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Inelastic Scattering of Atoms. I. Intermultiplet Transitions

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Electronic-translational energy transfer processes have minute cross sections for atoms with thermally attainable kinetic energies, unless the amount of energy converted from electronic to translational form (or vice versa if the threshold permits) is rather less than 1 ev. The transfer processes of interest to chemical kinetics, therefore, involve highly restricted sets of energy levels. Two situations are commonly encountered: (1) The "two-state" case, in which two energy levels of the diatomic system cross or approach closely in energy, so that a respectable probability of resonance transfer is achieved; cases of this type almost always involve transfer of most of the excitation from one atom to the other. (2) Transitions among the multiplet levels of a given Russell-Saunders term of an atom, induced by collision with an "inert" atom. Spin-orbit coupling is the electronic interaction splitting the levels. The present work is concerned with the latter case. The "high-energy approximation," a necessary modification of the Born approximation, and various "modified adiabatic approximations," which take account of the details of angular momentum coupling during collision, are described, and practical methods of calculation considered.

I. INTRODUCTION

INELASTIC collisions between atoms may be categorized as involving ionization of electrons, rearrangement of electrons, or electronic transitions. This work is concerned with the last, and in particular with rather restricted classes of them, to be outlined shortly.

General features of the problem of inelastic scattering have been discussed by Mott and Massey,[1] and Bates, Massey, and Stewart,[2] although a number of other workers have contributed to the subject. The application of the formal scattering theory to the problem has been made in one approximation by Mittleman and Watson.[3] (The formal theory indicates procedure and steps for systematic improvement when higher-order perturbation theory is desired.) All of these workers have been concerned with the most general class of electronic transitions and in practice have restricted any applications to the simplest prototypes, usually scattering of protons and hydrogen atoms at very high relative translational energies.

The physical interactions which establish energy differences between electronic states vary greatly in strength. Associated with each type of interaction there is a critical period, which one may think of as the time necessary to establish or resolve the energy separation. This "period of electronic motion" is defined by the quantity $\tau_e = (h/\Delta E_{ij})$, where ΔE_{ij} is the energy difference between i, j of the electronic system in some nuclear configuration. Often this period may be given an intuitive physical significance on a semiclassical basis; for example, when the interaction being considered is the electrostatic interaction of electrons with the self-consistent field in an atom, one may think of the period

τ_e as that associated with motion in a "Bohr orbit"; or, when the interaction is spin-orbit coupling, the relevant period is that for the precession of the vectors L and S about their resultant, J.

When the effective time of collision interaction τ_c, as measured by the quotient a/V, where a is an effective interaction distance, and V is the relative velocity in collision, is very long compared with τ_e, then one has what is termed adiabatic behavior; the electronic motion adjusts itself to each change in the slowly varying nuclear configuration without undergoing transitions. Only small nonadiabatic coupling terms in the Hamiltonian lead to transitions; the most important of these is proportional to V, and leads to resonant effects in the transition probability only when $(\tau_e/\tau_c) \sim 1$. For energy transfers of 1 ev or more, this condition of nonadiabatic resonance is not achieved until kinetic energies far greater than the threshold energy are attained. It is easy to show that if the energy transfer exceeds ~ 0.5 ev, the transition probabilities are easily calculable by first order perturbation theory in an adiabatic approximation, and are exceedingly small, so small as to be of no practical interest, for any thermally attainable kinetic energies, even for de-excitation processes where no threshold requirements exist. The implication of this fact is that inelastic scattering processes of chemical interest are those in which the amount of energy converted to translation is less than 1 ev, in most cases far less.

When $\tau_e \gg \tau_c$, the interaction associated with τ_e does not have time to adjust adiabatically to the nuclear motion. An appropriate description is to regard the zero-order states as *adiabatic eigenfunctions* of all those interactions whose periods τ_e' are still shorter than τ_c, and to treat as transition-producing perturbations those whose periods, like τ_e, are much longer than τ_c. The potential for elastic scattering of the atoms is a well-defined "adiabatic" surface, with solutions which deviate far from the free-particle description afforded by the first Born approximation. Only in the case that

[1] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), 2nd ed., Chap. VIII.
[2] D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. (London) **A216**, 437 (1953); D. R. Bates, *ibid.* **A240**, 437 (1957); **A243**, 15 (1958).
[3] M. Mittleman and K. F. Watson, Phys. Rev. **113**, 198 (1959).

τ_c is greater than all periods τ_e' associated with interactions of the atoms, is it legitimate to employ the first Born approximation; in general, the collision is "fast" with respect to some interactions, "slow" with respect to others. More special approximations treating such situations need to be developed.

In practice, cases in which ΔE_{ij} is substantially less than 1 ev arise in two ways. (1) In a diatomic collision, energy levels of one or both atoms may be close enough that under the influence of interaction they cross or nearly cross. Resonant transfer of most of the electronic energy from one excited state to another may then occur, with little or no conversion to translational energy. The probability of transfer depends on the closeness of approach in energy of the two states involved. We may refer to this general problem as the "two-state" problem. (2) A given Russell-Saunders term of an atom is split by spin-orbit coupling into multiplet levels. Characteristically, the multiplet separations are less than 1 ev. Under the influence of a perturbing collision with an "inert" atom, transitions between levels may occur.

As a rule of thumb, $\Delta E_{ij}(R)$ may sometimes be estimated by the value at infinite separation, $\Delta E_{ij}(\infty)$, for case (2), though obviously not for case (1), where most transition occurs at the crossing region, when $\Delta E_{ij}(R) \approx 0$.

When $(\tau_e/\tau_c) \sim 1$ for a given interaction, the coupling between the electronic and nuclear motions is at resonance. The inelastic scattering cross section may then become large, and the concept of motion on a single effective surface is not strictly valid since such motion leads only to elastic scattering. Motion for the heavy-particle system is inevitably complex, involving at least two effective "elastic potentials" and a "transition potential" as well. The estimates of the inelastic cross section afforded by either the high energy approximation or the adiabatic approximation in this resonance range are too high because the repeated strong interaction of the transition-causing perturbation causes scatterings that to first order are virtually inelastic, but are elastic in second and higher orders. It would be desirable to develop an approximation which gives a better first-order perturbation estimate of the cross section, near the resonance maximum. Physically, such an approximation would represent the electrons as moving in the field of moving nuclei, in which the nuclear motion is crudely approximated, say by a classical estimate. We hope to devote some further work to such an approximation in the case of two states.

The two-state problem has been treated phenomenologically by Landau[4] and Zener,[5] and the most thorough study has been made by Stueckelberg,[6] who developed a WKB type of approximation which is valid when the motion is semiclassical, the crossing

[4] L. D. Landau, Physik. Z. Sowjetunion **2**, 46 (1932).
[5] C. Zener, Proc. Roy. Soc. (London) **A137**, 696 (1932).
[6] E. C. G. Stueckelberg, Helv. Phys. Acta **5**, 369 (1932).

point being far from the classical turning points. A cruder solution is obtained by him for the near-resonance transfer problem.

II. RELATION OF APPROXIMATIONS TO FORMAL SCATTERING THEORY

Mittleman and Watson[3] developed the formal theory of scattering for atomic systems, using as the basis for treatment the compound states made up of products of electronic wave functions for isolated atoms and free particle functions for nuclear motion. They deduced formal expressions for an "elastic" scattering potential and for the inelastic transition matrix elements, and exhibited the possibility of variational expressions for these quantities which improve on the first-order theory. Their method is practical and yields improved results over the Born approximation at very high energies. They also deduce formal expressions for the adiabatic limit, but when these are examined from the standpoint of practical calculation, they prove to be at least equivalent in the amount of labor required to the solution of the adiabatic electronic problem by nth-order perturbation theory.

