule b move relative to it, except that the mass of molecule b is replaced by the reduced mass μ. It is important to note that in Eq. (1) the orientation of each of the internal and relative coordinate axes remains fixed with respect to a coordinate system fixed in space.

Exact solutions of Eq. (1) may be written in the form

$$\Theta_k=\sum_j \chi_{kj}(R)\psi_j(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R}), \quad (2)$$

where the ψ_k are called "adiabatic clamped" wave functions since they are solutions of the following Schrödinger equation in which the relative coordinates are held calmped or fixed

$$[H_a(\mathbf{r}_a)+H_b(\mathbf{r}_b)+\Phi(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})]\psi_k=E_k(\mathbf{R})\psi_k. \quad (3)$$

In the limit that the translational motion is slow compared to the motion of the internal coordinates, we may carry out a Born-Oppenheimer type separation which is equivalent to dropping all but a single term from the right hand side of Eq. (2). Deviations from the separation appear as the probability of transition to states described by other terms in the series of Eq. (2). In the absence of such transitions, the motion of the relative coordinates $\mathbf{R}$ is governed by the adiabatic clamped energies obtained from solutions of Eq. (3). That is, the $E_k(\mathbf{R})$ act as an intermolecular potential and the relative translational motion of the system may be described in terms of the frictionless motion of a point of mass μ on the potential energy surface $E_k(\mathbf{R})$.[7]

Any of these three separations of coordinates, and the associated concept of intermolecular force, is

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[5] J. O. Hirschfelder and J. S. Dahler, Proc. Natl. Acad. Sci. U. S. **42**, 363 (1956). The kinetic energy of the nuclei in the x direction, minus the kinetic energy of the center of gravity of the system (neglecting the masses of the electrons relative to the masses of the nuclei) is

$$\Sigma_i \tfrac{1}{2}m_{ai}\dot{x}_{ai}{}^2+\Sigma_j \tfrac{1}{2}m_{bj}\dot{x}_{bj}{}^2-(1/2M)[\Sigma_i m_{ai}\dot{x}_{ai}+\Sigma_j m_{bj}\dot{x}_{bj}]^2, \quad (a)$$

where m_{ai} and x_{ai} are the mass and x coordinate of the ith nucleus in molecule a, measured in a space-fixed coordinate system. Now in order for the classical trajectory to correspond to the motion of a single particle moving on a potential energy surface, it is it is necessary to find a set of relative coordinates q_k such that the kinetic energy of Eq. (a) can be transformed into the form $\frac{1}{2}\mu\Sigma_k \dot{q}_k{}^2$, where μ is some effective mass. It is easy to show that the q_k can always be taken as linear combinations of $x_{ai}-x_{a1}$ and $x_{bj}-x_{b1}$. This is the generalization of the skewing of Eyring potential energy surfaces for the case of an atom A colliding with a molecule BC. See J. O. Hirschfelder, dissertation, Princeton University, 1935 (unpublished), Appendix II, and Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[6] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1950), p. 140.

[7] T. Y. Wu and A. B. Bhatia, J. Chem. Phys. **24**, 48 (1956). Wu and Bhatia have pointed out that there is an additional small correction to the clamped energies which appears even in the limit of zero relative velocity, and which is due to the nuclear kinetic energy implied by the $\mathbf{R}$ dependence of $\psi_j(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})$. The term is important, however, only for very slight molecules.

meaningful only as long as the coupling between the coordinates is small enough so that quantum transitions are rare. When two potential energy surfaces come close together, from a quantum mechanical standpoint there is a probability of the system crossing from one energy surface to the other. Clearly a high probability of such a crossing would make the application of the semiclassical approach difficult. The probability of such a crossing is greatest when the relative kinetic energy in the particular degree of freedom is comparable to the energy difference between the two potential surfaces. Thus at very low velocities there are no crossings and at very high velocities there are few crossings. As a result, the concept of an intermolecular force might be restricted to apply to certain ranges of velocity away from these conditions of resonance.

From the oscillator strengths of the separated molecules, one can often tell a great deal about the coupling of the various degrees of freedom and determine what is the logical form of representation of the intermolecular forces. Consider, for example, the dispersion forces at large separations. The energy of interaction of two molecules at large separations is given in terms of the oscillator strengths for all the quantum transitions. Let us suppose that we are considering a collision between two diatomic molecules where there may be electronic, vibrational, and rotational transitions. Because of the Franck-Condon principle, there is usually a strong coupling between the electronic and vibrational transitions. Thus, if we tried to represent the intermolecular forces by treating vibrations classically, we would obtain oscillator strengths which were far too small, and the intermolecular forces calculated would also be too small. The Eyring type of potential energy surfaces (a) will thus not lead to satisfactory calculations of long-range dispersion forces. As far as short-range first order perturbation valence forces are concerned, the Eyring type of representation might still be useful.

In a semiclassical treatment, there will always be separate interaction potentials corresponding to all the possible internal quantum states, and when resonance degeneracy exists there will be a splitting into families of energy surfaces. For equilibrium or equation-of-state properties, there is a strong averaging tendency and it is frequently permissable to replace a family of energy surfaces by a single averaged potential energy. This is because the equilibrium properties are expressed in terms of the partition function which is the Boltzmann average of a point in the phase space of the system. For small energies, the difference between a Boltzmann average and an arithmetic average is small. Thus for equation-of-state calculations it is often satisfactory to use as a potential energy surface the intermolecular potential obtained by the arithmetic average over some of the quantum numbers which lead to splitting of the energy surface. Such average potentials are easy to calculate because they make use of quantum mechanical sum rules. Usually the averaged potentials correspond to forces which are of shorter range than those for the nonaveraged potentials. Often the concept of intermolecular force is clear from the standpoint of the averaged potentials even where it is no longer useful for the nonaveraged potentials because of frequent transitions.

However, if the theory is to be applied to nonequilibrium or transport properties, such averaging is not possible. In this case it is important that the dynamics corresponding to each potential energy surface be treated independently. This can be seen by considering the interaction between two dipoles. If the dipoles are pointed in one direction the molecules repel each other, and if pointed in the opposite direction they attract each other. In the first case the angle of deflection in the collision is positive, whereas in the second case it is negative. As far as the transport properties are concerned it is the cosine of the angle of deflection which matters, so that both the attractive and repulsive collisions would contribute in the same sense. This behavior is in contrast to that of the second virial coefficient, where the angle of deflection itself occurs to the first power so that the effect of the attractive collision would tend to counteract the effect of the repulsive collision.[8] Thus we see why the equation of state for polar molecules is not very different from the equation of state for nonpolar molecules, but why the viscosity, heat conductivity, and diffusion for polar species are very significantly different. For molecules in excited states where resonance splittings are truly large, this can be expected to be a large effect.

In the following sections we will consider in detail the possibility of developing the semiclassical theory of thermal energy collisions between polyatomic molecules in which only the relative translational motion of the molecules is handled classically. To preserve generality of the treatment, we will avoid introducing any averaged potential energy surfaces. From our meaning of semiclassical, it is clear that our conclusions will not necessarily apply to the classical-type approximations used by some authors for obtaining limiting values of integrals arising in purely quantum mechanical treatments.

II. LOW-VELOCITY LIMIT

(a) Clamped Energies

Solutions of Eq. (3) give the adiabatic clamped wave functions and the potential energy surfaces which are

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[8] The coefficient of viscosity $\eta(T)$ and the second virial coefficient $B(T)$ for monotonically varying intermolecular potentials are given by the expressions

$$\frac{RT}{\eta(T)}=\frac{8}{5}N\pi^{\frac{1}{2}}\int_0^\infty \exp(-\gamma^2)\gamma^7\int_0^\infty (1-\cos^2\chi)bdbd\gamma,$$

$$B(T)=\frac{12}{3}N\pi^{\frac{1}{2}}\int_0^\infty \exp(-\gamma^2)\gamma^4\int_0^\infty \chi b^2dbd\gamma,$$

where χ is the angle of deflection, b is the collision parameter, and γ is a reduced energy variable.

appropriate when the relative translational motion is to be treated classically. It is interesting to consider exact and approximate solutions of Eq. (3) in both space-fixed and body-fixed coordinate systems. Let xyz be a set of body-fixed coordinates oriented so that the z axis coincides with the line joining the mass centers, **R**, and let the exact wave functions and energies in this representation be ψ_k and E_k. Let successive approximate solutions be labeled $\psi_k^{(0)}, \psi_k^{(1)}, \cdots$ and $E_k^{(0)}, E_k^{(1)}, \cdots$. Let the primed symbols $\psi_k^{(0)\prime}$, $\psi_k^{(1)\prime}$, $\cdots\psi_k^{\prime}$ and $E_k^{(0)\prime}$, $E_k^{(1)\prime}$, $\cdots E_k^{\prime}$ have a corresponding significance in a space coordinate system $x'y'z'$ and let β and α be the polar coordinates of **R** in $x'y'z'$.

In the absence of external fields, the energy of interaction depends only on the relative orientation of the molecules and not on their location in space, so that the total Hamiltonian of the system is invariant under a rotation of the coordinates. Thus the exact eigenvalues of Eq. (3) can depend only on the magnitude of the intermolecular separation R, and the potential energy surfaces may be represented in terms of the kind of one dimensional energy curves used to describe atomic interactions. The energies $E_k(R)$ and $E_k'(R)$ are of course identical. The wave functions ψ_k and ψ_k' are also identical under the change of variables relating xyz and $x'y'z'$.

It will usually be necessary to use approximate methods of solution, however, and in this case the two representations can lead to different results. Suppose the zero-order solutions are obtained by solving Eq. (3) for larger **R**, where the interaction is zero. Then the first-order perturbation energies in the body-fixed coordinates,

$$E_k^{(1)} = (\psi_k^{(0)} | \mathcal{H} | \psi_k^{(0)}), \tag{4}$$

depend only on R because $\mathcal{H}$ is invariant under a rotation and the $\psi_k^{(0)}$ are not explicit functions of β or α. In the space-fixed representation, on the other hand,

$$E_k^{(1)\prime} = (\psi_k^{(0)\prime} | \mathcal{H} | \psi_k^{(0)\prime}) \tag{5}$$

may depend on β and α. The ψ_k are a complete set, so we may write

$$\psi_k^{(0)\prime} = \textstyle\sum_i a_{ki}(\beta,\alpha)\psi_i, \tag{6}$$

where the a_{ki} depend on β and α. Thus

$$\begin{aligned} E_k^{(1)\prime} &= (\textstyle\sum_i a_{ki}\psi_i | \mathcal{H} | \sum_j a_{kj}\psi_j) \\ &= \textstyle\sum_i |a_{ki}(\beta,\alpha)|^2 E_i(R). \end{aligned} \tag{7}$$

Thus if the approximate solutions are to have the same symmetry as the exact solutions, it is important that trial functions be chosen which have the proper symmetry with respect to the intermolecular axis. According to Eq. (4), this may be accomplished by working entirely in the body-fixed coordinate system. However, if one wishes to use trial functions defined in the space-fixed coordinates and first-order perturbation, then it is necessary to use a full set of first-order functions and to solve the resulting secular equation. Some authors have used only single terms in the space-fixed coordinate system for their approximate wave functions, and they have been led to the erroneous notion that the intermolecular forces depend on the angles β and α which give the orientation of **R**.