It is not difficult to prove that one may use any desirable alternative set of basis functions, provided they can be uniquely correlated with the solutions for the isolated atoms as $R \to \infty$. That is, one may arbitrarily divide the Hamiltonian into a part H_E, which has as solutions the desired basis set, and an interaction part H_I, which appears in the numerator of the formal theory prescription for the propagation-with-interaction operator. The first-order estimate of the transition probability then involves the matrix element $(\Psi_f^0, H_I \Psi_i^0)$, where Ψ_i^0 and Ψ_f^0 are the initial and final states, eigenfunctions of H_E.

The formal theory gives the method for higher-order estimates of scattering cross sections, but these always involve extensive iterations of integral equations, and for systems with many partial waves to consider, as is the case in atomic scattering, such a process is not practical at present. Therefore, it is of considerable value to choose, if possible, a judicious form of the elastic Hamiltonian H_E so that a good first-order estimate of the cross section may be obtained. This is the consideration which has guided our thinking on the special problems we consider.

It is worth pointing out also that inelastic cross sections, when correctly computed in any approximation, are always larger than the true values.

III. INTERMULTIPLET TRANSITIONS IN AN ATOM

Let us assume that one atom A, say, is in a given Russell-Saunders term state, and that collisions with "inert" B (i.e., the internal electronic structure of B is not considered except for its effect as a potential; all excitations in B require very high energies) cause transitions among the multiplet levels of A. Experimentally, for example, we might consider collisional

transfer among the multiplet levels in the excited ^2P term of an alkali atom in the presence of an inert gas, or the effect of an inert gas in the deactivation transition $^2P_{1/2} \rightarrow {}^2P_{3/2}$ in a halogen (iodine is of interest in connection with kinetic studies of the recombination of iodine atoms after photodissociation). When specific reference to an example is necessary, we shall have in mind a $^2P_{3/2} \leftrightarrow {}^2P_{1/2}$ transition.

At this point, it is necessary to define for clarity's sake the names for the various kinds of angular momenta appearing in the problem. Some definitions depart from the usual notation, but as the reader will appreciate, this is unavoidable without annoying defection to the use of subscripts of subscripts.

L is electronic orbital angular momentum; it has component M_L in the space-fixed axis system, component Λ on the molecule axis if separately quantized.

S is the electron spin angular momentum, M_s and Σ its components in space and molecule-fixed axes.

J is the total electronic angular momentum, M_J and Ω its space- and molecule-fixed axis components.

N is the nuclear rotational angular momentum, M_N its space-fixed component.

K=**N**+**L** is a partial sum of electronic and nuclear rotational angular momentum which is of use in Hund's case (b) coupling in diatomic molecules, and finds similar employment here. M_K is its space-fixed axis component.

P=**N**+**J** is the total angular momentum, M_p its component in the space-fixed axis system, and Ω (necessarily) its component on the molecule axis.

Electron coordinates in space-fixed axes are (x, y, z). Those in molecule-fixed axes are (ξ, η, ζ). The nuclear coordinates we measure by R, the internuclear distance; θ, ψ, the Eulerian angles, defined, respectively, in the same way as Edmonds[7] defines the Eulerian angles β, α. With this definition, the following transformation exists between (ξ, η, ζ) and (x, y, z) for an electron:

$$\xi_i = x_i \cos\theta \cos\psi + y_i \cos\theta \sin\psi - z_i \sin\theta$$

$$\eta_i = -x_i \sin\psi + y_i \cos\psi$$

$$\zeta_i = x_i \sin\theta \cos\psi + y_i \sin\theta \sin\psi + z_i \cos\theta. \quad (1)$$

The Hamiltonian is

$$H = -(\hbar^2/2M)\nabla_R^2 - (\hbar^2/2m)\sum_i \nabla_i^2 + V(\mathbf{r}, \mathbf{R}). \quad (2)$$

Here V is the interaction potential of all particles, including the spin-orbit coupling interactions; ∇_i^2 is the Laplacian with respect to the ith electron coordinates; and ∇_R^2 the Laplacian with respect to nuclear coordinates, with electron coordinates implied fixed in the space-fixed system. M is the reduced mass of the diatomic system for relative motion. Here it is implicitly assumed that the motion of the center of mass of the system has been separately treated, and that the

centers of mass of the atoms coincide with their respective nuclei. Small corrections to the treatment of the problem, arising out of the fact of finite electronic mass and related complexity in the definition of the center of mass of the system, have been considered by Jepsen and Hirschfelder.[8] We have not concerned ourselves with their inclusion because they are small.

Physically, the limiting approximations may be roughly categorized as follows:

(1) High-energy approximation. The collision occurs in a time $\tau_c \ll \tau_s$ (spin-orbit-axial field). The collision is, however, adiabatic with respect to all other interactions except those associated with axial field perturbations and the spin-orbit-interaction. The axial perturbation introduces transitions among the zero-order eigenfunctions of J^2, M_J. The nuclear motion occurs on an effective elastic scattering surface determined by the interaction energy of the filled shells of A and B. This approximation is identical to the "distorted wave" approximation of Mott and Massey.

(2) Adiabatic approximations. The collision is slow, so that electronic states of the diatomic system for fixed nuclei make an appropriate basis set. Transitions occur from the action of nonadiabatic coupling terms involving derivatives of electronic functions with respect to nuclear coordinates. As will be seen, some of these coupling terms must be handled carefully, and modify the form of the adiabatic approximations.

IV. HIGH-ENERGY APPROXIMATION

When the atoms A and B are well isolated, we may treat them as separate systems. We shall suppose that A has n_A electrons, n_v valence electrons, and B has n_B electrons in a filled shell structure or at least a spherically symmetric electron distribution with no low-lying energy levels near the ground level. We assume B to be in its ground state $\phi_B^0(\mathbf{r})$. We shall assume a one-electron Hartree-Fock form for the atomic wave functions, and that no transition occurs in the filled shell configurations of either atom. In the theory of atomic structure, all the multiplet states $(n\Gamma L S J M_J)$, (where $n\Gamma$ specify principal features of the atomic terms in question) are constructed out of the orbitals of a given configuration $\{n_i l_i\}$, where $i=1 \ldots n_v$. The eigenfunctions $\phi_A(n\Gamma J M_J)$ are specified linear combinations of the Russell-Saunders eigenfunctions $\phi_A'(n\Gamma L S M_L M_S)$, themselves again linear combinations of the basic antisymmetrized determinants $\phi_A''(\mu\{n_i l_i; m_{l_i} m_{S_i}\})$. The last notation means that the subscript μ here implies assignment of n_v orbitals as occupied, specifying the whole ordered set of numbers $\{n_i l_i m_{l_i} m_{S_i}\}$. We may summarize the foregoing by the expression

$$\phi_A(n\Gamma J M_J) = \sum_\mu (L S M_J | \mu) \phi_A''(n\Gamma \mu). \quad (3)$$

[7] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 7.

[8] D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. **32**, 1323 (1960).

The coefficients in the expansion are determined in the theory of atomic structure.