(b) Sample Calculation of Clamped Energies

As an example of the sort of problems which arise and of the approximations which may be made in order to obtain usable clamped energy functions, consider the problem of studying collisions between polar diatomic molecules. For this case, we assume a pure dipole-dipole energy of interaction between the molecules, so as to fix our attention on the interaction between the rotational motions of the molecules and the translational motion of the trajectory.

We may idealize the molecules as linear rigid rotators with moments of inertia I_a and I_b and with ideal electric dipoles $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$ located at the mass centers and oriented along the molecular axis. The energy levels $E_k(R)$ are now given by solutions of Eq. (3) where H_a and H_b are the Hamiltonians of the isolated rigid rotators, and $\Phi(\mathbf{r}_a,\mathbf{r}_b,\mathbf{R})$ is the energy of interaction between two ideal electric dipoles,

$$\Phi = \frac{\boldsymbol{\mu}_a \cdot \boldsymbol{\mu}_b}{R^3} - 3\frac{(\boldsymbol{\mu}_a \cdot \mathbf{R})(\boldsymbol{\mu}_b \cdot \mathbf{R})}{R^5}. \tag{8}$$

In the body-fixed coordinates, this takes the simple form

$$\Phi = \frac{\mu_a\mu_b}{R^3}[-2\cos\theta_a\cos\theta_b + \sin\theta_a\sin\theta_b\cos(\varphi_a - \varphi_b)], \tag{9}$$

where the angles θ_a, φ_a and θ_b, φ_b are the polar angles giving the orientation of the dipoles $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$. Clearly the operator for the component of the angular momentum in the z direction,

$$\mathcal{L}_z = \frac{\hbar}{i}\left[\frac{\partial}{\partial\varphi_a} + \frac{\partial}{\partial\varphi_b}\right], \tag{10}$$

commutes with Φ so that the solutions ψ_k may be chosen to be eigenfunctions of $\mathcal{L}_z$.

First, let us consider the nondegenerate case in which $I_a \neq I_b$. The wave function of each isolated molecule is simply a normalized spherical harmonic,[9] $Y_l^n(\theta,\varphi)$, so that at large separations the wave function for the system representing a collision between molecules a and b may be written (in body-fixed coordinates)

$$\psi_k^{(0)} = Y_l^m(a)Y_\lambda^\mu(b). \tag{11}$$

If we take the $\psi_k^{(0)}$ as the basis for a perturbation calculation, the matrix elements of the perturbing potential,

$$(Y_{l'}^{m'}(a)Y_{\lambda'}^{\mu'}(b) | \Phi | Y_l^m(a)Y_\lambda^\mu(b)), \tag{12}$$

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[9] Reference 1, p. 906.

may conveniently be evaluated from the recursion relations of the spherical harmonics,[10] and it is easily shown that the elements are zero unless all of the following conditions are satisfied:

$$\begin{gathered} l'=l\pm1, \qquad \lambda'=\lambda\pm1, \\ m'=m,\, m\pm1, \quad \mu'=\mu,\, \mu\pm1, \\ m'+\mu'=m+\mu. \end{gathered} \tag{13}$$

Clearly, all the diagonal matrix elements of the perturbing potential vanish, so that when the two molecules are different species and hence possess different moments of inertia, the first-order perturbation is necessarily zero.

In collisions between two identical molecules (whose moments of inertia are equal), the first-order perturbation energy is also zero except when the rotational quantub numbers bear certain resonance relations. If the molecules are identical then the spatial part of the wave function must be either symmetric or antisymmetric with respect to an interchange of the labels a and b Thus the single product of spherical harmonics, Eq. (11), no longer represents a suitable unperturbed wave function. Rather, the correct unperturbed wave function is formed from linear combinations of the $2(2l+1)(2\lambda+1)$ such terms corresponding to all allowed values of m and μ. Under such conditions a nonvanishing first-order perturbation energy results when $\lambda=l\pm1$ and in this case the two rotators are said to be in resonance. If $\lambda\neq l\pm1$ the first-order perturbation energy vanishes just as in the case of the two unlike rotators.

Consider the simplest resonance case, $l=0$, $\lambda=1$. The secular determinant is then formed from matrix elements of the six functions

$$\begin{aligned} \psi_1^{(0)}&=Y_0^0(a)Y_1^{-1}(b), & \psi_4^{(0)}&=Y_1^{-1}(a)Y_0^0(b), \\ \psi_2^{(0)}&=Y_0^0(a)Y_1^0(b), & \psi_5^{(0)}&=Y_1^0(a)Y_0^0(b), \\ \psi_3^{(0)}&=Y_0^0(a)Y_1^1(b), & \psi_6^{(0)}&=Y_1^1(a)Y_0^0(b). \end{aligned} \tag{14}$$

It is easily verified that the first-order perturbation energies obtained from solutions of the secular equation are

$$\begin{gathered} E_k^{(1)}(R)=a_k\mu_a\mu_b/R^3, \\ a_1=\tfrac{2}{3}, \quad a_2=a_3=\tfrac{1}{3}, \quad a_4=a_5=-\tfrac{1}{3}, \quad a_6=-\tfrac{2}{3} \end{gathered} \tag{15}$$

and that the wave functions belonging to these energies are

$$\begin{aligned} \psi_1^{(1)}&=\psi_2^{(0)}-\psi_5^{(0)}=Y_0^0(a)Y_1^0(b)\ -Y_1^0(a)Y_0^0(b), \\ \psi_2^{(1)}&=\psi_1^{(0)}+\psi_4^{(0)}=Y_0^0(a)Y_1^{-1}(b)+Y_1^{-1}(a)Y_0^0(b), \\ \psi_3^{(1)}&=\psi_3^{(0)}+\psi_6^{(0)}=Y_0^0(a)Y_1^1(b)\ +Y_1^1(a)Y_0^0(b), \\ \psi_4^{(0)}&=\psi_1^{(0)}-\psi_4^{(0)}=Y_0^0(a)Y_1^{-1}(b)-Y_1^{-1}(a)Y_0^0(b), \\ \psi_5^{(0)}&=\psi_3^{(0)}-\psi_6^{(0)}=Y_0^0(a)Y_1^1(b)\ -Y_1^1(a)Y_0^0(b), \\ \psi_6^{(0)}&=\psi_2^{(0)}+\psi_5^{(0)}=Y_0^0(a)Y_1^0(b)\ +Y_1^0(a)Y_0^0(b). \end{aligned} \tag{16}$$

For resonant interactions with higher values of l, the solution of the secular equation may be difficult. For approximating the energy in such cases, as well as for calculating the first nonvanish terms arising from nonresonant interactions, the method of "unsharp resonance" developed and applied to this problem by London[11] may be used. The method is essentially a variation procedure in which a given unperturbed function $\psi_k^{(0)}$ is replaced by a linear combination composed of $\psi_k^{(0)}$ and the twelve (at most) $\psi_i^{(0)}$ with which it forms nonvanishing matrix elements of Φ. The secular equation can be solved, and for the nonresonance case yields energies which for large R have the form

$$E_k^{(1)}=\frac{\hbar^2}{2}\left[\frac{l(l+1)}{I_a}+\frac{\lambda(\lambda+1)}{I_b}\right]-B_k\frac{\mu_a^2\mu_b^2}{R^6}. \tag{17}$$

The constants B_k depend on the quantum numbers l, m, λ, and μ, and can be calculated easily.[12] London concludes that these forces are smaller than the dispersion forces, even for such strongly polar molecules as HCl.

For resonance cases the energies have the form, for large R,

$$E_k^{(1)}=\frac{\hbar^2}{2I}[l(l+1)+\lambda(\lambda+1)]\pm A_k\frac{\mu_a\mu_b}{R^3}, \tag{18}$$

where again the A_k are easily calculated.[12] Energies obtained from Eq. (18) will in general not be as good as those obtained from a solution of the secular equation because the variation function does not include the entire degenerate set. It is to be noted, however, that Eq. (18) will give the proper number of energies for a given degenerate set, and that the variation functions are eigenfunctions of $\mathcal{L}_z$ in the body-fixed coordinates.

III. REGION OF MODERATE RELATIVE VELOCITY

The relative motion of the two molecules introduces new terms in the Hamiltonian of the system, corresponding to the kinetic energy of the relative motion and resulting in coupling and transitions among the clamped internal wave functions. In the equation for the radial motion, the centrifugal potential $\frac{1}{2}\mu g^2(b/R)^2$ must be added to the potential energy for the clamped molecules. Here b is the collision parameter and $\frac{1}{2}\mu g^2$ is the relative kinetic energy of the molecules at the beginning of the collision. In the equations for the angular motion of the trajectory, there are velocity-dependent terms which correspond to torques. These additional terms in the Hamiltonian can be treated as perturbations which result in transitions between our previously calculated clamped potential energy surfaces. We shall define the region of moderate relative velocity as the region where such quantum mechanical

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[10] Reference 1, p. 907.

[11] F. London, Z. Physik **63**, 245 (1930); see also H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

[12] Explicit formulas and some tabulated values may be found in reference 1, p. 997.

transitions are rare enough so that they may be treated by perturbation theory. When the quantum numbers describing the internal motion do not change during a collision, the entire motion lies on a single potential energy surface and the relative motion is called an adiabatic trajectory. When such transitions do occur, the semiclassical theory must give both the probability of transition and the effect of the transition on the trajectory.

(a) Adiabatic Trajectories

In the classical mechanical solution of the two-particle problem, the trajectory of relative motion is characterized by the fact that both the total energy and the total angular momentum of the system are conserved at every point of the trajectory. In the semiclassical formulation the energy is always a well defined quantity, so that it is conserved along the trajectory. If $\mathbf{g}(\mathbf{R})$ is the relative translational velocity, the conservation of energy becomes

$$E_k^{\mathrm{tot}}=\tfrac{1}{2}\mu g^2(\mathbf{R})+E_k(\mathbf{R}). \qquad (19)$$

In general, only the magnitude and one component of the angular momentum associated with the internal motions are specified in the semiclassical description, so that it is not possible to carry over the conservation law of angular momentum directly. An interpretation of the angular momentum consistent with the semiclassical approximation would be the requirement that the trajectory be characterized by conservation of the known angular momentum, so that the quantity

$$\mathbf{L}=\mu(\mathbf{R}\times\mathbf{g}(\mathbf{R}))+M\hbar\mathbf{i}_{\mathbf{R}} \qquad (20)$$

remain constant along the trajectory.[13]

The characteristics of a semiclassical trajectory for which the energy is given by Eq. (19) and the angular momentum by Eq. (20) may be deduced from a mechanical analog. In place of the two rotating molecules moving with respect to each other, we have a flywheel constrained to rotate about a radial axis and bound to the origin by the intermolecular forces which we calculated for the clamped molecules. This mechanical analog is shown in Fig. 1. The flywheel A has a mass μ and angular momentum $\hbar M$ in the direction of its axis of rotation. The flywheel slides and rotates without friction on the massless rod B and it has a potential energy $E_k(R)$. The moments of inertia of the flywheel about any axis perpendicular to B, as well as the moment of inertia about the z axis, are vanishingly small, but the initial speed of rotation about the z axis, $\dot{\psi}$, is large such that the product $I_z\dot{\psi}$ is equal to the desired angular momentum, $\hbar M$.

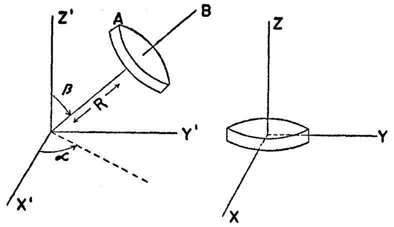

FIG. 1. A mechanical analog which illustrates the dynamics of a collision in which the internal angular momentum is constant relative to body-fixed coordinates.