Small differences in the calculation can arise depending on whether electronic functions for the entire system are antisymmetrized with respect to all possible electron interchanges, or only with respect to the interchanges of electrons in individual atoms. Strictly speaking, the former procedure is correct, including the exchange interactions between A and B. In the development given here, we ignore the complete antisymmetrization. It may be included in an obvious but tedious extension. When final results are given, we shall modify them to include the results of exchange.

Accordingly, we represent the electronic states for the system as

$$\phi_{AB}(n\Gamma JM_J) = \phi_A(n\Gamma JM_J)\phi_B^0. \qquad (4)$$

When A and B interact at a finite distance R, there is a self-consistent field interaction energy $V_{core}^{AB}(R)$, which is spherically symmetric and independent of the values J, M_J. We may evaluate it as the average of the SCF interaction energy of A and B in states J, M_J, over all angles θ, ψ, and the possible values of J, M_J. This interaction energy is not small. It is diagonal in J, M_J, and, therefore, leads to elastic scattering. Because it involves the filled-shell interactions, it is usually considerably larger than the remaining "elastic" interactions, which are specifically angle dependent

and J, M_J dependent, though diagonal in J. In addition, the interaction between A and B has matrix elements which are nondiagonal in J and M_J, and it is these which can lead to inelastic scattering.

The potential $V_{core}^{AB}(R)$ represents mutual polarizations of the atoms, and it is of course true that the one-electron orbitals are polarized as well, having a different self-consistent field from that in the free atom. However, the conditions of the approximation are, that the wave functions to be used are the zero-order functions, unperturbed by the axial field. If perturbations on the functions by the axial field are considered, this amounts to moving toward an adiabatic approximation. It is essential to the high energy approximation that the electronic functions are the zero-order functions of the isolated atoms, and that $V_{core}^{AB}(R)$ is the average first-order perturbation energy of the A-B interaction, diagonal in J, M_J, and averaged over J, M_J and space orientations θ, ψ; the nondiagonal elements of the interaction energy lead to inelastic scattering if they are nondiagonal in J. Additional elastic scattering arises from terms diagonal in J but not in M_J, but we do not consider these here.

The basic difference between this approximation and the first Born approximation is that the size of $V_{core}^{AB}(R)$ is taken into account, and the radial functions for the nuclear motion are solutions to the problem of motion in the potential V_{core}^{AB}.

The expression for $V_{core}^{AB}(R)$, then, is

$$V_{core}^{AB}(R) = [1/4\pi \sum_J (2J+1)] \sum_{J,M_J} \int_0^\pi \int_0^{2\pi} V_{AB}(n\Gamma JM_J; R, \theta, \psi) \sin\theta d\theta d\psi, \qquad (5)$$

where $V_{AB}(n\Gamma JM_J; R, \theta, \psi)$ is the interaction energy of A and B at R, θ, ψ in $(n\Gamma JM_J)$:

$$V_{AB}(n\Gamma JM_J) = (n\Gamma JM_J | H_e - \epsilon_A^0(n\Gamma JM_J) - \epsilon_B^0 | n\Gamma JM_J),$$

$$= \sum_\mu (n\Gamma JM_J/\mu)\{(Z_A Z_B e^2/R) - \sum_{i=1}^{\eta_A}[\phi_{i\mu}(1)|Z_B e^2/r_{B1}|\phi_{i\mu}(1)]$$

$$- \sum_{j=1}^{\eta_B}[\phi_j(1)|Z_A e^2/r_{A1}|\phi_j(1)] + \sum_{i=1}^{\eta_A}\sum_{j=1}^{\eta_B}[\phi_{i\mu}(1)\phi_j(2)|e^2/r_{12}|\phi_{i\mu}(1)\phi_j(2)]$$

$$- \sum_{\substack{i=1 \\ (\text{same spin})}}^{n_A}\sum_{j=1}^{n_B}[\phi_{i\mu}(1)\phi_j(2)|e^2/r_{12}|\phi_j(1)\phi_{i\mu}(2)]\}.^{8a} \qquad (6)$$

This expression already contains the results of exchange, as may readily be seen in the presence of the exchange integrals with orbitals of the same spin. Derivation following the simple product function quoted in Eq. (4) would lead to a result without the exchange integrals. In the above expressions, H_e is the electronic Hamiltonian, $\epsilon_A^0(n\Gamma JM_J) + \epsilon_B^0$ the energy of the

isolated atoms; $\varphi_{i\mu}$ is the ith one-electron orbital in the μth antisymmetrized determinant $\phi_A''(\mu)$; φ_j is the jth one-electron orbital in ϕ_B^0.

An alternative way to obtain $V_{core}^{AB}(R)$ could be to employ experimental values obtained, say, from accurate elastic scattering. Such information is not presently available in the region of interest. High-

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[8a] Equation (6) is not correct because it neglects overlap of orbitals on different atoms; it is necessary to include the overlap to get reliable results for V_{core}^{AB}.

energy molecular beam data deal with portions of the curve too high in energy for the kinetic energies we are considering, in the thermally accessible range. Second, even if such potentials were available, they actually include adiabatic effects in the polarization. Some preliminary computed results show that an accurate correlation between the magnitude of $V_{core}^{AB}(R)$ and the magnitude of the interaction matrix element, to be discussed shortly, is vital to the calculations; variations of 5% to 10% in the location of the classical turning point on $V_{core}^{AB}(R)$, with the same value for the interaction matrix element as a function of R, can produce as much as 200 to 300% variation in the inelastic scattering cross section. Therefore, it seems desirable to use the same approximation to calculate both $V_{core}^{AB}(R)$ and the interaction matrix elements, rather than two unrelated calculations, or estimates.

The interaction matrix elements are

$$V_{int}^{AB}(J'M_J'JM_J; R, \theta, \psi)$$
$$= (n\Gamma J'M_J' | H_e | n\Gamma JM_J). \quad (7)$$

There are, of course, other perturbations, leading in first order to elastic scattering, arising from matrix elements diagonal in J:

$$V_{int}^{AB}(JM_J'M_J; R, \theta, \psi) = (n\Gamma JM_J' | H_e | n\Gamma JM_J);$$
$$(8a)$$

$$V_{int}^{AB}(JM_J; R, \theta, \psi) = V_{AB}(n\Gamma JM_J; R, \theta, \psi)$$
$$- V_{core}^{AB}(R); \quad (8b)$$

but, since we are not interested in the detailed elastic scattering, we neglect them.

We now treat the nuclear motion. The total Hamiltonian appears as a second-order differential operator in the nuclear coordinates R, θ, ψ, and as a matrix in the electronic eigenfunction vector space, with the basis $\{\phi_{AB}(n\Gamma JM_J)\}$:

$$H = [- (\hbar^2/2M)\nabla_R^2 + V_{core}^{AB}(R)]\mathbf{1} + \mathbf{\epsilon}^0$$
$$+ \mathbf{V}_{int}^{AB}(R, \theta, \psi). \quad (9)$$

Here $\mathbf{1}$ is the unit matrix, $\mathbf{V}_{int}^{AB}$ is a matrix with the elements quoted in Eqs. (7) and (8), and $\mathbf{\epsilon}^0$ is the diagonal matrix with the elements $\epsilon^0(n\Gamma J) = \epsilon_A^0(n\Gamma J) + \epsilon_B^0$. If the general solution Ψ is written as a vector in the electronic basis set,

$$\Psi = \sum_{JM_J} \phi_{AB}(n\Gamma JM_J) \{ \sum_{NM_N} a(n\Gamma JM_J NM_N) F(n\Gamma JN; R) P_N^{M_N}(\cos\theta) \exp(iM_N\psi/R) \}, \quad (10)$$

a set of coupled differential equations for the functions F results. This approximation is the same as the "distorted wave" approximation of Mott and Massey[1] and Bates, Massey, and Stewart.[2] For the purpose of clarity we prefer, however, to use the formal theory of scattering as the framework for calculating the cross section.