Subject to these restrictions, the solution of the mechanical problem may be written

$$I_z\dot{\psi}=\hbar M, \qquad (21)$$

$$\mu d^2R/dt^2-\mu R[\dot{\beta}^2+\sin^2\beta\,\dot{\alpha}^2]=-\partial E_k(R)/\partial R, \qquad (22)$$

$$\mu[2\dot{R}\dot{\beta}+R\,d^2\beta/dt^2-R\sin\beta\cos\beta\,\dot{\alpha}^2]=-I_z\dot{\psi}\dot{\alpha}\sin\beta/R, \qquad (23)$$

$$\mu[2\sin\beta\,\dot{R}\dot{\alpha}+2R\cos\beta\,\dot{\alpha}\dot{\beta}+R\sin\beta\,d^2\alpha/dt^2]=I_z\dot{\psi}\dot{\beta}/R. \qquad (24)$$

Equation (21) indicates that the internal angular momentum does remain constant, so that the mechanical system is indeed the desired analog of the semiclassical problem. The left-hand sides of Eqs. (22), (23), and (24) are the components of the vector quantity $\mu d^2\mathbf{R}/dt^2$ in R, β, and α directions, and the right-hand sides are force-like terms. The force in the radial direction is the true force $-(\partial/\partial R)[E_k(R)]$. In addition there is a virtual force in the β direction proportional to $(\dot{\alpha}\sin\beta)/R$, and a virtual force in the α direction proportional to $\dot{\beta}/R$. Considered together, these comprise a virtual force which is perpendicular to the plane containing the instantaneous motion, and which is proportional to the component of the velocity perpendicular to $\mathbf{R}$.

Thus the correct semiclassical trajectories may be obtained as solutions of the classical equations of motion

$$\mu d^2\mathbf{R}/dt^2=-\nabla E_k(R)+\hbar M\mathbf{R}\times\mathbf{g}/R^3, \qquad (25)$$

with the usual boundary conditions of initial relative velocity and collision parameter.

At first sight it might seem that this virtual force proportional to R^{-2} is energetically inconsistent with the fact that the true intermolecular forces will generally fall off much more rapidly. Since the deflection due to the virtual force is always perpendicular to the force, as in gyroscopic motion, the virtual force does no work, and the skewing of the trajectory out of the plane is consistent with the conservation laws.

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[13] On the other hand, one might interpret the internal angular momentum in the correspondence limit as a definite vector of length $\hbar[J(J+1)]^{\frac{1}{2}}$ which lies on a cone about the z axis such that its component in the z direction is $\hbar M$. For each particular orientation on the cone, one could assign a precise angular momentum to the internal coordinates and construct a classical trajectory which conserved energy and angular momentum. Letting all orientations on the cone appear with equal *a priori* probability would yield an infinite family of classical trajectories for each solution of the clamped equation. Using such families of trajectories, it would be very difficult to evaluate the differential scattering cross sections.

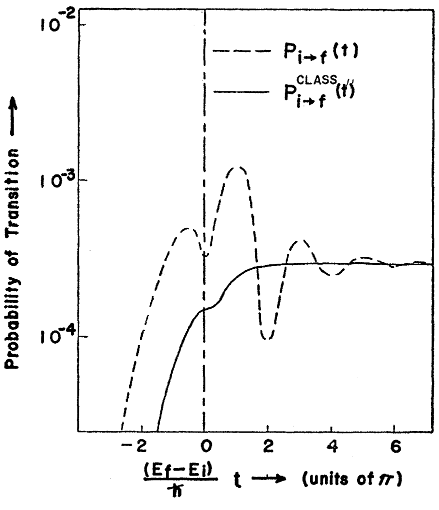

FIG. 2. The probability of transition during a collision. The broken curve is calculated from the quantum mechanical expression, Eq. (26); the solid curve is calculated from the approximate expression, Eq. (27), which is more suitable for a semiclassical interpretation.

(b) Probability of Transition

The adiabatic trajectories obtained from solutions of Eq. (25) give the relative separation $\mathbf{R}$ of the two molecules as a function of time, so that the method of time-dependent perturbations as an unperturbed set is indicated for an investigation of the probability of transition. Usually one takes the wave functions describing the system when R is very large. In our formulation of the collision problem, beginning from the Born-Oppenheimer type separation, the relative motion of the molecules is the perturbation, and the correct unperturbed functions are the adiabatic clamped functions ψ_k obtained as solutions of Eq. (3). Using this basis, it may be shown[14] that the probability that a system which at time $t=-\infty$ was in the pure initial state ψ_i is found in the final state ψ_f at time t, is given by

$$P_{i\to f}(t)=\left|\int_{-\infty}^{t}\frac{\exp\left(-\frac{i}{\hbar}\int_0^{t'}[E_i(t'')-E_f(t'')]dt''\right)}{E_i(t')-E_f(t')}\cdot\times\left(\psi_f\left|\frac{d\Phi}{dt'}\right|\psi_i\right)dt'\right|^2 \quad (26)$$

It is characteristic that in this nearly adiabatic form of time-dependent perturbation theory the matrix elements of $d\Phi/dt$ rather than those of the potential itself appear in the integrand. As Bohm points out, this use of adiabatic functions as a basis for the perturbation allows one to consider systems in which the interaction is large, as long as the rate of change of the interaction is small. Unfortunately, the probability that a transition occurs between time t and $t+\Delta t$, as given by Eq. (26), is not satisfactory for the semiclassical theory, as may be seen from Fig. 2 where the function $P_{i\to f}(t)$ is pictured for the case:

Initial quantum numbers: $l=2,\ m=0;\ \lambda=5,\ \mu=0,$
Final quantum numbers: $l'=3,\ m'=0;\ \lambda'=6,\ \mu'=0,$
Initial relative velocity: $g=3.19\times10^5$ cm/sec,
Impact parameter: $b=4.89\times10^{-8}$ cm.

These constants correspond to a typical encounter for HCl molecules at room temperature. The calculation was made assuming that the trajectory was a straight line traversed at constant velocity, and that $E_i(R)-E_f(R)$ was constant and equal to $(\hbar/2I)[l(l+1)+\lambda(\lambda+1)-l'(l'+1)-\lambda'(\lambda'+1)]$. Although these approximations would not in general be valid if we were seeking precise numerical results, they are adequate for illustrating the general behavior of the function.

The probability that the transition occurs between t and $t+\Delta t$ is given by $(d/dt)[P_{i\to f}(t)]\,\Delta t$. Because of the oscillating behavior of $P_{i\to f}(t)$, there are regions where such a procedure would give negative probabilities which would be difficult to interpret in a semiclassical theory. Such oscillations are caused by diffraction effects, and the apparent ambiguity of a negative transition probability arises from the fact that the semiclassical theory violates the uncertainty principle in asking about the simultaneous values of the energy and the time. The relatively long period and large amplitude of the oscillations make it impossible to construct a satisfactory curve by connecting corresponding points on the curve separated by one period. In the absence of a satisfactory derivation of the classical analog of the transition probability, we suggest that the following function may serve as a satisfactory approximation:

$$P_{i\to f}{}^{\text{class}}(t)=\frac{\displaystyle\int_{-\infty}^{t}\left(\psi_f\left|\frac{d\phi}{dt'}\right|\psi_i\right)^2\left|\frac{dR}{dt'}\right|^{-1}dt'}{\displaystyle\int_{-\infty}^{\infty}\left(\psi_f\left|\frac{d\phi}{dt'}\right|\psi_i\right)^2\left|\frac{dR}{dt'}\right|^{-1}dt'}P_{i\to f}(\infty). \quad (27)$$

This function has the following desirable properties:

1. It is zero at $t=-\infty$ and equal to $P_{i\to f}(\infty)$ at $t=\infty$, in agreement with the exact quantum mechanical expression.

2. It is a nondecreasing function of the time, corresponding to the classical picture that if transitions are rare, there is negligible chance of multiple or reverse transitions, so that there should be a steadily increasing probability of finding the system in the final state.

3. The probability that a transition occurs during the approaching half of a symmetric trajectory is equal to the probability that it occurs during the receding half,

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[14] D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., New York, 1951), p. 496.

corresponding to the fact that as a first approximation the quantum mechanical expression does not distinguish between $d\Phi/dt$ and $-d\Phi/dt$.

4. The transition probability increases most rapidly in regions where the perturbation potential is changing most rapidly in time, consistent with the adiabatic theorem.

5. $P_{i\to f}^{\text{class}}(t)$ agrees with the general form of $P_{i\to f}(t)$ if both are considered as functions of R, in that both indicate that the region about the distance of closest approach is a likely region for the transition.

The function $P_{i\to f}^{\text{class}}(t)$, applied to the special case already calculated, is given as the dotted line in Fig. 2.

In the semiclassical approximation, then, the probability that a particular quantum transition of the internal coordinates occurs on some element Δs of a collision trajectory is given by the function

$$\frac{1}{g(s)}\frac{d}{dt}[P_{i\to f}^{\text{class}}(t)]\,\Delta s \tag{28}$$

evaluated along an adiabatic trajectory.

(c) Nonadiabatic Trajectories

If at some point $\mathbf{R}^*$ along an adiabatic trajectory, a transition does occur such that the wave function describing the internal motions changes from ψ_i to ψ_f, then the remainder of the motion is a segment of an adiabatic trajectory on the new potential energy surface $E_f(R)$, calculated according to Eq. (25). This trajectory is uniquely specified by the speed and direction of motion immediately after the transition. To be consistent with the semiclassical development so far, these boundary conditions must be determined from the conservation laws Eqs. (19) and (20). Letting the subscript i denote quantities before the transition and f those after, the conservation laws may be written

$$E^{\text{tot}}=\tfrac{1}{2}\mu g_i^2(\mathbf{R}^*)+E_i(\mathbf{R}^*)=\tfrac{1}{2}\mu g_f^2(\mathbf{R}^*)+E_f(\mathbf{R}^*), \tag{29}$$

$$\begin{aligned}\mathbf{L}&=\mu[\mathbf{R}^*\times\mathbf{g}_i(\mathbf{R}^*)]+\hbar M_i\mathbf{i}_{\mathbf{R}^*}\\&=\mu[\mathbf{R}^*\times\mathbf{g}_f(\mathbf{R}^*)]+\hbar M_f\mathbf{i}_{\mathbf{R}^*}.\end{aligned} \tag{30}$$

The energy equation may be solved immediately to give the new relative speed

$$g_f(\mathbf{R}^*)=\left[\frac{E_i(R^*)-E_f(R^*)+\frac{1}{2}\mu g_i^2(\mathbf{R}^*)}{\frac{1}{2}\mu}\right]^{\frac{1}{2}}. \tag{31}$$

If the increase in internal energy is larger than the initial relative kinetic energy, Eq. (31) yields an imaginary value of the final relative velocity, and this is to be regarded as a sort of "selection rule" peculiar to the semiclassical theory. Actually, the quantum mechanical probability of transition, Eqs. (26) and (27), becomes small in such a situation, so that this semiclassical selection rule would not be expected to rule out any important fraction of the possible transitions.