In the formal theory, initial and final states are presumed eigenfunctions of a zero-order Hamiltonian H_E, which in our case is the matrix operator

$$H_E = [- (\hbar^2/2M)\nabla_R^2 + V_{core}^{AB}(R)]\mathbf{1} + \mathbf{\epsilon}^0. \quad (11)$$

The cross section for scattering into any final state is proportional to the absolute square of the transition matrix element T_{fi} defined as

$$T_{fi} = (\Psi_f, H_I \Psi_i^{(+)}), \quad (12)$$

where Ψ_f is the properly normalized final state, and H_I is the interaction Hamiltonian, which in our case is

$$H_I = \mathbf{V}_{int}^{AB}(R, \theta, \psi). \quad (13)$$

The $\Psi_i^{(+)}$ is a state prepared from the initial state Ψ_i by summing up the results of all orders of interactions with H_I, separated by propagation with H_E between interactions. An integral equation exists for $\Psi_i^{(+)}$; it is

$$\Psi_i^{(+)} = \Psi_i + (1/E + i\epsilon - H_E) H_I \Psi_i^{(+)}. \quad (14)$$

The meaning of this formal expression is explained in the paper by Lippmann and Schwinger,[9] for example. The first approximation to the scattering is given, then, by the substitution of Ψ_i for $\Psi_i^{(+)}$,

$$T_{fi} = (\Psi_f, H_I \Psi_i); \quad (15)$$

Ψ_i is properly normalized (the normalization will be given later) and its detailed form is determined by boundary conditions in the elastic scattering problem.

Eigenfunctions to the equation

$$H_E \Psi = E\Psi \quad (16)$$

are composed of linear combinations of solutions of the form

$$\chi(n\Gamma JM_J NM_N)$$
$$= (C/R)\phi_{AB}(n\Gamma JM_J) E(n\Gamma JN; R) P_N^{M_N}(\cos\theta)$$
$$\times \exp(iM_N\psi). \quad (17)$$

The value of the constant C will be discussed later; F satisfies the equation

$$- (\hbar^2/2M)(d^2F/dR^2)$$
$$+ [V_{core}^{AB}(R) + N(N+1)\hbar^2/2MR^2]F$$
$$= [E - \epsilon^0(n\Gamma J)]F, \quad (18)$$

and it has the property of being everywhere finite. Asymptotically, as $R \rightarrow \infty$, we take it to be

$$\lim_{R \to \infty} F = [\sin(kR - \tfrac{1}{2}N\pi + \delta_N)]/k, \quad (19)$$

[9] B. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).

where k satisfies the relation

$$(\hbar^2/2M)k^2 = E - \epsilon^0(n\Gamma J). \qquad (20)$$

The final states we consider are eigenfunctions χ. The initial state will be a specified linear combination of them. It may be found by solving the elastic scattering problem in the usual fashion. The result is

$$\Psi_i = (1/\mathbb{U}^{\frac{1}{2}}R)\phi_{\mathrm{AB}}(n\Gamma JM_J)\Big[\sum_N (2N+1)F(n\Gamma JN; R)P_N^0(\cos\theta)\exp i(N\pi/2 + \delta_N)\Big]. \qquad (21)$$

It will be found that this function has the following asymptotic behavior for $R\to\infty$,

$$\lim_{R\to\infty}\Psi_i = (1/\mathbb{U}^{\frac{1}{2}})\phi_{\mathrm{AB}}(n\Gamma JM_J)\big[\exp(ikR\cos\theta) + \exp(ikR)[f(\theta)/R]\big], \qquad (22)$$

and, therefore, it has the property of being normalized in volume $\mathbb{U}$. A properly normalized final state is so defined that the constant C takes the value

$$C = (1/\mathbb{U})^{\frac{1}{2}}[(2N'+1)(N'-M_{N'})!/4\pi(N'+M_{N'})!].(23)$$

It should be noted that this formulation for the final state is for use only in connection with evaluating the matrix element T_{fi}; the asymptotic form for inelastically scattered waves must of course contain only the outgoing wave e^{ikR}/R, and a calculation of the propagated state $\Psi_i^{(+)}$ will show such behavior.

The cross section for scattering from J, M_J to the partial wave final state $(n\Gamma J'M_J'N'M_N')$ is given by

$$\sigma(n\Gamma, JM_JJ'M_J'N'M_N')$$
$$= (M^2k_f\mathbb{U}^2/4\pi^2\hbar^4k_i)\,|\,T_{fi}(n\Gamma JM_JJ'M_J'N'M_N')\,|^2. \qquad (24)$$

We may obtain the total cross section by evaluating the sum over all values of N' and M_J', and averaging over all M_J:

$$\sigma(n\Gamma, J\to J')$$
$$= (1/2J+1)\sum_{M_J}\sum_{M_J'}\sum_{N'}\sigma(n\Gamma, JM_J, J'M_J'N'M_N'). \qquad (25)$$

The selection rules, are in general,

$$M_J'-M_J = 0, \pm1, \pm2; \qquad M_{N'}+M_J' = M_J;$$

$$N' = N, N\pm2. \qquad (26)$$

As an example, we shall work out in somewhat greater detail the expression for $\sigma(1^2P, \frac{1}{2}\to\frac{3}{2})$ in an alkali atom, say, colliding with a rare gas atom. (We assume the configuration $2p$ for the outer electron.) The electronic matrix elements may all be expressed in terms of two simple interaction integrals; Let $p\pi$ be a real $2p$ orbital perpendicular to the internuclear axis, and let $p\sigma$ be the $2p$ orbital along it. Define

$$V_\pi(R) = \int p\pi(1)H_{\mathrm{int}}p\pi(1)d\tau_1; \qquad (27a)$$

$$V_\sigma(R) = \int p\sigma(1)H_{\mathrm{int}}p\sigma(1)d\tau_1. \qquad (27b)$$

The H_{int} includes the exchange interaction if exchange is desired. The matrix elements $V_{\mathrm{int}}^{\mathrm{AB}}(R, \theta, \psi)$ then turn out to be

$$\left(\begin{matrix}3 & 3\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}1 & 1\\2 & 2\end{matrix}\right) = [(V_\sigma-V_\pi)(6)^{\frac{1}{2}}]P_2'(\cos\theta)\exp(-i\psi) = \left(\begin{matrix}1 & \bar{1}\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}3 & \bar{3}\\2 & 2\end{matrix}\right)$$

$$\left(\begin{matrix}3 & 1\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}1 & \bar{1}\\2 & 2\end{matrix}\right) = [-(V_\sigma-V_\pi)/\sqrt{2}]P_2'(\cos\theta)\exp(-i\psi) = \left(\begin{matrix}1 & 1\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}3 & \bar{1}\\2 & 2\end{matrix}\right)$$

$$\left(\begin{matrix}3 & 3\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}1 & \bar{1}\\2 & 2\end{matrix}\right) = [(V_\sigma-V_\pi)(6)^{\frac{1}{2}}]P_2^2(\cos\theta)\exp(-2i\psi) = -\left(\begin{matrix}1 & 1\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}3 & \bar{3}\\2 & 2\end{matrix}\right) \qquad (28)$$

$$\left(\begin{matrix}3 & 1\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}1 & 1\\2 & 2\end{matrix}\right) = [-2(V_\sigma-V_\pi)/3\sqrt{2}]P_2^0(\cos)\theta = -\left(\begin{matrix}3 & \bar{1}\\2 & 2\end{matrix}\Big|V_{\mathrm{int}}^{\mathrm{AB}}\Big|\begin{matrix}1 & \bar{1}\\2 & 2\end{matrix}\right).$$

These matrix elements lead to nonvanishing integrals for $N'=N$, $N\pm2$. It is easily seen that the final result will contain the elastic phase shifts in the initial state, but not those of the final state. The necessary radial integrals are all of the form

$$\int_0^\infty F(n\Gamma J'N'; R)[V_\sigma(R) - V_\pi(R)]F(n\Gamma JN; R)dR.$$

$$(29)$$

We shall defer until later a discussion of practical calculations in this approximation.