In the angular momentum equation we note that the angular momentum due to the relative motion is always perpendicular to the known component of the internal angular momentum, so that Eq. (30) may immediately be written as the two equations

$$\hbar M_i=\hbar M_f \tag{30a}$$

$$\mu[\mathbf{R}^*\times\mathbf{g}_i(\mathbf{R}^*)]=\mu[\mathbf{R}^*\times\mathbf{g}_f(R^*)]. \tag{30b}$$

Equation (30a) contains the second semiclassical selection rule, namely that the total magnetic quantum number of the two molecule system does not change in a transition. To understand this selection rule and its limitations, it is instructive to review the assumptions of our development. Proceeding from the Born-Oppenheimer type separation of coordinates, we have supposed that the best instantaneous wave functions were those obtained from solutions of the clamped system, Eq. (3). This led us to a meaning of "adiabatic" which was defined in terms of quantum numbers referring to the body-fixed coordinate system, so that an adiabatic function was one for which the component of angular momentum in the radial direction remained constant during an encounter. This meaning of adiabatic is illustrated by the trajectory of Fig. 3(a) where the motion of molecule b is pictured relative to molecule a. The body-fixed wave function ψ_k remains unchanged during the collision and is an eigenfunction of $\mathcal{L}_z$. The vector representing the expectation value of $\mathcal{L}_z$ is indicated at several points of the trajectory.

Clearly, from the point of view of a space fixed coordinate system this does not represent an adiabatic trajectory, for the direction of the known component of the angular momentum has changed continuously during the encounter. To differentiate between these two points of view, one must distinguish between "elastic

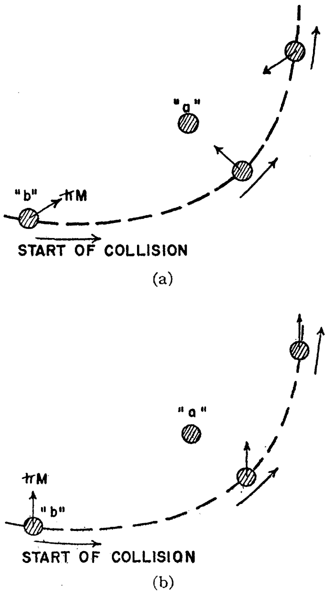

FIG. 3(a). Internal angular momentum specified relative to body-fixed coordinates throughout an encounter. (b) Internal angular momentum specified relative to space-fixed coordinates throughout an encounter.

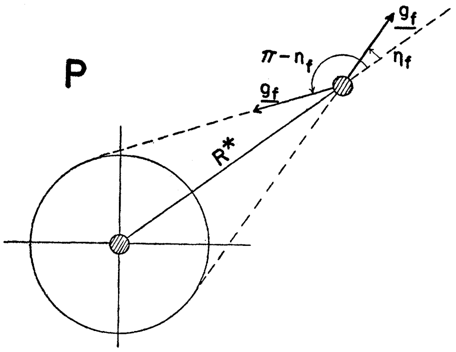

FIG. 4. Illustration of the two possible trajectories which conserve angular momentum after a transition.

adiabatic" and "elastic nonadiabatic" wave functions. From the point of view of the body fixed representation, Fig. 3(a) depicts an elastic adiabatic trajectory; from the space fixed point of view it is elastic nonadiabatic.

One could also formulate a semiclassical theory by defining adiabatic functions with reference to a space fixed coordinate system. In this case they would be eigenfunctions of $\mathcal{L}_{z'}$, and the known component of the angular momentum during an encounter would be depicted as in Fig. 3(b). From a space-fixed point of view we would call this an elastic adiabatic trajectory, but from the body-fixed coordinate system, we would call it elastic nonadiabatic.

Each of these representations is useful for particular kinds of collisions. When the interaction between the molecules is strong, the representation of Fig. 3(a) will be the best. Since we are interested in applying our results to kinetic theory problems, where collisions are important only when the interaction is strong enough to produce an angular deflection, we have chosen this representation.

In a grazing collision, where the trajectory may be approximated as a straight line, the representation of Fig. 3(b) will be the best. This is the approximation made by Anderson[15] and by Smith, Lackner, and Volkov[16] in their calculations of the pressure broadening of microwave spectra. The collision cross sections for pressure broadening are generally much larger than the kinetic theory cross sections[17] so that it is just the grazing collisions, represented by straight-line trajectories, which are important. Note, however, that if one were to attempt to use this representation for describing collisions with small impact parameters, the interaction energies calculated from perturbation theory might no longer be spherically symmetric, as was shown in Eq. (7).

Thus for collisions with large impact parameters the intermolecular forces are best expressed in terms of space-fixed coordinates, whereas for collisions in which the molecules come close together the body-fixed representation is superior. This situation is reminiscent of the two types of coupling, *LS* and *JJ* coupling, in atomic structure. The essential difference here is that during the course of a collision the molecules start out in a region of loose coupling, then as they come close together the coupling can become tight.

For grazing collisions, the second semiclassical selection rule, Eq. (30), is no longer valid, for as the coupling decreases there is an increasing tendency for the type of adiabatic collisions depicted in Fig. 3(b) to predominate. It is not clear whether this breakdown of the selection rule will appear before the angle of deflection has become so small that the collisions are no longer important for kinetic theory purposes.

When the magnetic quantum number does not change, Eq. (30b) may be used to construct a satisfactory final trajectory. It is clear from Eq. (30b) that $\mathbf{g}_f$ must lie in the plane of $\mathbf{R}^*$ and $\mathbf{g}_i$. Call this the plane P and let η be the angle from $\mathbf{R}^*$ to $\mathbf{g}$. Then the orientation of $\mathbf{g}_f$ relative to $\mathbf{R}^*$ is given by the relation

$$\sin\eta_f = \frac{g_f(\mathbf{R}^*)}{g_i(\mathbf{R}^*)} \sin\eta_i. \tag{32}$$

Clearly if η_f is a solution of Eq. (32), so is $\pi - \eta_f$. The significance of these two solutions may be seen in Fig. 4 where the final velocities are pictured in the plane P. The two possible directions of $\mathbf{g}_f$ are the two tangents to the circle of radius $R^* \sin\eta_f$. One of these represents an encounter in which the molecules are approaching each other, the other an encounter in which they are receding. By viewing the discontinuous change in velocity at the point of transition as a series of infinitesimal changes which gradually distort the trajectory, it is clear that the distinction between approaching and receding paths remains distinct. Thus if $\mathbf{g}_i(\mathbf{R}^*)$ is an approaching trajectory, $\mathbf{g}_f(\mathbf{R}^*)$ must also be chosen as an approaching trajectory and similarly for receding trajectories.