V. ADIABATIC APPROXIMATIONS

A. Approximation (A)

The electronic basis vectors for the first adiabatic approximation are eigenfunctions of the complete electronic Hamiltonian $H_e(\mathbf{r}, \mathbf{R})$ in the molecule-fixed coordinate system. Perturbations resulting from nuclear motion, both radial and angular, couple the states. Angular momentum couplings have both elastic and inelastic effects; the elastic parts dominate as $R\to\infty$ and rotational angular momentum increases, and represent the physical fact that adiabatic "following" of the diatomic axis does not occur for distant collisions. The modified adiabatic approximation presented here takes account of this partial following, and brings the approximation to a form which gives a valid description for "slow" collisions.

The Hamiltonian for electron motion in the space-fixed axis system and the relative nuclear motion is

$$H = -(\hbar^2/2M)\nabla_R^2 - (\hbar^2/2m)\sum_i \nabla_i^2 + V(\mathbf{r}, R). \quad (30)$$

Derivatives with respect to the nuclear coordinates are to be performed holding the space-fixed electron coordinates (x_i, y_i, z_i) fixed, and supposing their spins quantized with respect to the Z axis. If the electronic Hamiltonian is to be written in molecule-fixed coordinates (ξ_i, η_i, ζ_i) and spins are quantized with respect to the diatomic axis, and derivatives with respect to nuclear coordinates R, θ, ψ are taken holding electrons fixed in the molecule-fixed system, the Hamiltonian must be appropriately transformed. The general lines of the transformation are given, for example, by Kronig.[10] The resulting transformed Hamiltonian is

$$H' = H_e(\xi_i, \eta_i, \zeta_i, R) - (\hbar^2/2MR^2)(\partial/\partial R)[R^2(\partial/\partial R)]$$

$$- (\hbar^2/2MR^2)\{(1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)]$$

$$+ (1/\sin^2\theta)[(\partial/\partial\psi) - (i\cos\theta/\hbar)J_\zeta]^2\}$$

$$+ (1/2MR^2)[J_\xi^2 + J_\eta^2 - J_+Q_+ - J_-Q_-], \quad (31)$$

where

$$J_\pm = J_\xi \pm iJ_\eta;$$

$$Q_\pm = \hbar[\mp(\partial/\partial\theta) + (i/\sin\theta)(\partial/\partial\psi) + (\cot\theta/\hbar)J_\zeta], \quad (32)$$

[10] R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, New York, 1930), pp. 6–16, 40–44.

and $H_e(\mathbf{r}, R)$ expressed in the coordinates (ξ, η, ζ) is only a parametric function of R. Let us now define the functions $\phi(n\Gamma\Omega; \mathbf{r}, R)$, eigenfunctions of H_e and J_ζ:

$$H_e(\mathbf{r}, R)\phi(n\Gamma\Omega; \mathbf{r}, R) = \epsilon(n\Gamma\Omega; R)\phi(n\Gamma\Omega; \mathbf{r}, R); \quad (33)$$

$$J_\zeta\phi(n\Gamma\Omega; \mathbf{r}, R) = \Omega\hbar\phi(n\Gamma\Omega; \mathbf{r}, R); \quad (34)$$

$H_e(\mathbf{r}, R)$ includes the spin-orbit interaction. Let $\mathcal{K}(PM_P\Omega; \theta, \psi)$ be functions which satisfy the equations

$$\{(1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)]$$

$$+ (1/\sin^2\theta)[(\partial/\partial\psi) - i\Omega\cos\theta]^2\}\mathcal{K}$$

$$= -[P(P+1) - \Omega^2]\mathcal{K}. \quad (35)$$

Kronig[10] discusses these functions. They are normalized to unity when integrated over θ, ψ, and have the property

$$\mathcal{K}(P, M_P, -\Omega; \theta, \psi) = (-1)^{P-\Omega}\mathcal{K}(PM_P\Omega; \theta-\pi, \psi); \quad (36)$$

they are Jacobi polynomials in $\cos\theta$ with appropriate phases, multiplied by $\exp(iM_P\psi)$. We wish to use the representations of finite rotations defined in Edmonds[11] and having the symbol $d_{M_P\Omega}^P(\theta)$; the connecting definition is

$$\mathcal{K}(pM_P\Omega; \theta, \psi)$$

$$= [(2P+1)/4\pi]^{\frac{1}{2}}d_{M_P\Omega}^P(\theta)\exp(iM_P\psi). \quad (37)$$

The angular matrix elements of $Q_\pm$ are of interest; the only nonvanishing elements are

$$(PM_P\Omega\pm1|Q\pm|PM_P\Omega)$$

$$= \hbar[(P\pm\Omega+1)(P\pm\Omega)]^{\frac{1}{2}}. \quad (38)$$

The simple adiabatic approximation (called the "perturbed stationary states" approximation by Mott and Massey[1] and Bates, Massey, and Stewart[2]) consists of using as the zero-order eigenfunctions the products

$$\psi = (1/R)\phi(n\Gamma\Omega; \mathbf{r}, R)\mathcal{K}(PM_P\Omega; \theta, \psi)f(n\Gamma P\Omega; R)$$

$$(39)$$

and in neglecting the terms in $d\phi/dR$ and those arising from the last term in the Hamiltonian of Eq. (31). f satisfies the equation

$$-(\hbar^2/2M)(d^2f/dR^2)$$

$$+ [\epsilon(n\Gamma\Omega; R) + (\hbar^2/2MR^2)(P(P+1) - \Omega^2)]f = Ef.$$

$$(40)$$

The neglected terms lead to coupling between different states. The validity of approximation depends on their magnitude. At very large distances, the simple adiabatic electronic states tend to unperturbed atomic eigenfunctions, but they are rotating with the diatomic

[11] A. R. Edmonds, see footnote 7, Secs. 4.2–4.7.

axis. Obviously, such a basis set is an unrealistic one as $R \to \infty$. Intuitively, one expects that physically appropriate states are the "uncoupled" functions which form the basis of the high energy approximation; certainly the initial state must be so described, and a correct treatment of the collision should give an account of the onset of angular momentum coupling, with its resultant "following" of the diatomic axis by the electron cloud. The simple adiabatic approximation is, therefore, not suitable as $R \to \infty$, this fact seems to have been the reason for its rejection in the more recent work of Bates.[12] However, the adiabatic approximation may be revised in a manner which takes account of the partial "following."

Before and after collision, atom A has a definite electronic angular momentum quantum number J and a space-fixed z-component M_J. We are not concerned with the final value of M_J, but that of J. The collision is elastic if $J_{\text{final}} = J_{\text{initial}}$, inelastic otherwise. What are of interest are the "intermanifold" transitions, in which not merely M_J, but J, is finally altered.

The perturbation in the last square brackets of Eq. (31) has both *inter-* and *intra*manifold coupling effects. In fact, as $R \to \infty$, since J then becomes a good quantum number, it is obvious that the *inter*manifold effects tend to zero, while the *intra*manifold effects remain and couple the adiabatic states for large R and P. From a physical point of view, we may expect that this perturbation will be diagonal in an "uncoupled" representation.

As $R \to \infty$, the adiabatic functions may be correlated uniquely with limiting values of J. We shall designate each manifold by its limiting J value

$$\lim_{R \to \infty} \phi(n\Gamma(J)\Omega; \mathbf{r}, R) = \phi^{(\infty)}(n\Gamma J\Omega; \mathbf{r}). \quad (41)$$

In the "coupled" description, the basis states as $R \to \infty$ are the products

$$\phi^{(\infty)}(n\Gamma J\Omega; \mathbf{r})\mathfrak{X}(PM_p\Omega; \theta, \psi), \quad (42)$$

but in an "uncoupled" description they are

$$\phi^{(\infty)}(n\Gamma JM_J; \mathbf{r})Y(NM_N; \theta, \psi), \quad (43)$$

where $Y(NM_N; \theta, \psi)$ is the properly defined spherical harmonic. The relation between these basis sets is obtained by using the properties of the representations of finite rotation:

$$\phi(n\Gamma JM_J; \mathbf{r})Y(NM_N; \theta, \psi) = (-1)^{M_N}\sum_{\Omega}\sum_{P}\left[\left(\frac{2N+1}{2P+1}\right)^{\frac{1}{2}}(NM_N JM_J | NJPM_p)(NJP\Omega | N0J\Omega)\right]\phi(n\Gamma J\Omega; \mathbf{r})$$

$$\times \mathfrak{X}(PM_p\Omega; \theta, \psi); \quad (44)$$

$$\phi(n\Gamma J\Omega; \mathbf{r})\mathfrak{X}(PM_p\Omega; \theta, \psi)$$

$$= \sum_{M_J}\sum_{N}(-1)^{M_N}\left[\left(\frac{2N+1}{2P+1}\right)^{\frac{1}{2}}(NJPM_p | NM_N JM_J)(N0J\Omega | NJP\Omega)\right]\phi(n\Gamma JM_J; \mathbf{r})Y(NM_N; \theta, \psi). \quad (45)$$

The Hamiltonian is diagonal in P, M_P, and, therefore, whether or not the uncoupling of states succeeds in diagonalizing the perturbing terms of the simple adiabatic approximation as $R \to \infty$, depends on the accomplishment of that diagonalization by the transformation

$$\sum_{\Omega=-J}^{J}(NJP\Omega | N0J\Omega)\phi(n\Gamma J\Omega; \mathbf{r})\mathfrak{X}(PM_p\Omega; \theta, \psi). \quad (46)$$

There are $2J+1$ such combinations for each J, P, one for each of the possible consistent values of N such that $N + J = P$. It is easily shown directly that the Hamiltonian is indeed diagonalized by such transformations, and for given J, P, there are $2J+1$ eigenvalues,

$$\epsilon \to \epsilon^0(n\Gamma J) + [N(N+1)\hbar^2/2MR^2]. \quad (47)$$

This transformation indicates a procedure for treating the coupling at finite R. The states $\phi[n\Gamma(J)\Omega; \mathbf{r}, R]$ all have the energy $\epsilon^0(n\Gamma J)$ as $R \to \infty$. For a

[12] D. R. Bates, Proc. Roy. Soc. (London) **A245,** 299 (1958); Proc. Phys. Soc. (London) **A73,** 227 (1959).

given J, P, the $(2J+1) =$ dimensional space spanned by the products

$$\phi[n\Gamma(J)\Omega; \mathbf{r}, R]\mathfrak{X}(PM_p\Omega; \theta, \psi) \quad (48)$$

is called the *manifold* of J for the given total angular momentum P. For general values of R, P we elect to use as the zero-order basis the "electronic-rotational" functions $Z[n\Gamma(J)P\mu; \mathbf{r}, R, \theta, \psi]$, defined by the transformation which diagnalizes the electronic-rotational Hamiltonian H_A *within a given manifold*;

$$H_A = H_e(\mathbf{r}, R) - (\hbar^2/2MR^2)$$

$$\times \left[(1/\sin\theta)\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + (1/\sin^2\theta)\left(\frac{\partial}{\partial\psi} - (i/\hbar)\cos\theta J_\zeta\right)^2\right]$$

$$+ (1/2MR^2)[J_\xi^2 + J_\eta^2 - J_+Q_+ - J_-Q_-]. \quad (49)$$

It is evident that the functions Z_μ are identical with the linear combinations of Eq. (46) as $R \to \infty$, and are, therefore, also then related to the uncoupled eigen-

functions as follows:

$$\phi(n\Gamma M_J; \mathbf{r})\, Y(NM_N; \theta, \psi)$$

$$= (-1)^{M_N}\sum_P (NM_N JM_J | NJPM_p)\left(\frac{2N+1}{2P+1}\right)^{\frac{1}{2}}$$

$$\times Z[n\Gamma P(J)\mu(N_\mu)].\quad (50)$$

At arbitrary R the functions Z_μ which form this new basis are thus defined by a separate matrix diagonalization for each manifold $(n\Gamma JP)$. The limiting behavior at $R\to\infty$ links each Z_μ within the manifold with a value of N, (N_μ), and at strong coupling with a value of Ω. Over the whole range neither quantum number is valid and we merely use the index μ. The associated energy eigenvalues are $\lambda[n\Gamma P(J)\mu; R]$.

Transitions $(n\Gamma JP \to n\Gamma J'P)$ take place by virtue of the remaining perturbations (H_I):

(1) the electrorotational Hamiltonian H_A has *inter*manifold matrix elements which genuinely represent inelastic scattering due to angular "drag effects."

(2) There are intermanifold terms in $(\partial\phi/\partial R)$.

(3) There are intramanifold terms in $(\partial Z_\mu/\partial R)$ which arise from the fact that the coefficients of transformation to the Z_μ representation are functions of R.