It is to be noted that if $[g_i(\mathbf{R}^*)/g_f(\mathbf{R}^*)] \sin\eta_i > 1$, no sstisfactory final trajectory exists, and this constitutes the third semiclassical selection rule. This selection rule can be operative only when there is a net transfer of energy from the translational motion to the internal degrees of freedom, so that $g_i(\mathbf{R}^*) > g_f(\mathbf{R}^*)$, and then only when the transition occurs near the distance of closest approach.

IV. HIGH-VELOCITY REGION

When the relative velocity of the encounter increases to a point where internal transitions become likely, the concept of intermolecular force and the semiclassical description of molecular collisions as developed in this paper are no longer useful. In this case we must rely on a strictly quantum mechanical formulation and seek to determine the differential scattering cross sections

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[15] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[16] Smith, Lackner, and Volkov, J. Chem. Phys. **23**, 389 (1955).

[17] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

directly. There are a number of variations of the distorted wave treatment which are being developed at the present time to handle such cases. It is to be expected that at extremely high velocities the problem again becomes tractable by semiclassical methods, as in the case for the stopping powers of alpha particles passing through matter. Unfortunately high-temperature thermal collisions and collisions resulting in chemical reactions are usually in the intermediate velocity range which is most difficult to handle.

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Radioactive Decay of La^{137} and Ce^{137}

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A long-lived radioactive isotope of lanthanum has been produced by neutron bombardment of natural cerium. It decays with emission of Ba x-rays and has been assigned as La^{137}. The K-electron capture half-life is $(6\pm2)\times10^4$ yr calculated from the Ba K x-ray intensity and the yield of mass 137 atoms in the bombardment. Approximate measurements of neutron cross sections of Ce^{136} gave 6.3 barns for activation of Ce^{137} and 0.6 barn for activation of Ce^{137m}. A previously unobserved 10-kev $M1$ transition has been discovered in the decay of Ce^{137}. A decay scheme is proposed which has a $g_{7/2}$ ground-state spin assignment for La^{137}. Electron capture to the $d_{3/2}$ ground state of Ba^{137} on the basis of this assignment is second-forbidden.

I. INTRODUCTION

CHUBBOCK and Perlman[1] estimated that the half-life of La^{137} must be longer than 400 yr. Their estimate was based on the K x-ray counting rate of a Ce^{137} sample, the x-ray detection efficiency of their counter, and the fact that they found no evidence of radioactivity which could be attributed to a lanthanum daughter. In some recent work on the Ce^{137} isomers, the present authors[2] estimated that the La^{137} half-life must be longer than 10^5 yr if it decayed by K electron capture. However, spin assignments consistent with the experimental data indicated that the transition between the La^{137} and the Ba^{137} ground states should be allowed.

In the present work, La^{137} has been identified and found to decay by K electron capture. Since the half-life was found to be very long for an allowed transition with enough energy to permit K capture, further work was done on the Ce^{137} decay scheme in order to understand the apparent anomaly. This work has led to the discovery of a low-energy transition and to the addition of a new energy level below the ground state in the previous Ce^{137} decay scheme. On the basis of the spin assigned to the new ground state, electron capture decay of La^{137} would be second-forbidden.

II. IDENTIFICATION OF La^{137}

La^{137} was produced by bombardment of 880 mg of CeO_2 in the ORNL graphite reactor with an integrated flux of 1.3×10^{23} neutrons/cm^2. After dissolving the CeO_2 in nitric acid, a known amount of La^{140} tracer was added. Most of the cerium was removed from the lanthanum by extraction with tributyl phosphate. Final purification of the lanthanum fraction was accomplished by adsorption on a cation exchange column and elution under conditions which gave essentially complete separation of lanthanum from cerium and other rare earths.[3] Measurement of the La^{140} activity in the final sample showed that it contained 60% of the original lanthanum.

After the La^{140} tracer had decayed, scintillation spectrometer measurements showed the presence of x-rays with an energy of about 32 kev and the absence of gamma rays of higher energy. The intensity of these x-rays has remained constant for a period of more than six months, indicating a half-life longer than twenty years. The proportional counter pulse-height spectra in Fig. 1 were used to identify the radiation from the long-lived lanthanum source as barium K x-rays. These spectra were taken with a xenon filled counter and show the "escape"[4] peaks that result from critical absorption of x-rays in xenon with escape of Xe, $K\alpha$, or $K\beta$ x-rays from the counter.

In the upper curve of Fig. 1 taken with a Pm^{145} source, which emits Nd K x-rays, both the $K\alpha$ and the $K\beta$ lines are critically absorbed in xenon. In each case either xenon $K\alpha$ or $K\beta$ x-rays may escape resulting in a pulse height spectrum with four escape peaks. The most intense peak at 7.6 kev results from Nd $K\alpha$ absorption followed by Xe $K\alpha$ escape. The peak at 8.6 kev which results from Nd $K\beta$ absorption with Xe $K\beta$ emission is not resolved from the peak at 7.6 kev and hence only

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[4] S. C. Curran, *Beta and Gamma Ray Spectroscopy*, edited by K. Siegbahn (Interscience Publishers, Inc., New York, 1955), p. 176.