The general solution Ψ to a scattering problem may be expanded in the products

$$\chi = (1/R)Z[n\Gamma P(J)\mu; \mathbf{r}, R, \theta, \psi]F[n\Gamma P(J)\mu; R],$$
$$(51)$$

where $F_\mu(R)$ satisfies the equation

$$-(\hbar^2/2M)(d^2F_\mu/dR^2)+\lambda_\mu(R)F_\mu = EF_\mu;\quad (52)$$

in the limit of weak coupling,

$$\lambda_\mu \to \epsilon^0(n\Gamma J)+[N_\mu(N_\mu+1)\hbar^2/2MR^2],\quad (53)$$

and for strong coupling,

$$\lambda_\mu \to \epsilon(n\Gamma\Omega; R)+[P(P+1)-\Omega^2]\hbar^2/2MR^2.\quad (54)$$

The functions F_μ are those solutions of (52) which are everywhere finite, and in the limit of large R have the asymptotic behavior

$$\lim_{R\to\infty} F_\mu(R) = (1/k_s)\sin(k_J R+N_\mu\pi/2+\delta_\mu).\quad (55)$$

The basis eigenvectors Z_μ may be expressed as normalized linear combinations,

$$Z[n\Gamma P(J)\mu]=\sum_\Omega A[n\Gamma P(J)\mu\Omega; R]$$

$$\times \phi[n\Gamma(J)\Omega; \mathbf{r}, R]\mathcal{K}(PM_p\Omega; \theta, \psi).\quad (56)$$

Expressions for the eigenvalues λ_μ and coefficients $A_{\mu\Omega}$ are readily obtained by rapid diagonalization of matrices of small dimensions; for machine computation this problem does not complicate the calculation, since other features of a scattering calculation require detailed results for each value of the total angular mo-

mentum in any case (i.e., the functions F_μ). In the basis set of the simple adiabatic approximation, the intramanifold matrix elements of H_A are

$$[n\Gamma(J)P\Omega | H_A | n\Gamma(J)P\Omega]=\epsilon(n\Gamma\Omega; R)$$
$$+[P(P+1)-\Omega^2]\hbar^2/2MR^2$$
$$+(1/2MR^2)\{\phi[n\Gamma(J)\Omega] | J^2 | \phi[n\Gamma(J)\Omega]\};\quad (57a)$$
$$[n\Gamma(J)P\Omega\pm1 | H_A | n\Gamma(J)P\Omega]$$
$$= -(\hbar/2MR^2)[(P\pm\Omega+1)(P\mp\Omega)]^{\frac{1}{2}}$$
$$\times\{\phi[n\Gamma(J)\Omega\pm1] | J\pm | \phi[n\Gamma(J)\Omega]\}.\quad (57b)$$

All inelastic transitions are *inter*manifold transitions. These can arise only from perturbations of types (1) and (2) mentioned earlier; those of type (3) vanish because of the orthogonality of functions $\phi[n\Gamma(J)\Omega]$ of different manifolds.

There remains only the problem of nuclear motion in the initial and final states. The initial state is to represent the elastic scattering, and asymptotically has the form

$$\Psi_i \to \phi(n\Gamma JM_J)\exp(ik_i R\cos\theta)$$
$$+[\exp(ik_i R)/R]\sum_{M_J'}\phi(n\Gamma JM_J')f(JM_J'; \theta, \psi).\quad (58)$$

The plane wave may be expanded under asymptotic conditions in the functions Z_μ:

$$\lim_{R\to\infty}\phi(n\Gamma JM_J)\exp(ik_i R\cos\theta)$$

$$= (1/k_i R)\sum_N\sum_P (4\pi/2P+1)^{\frac{1}{2}}(2N_\mu+1)$$

$$\times\exp(iN_\mu\pi/2)(N_\mu 0 JM_J | N_\mu JPM_J)$$

$$\times Z[n\Gamma P(J)\mu(N_\mu)]\sin(k_i R+N_\mu\pi/2).\quad (59)$$

The general elastic scattering solution Ψ_i may be expanded at any value of R, as

$$\Psi_i = (1/R)\sum_P\sum_\mu \alpha[n\Gamma P(J)\mu]F_\mu(R)Z_\mu(\mathbf{r}, R, \theta, \psi).\quad (60)$$

Comparing coefficients in the asymptotic limit $R\to\infty$, and applying the condition of outgoing waves only in the scattered waves, one obtains

$$\alpha[n\Gamma P(J)\mu]=(4\pi/2P+1)^{\frac{1}{2}}(2N_\mu+1)$$

$$\times(N_\mu 0 JM_J | N_\mu JPM_J)\exp(i\delta_\mu+iN_\mu\pi/2).\quad (61)$$

A normalizing factor $(\mathcal{U})^{-\frac{1}{2}}$ is included in the initial state to normalize it to unity in a box of volume $\mathcal{U}$. The properly normalized final states are

$$\Psi_f = (1/\mathcal{U}^{\frac{1}{2}}R)Z_\mu(\mathbf{r}, R, \theta, \psi)F_\mu(R).\quad (62)$$

The transition matrix elements for $(n\Gamma; JM_J \to PJ'\mu')$ are

$$T(n\Gamma; JM_J \to PJ'\mu')=(1/\mathcal{U})[\Psi_f(\mu', PJ'), H_I\Psi_i].\quad (63)$$

and the cross section for that transition is

$$\sigma(n\Gamma; JM_J \rightarrow PJ'\mu')$$
$$= (M^2 k_{J'}/4\pi^2\hbar^4 k_J) \mid T(n\Gamma; JM_J \rightarrow PJ'\mu') \mid^2. \quad (64)$$

The total cross section is obtained by summing over all μ' within the manifold of J', P, summing over P, and averaging over M_J,

$$\sigma(J \rightarrow J') = (1/2J+1) \sum_{M_J} \sum_P \sum_{\mu'} \sigma(n\Gamma; JM_J \rightarrow J'P\mu').$$
$$(65)$$

B. Approximation (B)

In approximation A, it was implicitly assumed that spin-orbit interaction is strong enough to couple the electron spin to the diatomic axis if the axial field is able to couple the orbital momentum. However, many cases arise in which the spin-orbit coupling is not large, and one should consider a "Hund's case (b)" approximation in which the electronic polarization by the axial field occurs adiabatically, but spins remain quantized in a space-fixed axis system. As will be seen, development of the zero-order Hamiltonian in such an approximation leads not only to elastic scattering, but to inelastic scattering as well, because the spin-orbit interaction is not a part of the zero-order Hamiltonian, and is to be treated as a perturbation.

A brief physical description of a collision will be helpful in understanding the mathematical analysis and in approximation (C). When a collision commences, axial fields are substantially weaker than the spin-orbit interactions, and the slight partial following of the diatomic axis by the orbital angular momentum which occurs is accompanied by strong coupling of spin and orbital momenta. As the axial field increases, however, for rapid passage and strong axial fields and orbital angular momentum is wrenched free from the spin and reoriented. Only at the end of collision is the spin-orbit interaction again able to restore the separation into eigenstates of J and its z component.

A discussion of the role of the zero-order Hamiltonian in producing inelastic scattering is only appropriate after it has been defined. The Hamiltonian for approximation (B) is obtained by a transformation of the electron coordinates to molecule-fixed axes, as in Sec. A, but the spin transformation is omitted and the electronic states have characteristic values of M_s. The Hamiltonian is, then,

$$H'' = H_e^0(\xi, \eta, \zeta; R) + H_{s.o.}(\xi, \eta, \zeta, m_s; R, \theta, \psi)$$
$$- (\hbar^2/2MR^2)(\partial/\partial R)[R^2(\partial/\partial R)]$$
$$- (\hbar^2/2MR^2)\{(1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)]$$
$$+ (1/\sin^2\theta)[(\partial/\partial\psi) - (i/\hbar)\cos\theta L_\zeta]^2\}$$
$$+ (1/2MR^2)[L_\xi^2 + L_\eta^2 - L_+U_+ - L_-U_-], \quad (66)$$

where

$$L_\pm = L_\xi \pm iL_\eta;$$
$$U_\pm = \hbar[\mp(\partial/\partial\theta) + (i/\sin\theta)(\partial/\partial\psi) + (\cot\theta/\hbar)L_\zeta], \quad (67)$$

H_e^0 is the electronic Hamiltonian exclusive of spin-orbit interaction, and $H_{s.o.}$ is the spin-orbit interaction itself. Derivatives with respect to R, θ, ψ, are understood to be taken with ξ, η, ζ fixed.

We now define an operator H_B, analogous in this approximation to H_A of approximation (A):

$$H_B = H_e^0 - (\hbar^2/2MR^2)\{(1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)]$$
$$+ (1/\sin^2\theta)[(\partial/\partial\psi) - (i/\hbar)\cos\theta L_\zeta]^2\}$$
$$+ (1/2MR^2)[L_\xi^2 + L_\eta^2 - L_+U_+ - L_-U_-]. \quad (68)$$

The matrix elements of H_B are readily defined in the representation provided by the vectors

$$\phi[n\Gamma M_s(L)\Lambda; \mathbf{r}, R]\mathfrak{IC}(KM_k\Lambda; \theta, \psi), \quad (69)$$

where ϕ is an eigenfunction of H_e^0, L_ζ, S, and M_s:

$$H_e^0\phi(n\Gamma M_s\Lambda; \mathbf{r}, R) = \epsilon'(n\Gamma\Lambda; R)\phi(n\Gamma M_s\Lambda); \quad (70)$$

$$L_\zeta\phi = \Lambda\hbar\phi. \quad (71)$$

The $\mathfrak{IC}(KM_k\Lambda; \theta, \psi)$, entirely analogous to $\mathfrak{IC}(PM_p\Omega; \theta, \psi)$ in approximation (A), satisfies the equation

$$\{(1/\sin\theta)(\partial/\partial\theta)[\sin\theta(\partial/\partial\theta)]$$
$$+ (1/\sin^2\theta)[(\partial/\partial\psi) - i\Lambda\cos\theta]^2\}\mathfrak{IC}$$
$$= -[K(K+1) - \Lambda^2]\mathfrak{IC}. \quad (72)$$

The matrix elements of $U_\pm$ between the functions $\mathfrak{IC}$ are

$$(KM_k\Lambda\pm1 \mid U_\pm \mid KM_k\Lambda) = \hbar[(K\pm\Lambda+1)(K\mp\Lambda)]^{\frac{1}{2}}.$$
$$(73)$$

Just as in approximation (A), a relation exists between the "uncoupled" electronic-rotational basis set and this "coupled" set, as $R \rightarrow \infty$:

$$\phi^{(\infty)}(n\Gamma M_s M_L; \mathbf{r}) Y(NM_N; \theta, \psi)$$
$$= (-1)^{M_N} \sum_K \sum_\Lambda \left(\frac{2N+1}{2K+1}\right)^{\frac{1}{2}} (NM_N LM_L \mid NLKM_k)$$
$$\times (NLK\Lambda \mid N0L\Lambda)\phi^{(\infty)}(n\Gamma M_s\Lambda; \mathbf{r})\mathfrak{IC}(KM_k\Lambda; \theta, \psi).$$
$$(74)$$

Furthermore, it is easily shown that the transformation

$$\sum_\Lambda (NLK\Lambda \mid N0L\Lambda)\phi^{(\infty)}(n\Gamma\Lambda; \mathbf{r})\mathfrak{IC}(KM_k\Lambda; \theta, \psi) \quad (75)$$

diagonalizes H_B as $R \rightarrow \infty$. The eigenvalues are asymptotically

$$\epsilon \rightarrow \epsilon^0(n\Gamma LS) + N(N+1)\hbar^2/2MR^2, \quad (76)$$

where N takes on the $2L+1$ possible values consistent with given K, and $\epsilon^0(n\Gamma LS)$ is the Russell-Saunders

atomic term value (omitting spin-orbit interaction energies).

At finite R, we now define the zero-order basis set for this approximation as the set of eigenfunctions $X(n\Gamma K\mu)$ which diagonalize the matrix H_B. Since H_B is diagonal in K, S, M_s this basis set is obtained by the diagonalization of the noninteracting $(2L+1)$-dimensional matrices for each K value, and the given values of S, M_s. The eigenvalues we shall define by the symbol $\omega(n\Gamma K\mu; R)$.

The solution to the scattering problem is chosen to be expanded using X_μ as a basis:

$$\Psi = (1/R)\sum C(n\Gamma K\mu) X(n\Gamma K\mu; \mathbf{r}, R, \theta, \psi) F(n\Gamma K\mu; R);$$

(77)

the functions F are chosen to satisfy the equation,

$$-(\hbar^2/2M)d^2F/dR^2 + \omega_\mu(R)F = EF,$$

(78)

and to be finite everywhere with the asymptotic property

$$\lim_{R\to\infty} F(n\Gamma K\mu; R) = (1/k)\sin(kR + N_\mu\pi/2 + \delta_\mu).$$

(79)

Because the spin-orbit coupling is not included in H_B, the electronic states of the system are all degenerate as $R\to\infty$. Splitting between states of distinct J is only introduced by the spin-orbit interaction.

The spin-orbit interaction, and the matrix elements arising from the terms in $(dX_\mu/dK)\cdot(dF_\mu/dk)$, lead to perturbations of the zero-order states. The effect of these will be considered later, after the results of the zero-order scattering are treated.

In this approximation, the collision is assumed to be "fast" with respect to spin-orbit interaction. The initial state of the system is an eigenfunction of the entire electronic Hamiltonian H_e, including spin-orbit coupling. In the treatment of this approximation, it is imagined that the spin-orbit interaction is suddenly "turned off," and the eigenstate is expanded in eigenstates $\phi'(n\Gamma M_J M_L; \mathbf{r})$. This expansion is the "initial state" for the formal theory treatment, and propagates itself under the zero-order Hamiltonian in terms of the basis set X_μ. Neglecting the perturbations, no transitions in the X_μ occur, and the final amplitude at each θ, ψ solid angle for scattering into various values of M_L is determined by the boundary conditions and phase shifts. These "final states" are then re-expanded in terms of eigenfunctions of H_e; i.e., the spin-orbit interaction is suddenly "turned on" again. Therefore, because of the sudden approximation treatment of the spin-orbit interaction at the beginning and end of a collision, "elastic" scattering in terms of the zero-order Hamiltonian is inelastic scattering in actuality.

The initial electronic state is $\phi(n\Gamma JM_J; \mathbf{r})$; it may be written as a linear combination of the Russell-Saunders eigenfunctions:

$$\phi(n\Gamma JM_J; \mathbf{r})$$

$$= \sum_{M_s}(LS\,JM_J\,|\,LM_L SM_s)\phi'(n\Gamma M_L M_s).$$

(80)

Since the spin-orbit interaction is neglected, the value of M_s may not change, and the solution to the scattering problem must have the asymptotic form

$$\Psi\to\sum_{M_s}(LS JM_J\,|\,LM_L SM_s)\{\phi'(n\Gamma M_L M_s)\,\exp(ikR\cos\theta) + (\exp ikR/R)\sum_{M_L'}f(M_L', \theta, \psi)\phi'(n\Gamma M_L' M_s)\}.$$

(81)

For each value of M_s, we shall consider the problem separately $(M_L = M_J - M_s)$. The plane wave may be expanded for each M_L in the basis X_μ as $R\to\infty$:

$$\lim_{R\to\infty}\phi'(n\Gamma M_L M_s)\,\exp(ikR\cos\theta)$$

$$= \sum_N\sum_K(4\pi/2K+1)^{\frac{1}{2}}(2N_\mu+1)\,\exp(iN_\mu\pi/2)\,(N_\mu 0LM_L\,|\,N_\mu LKM_L)X(n\Gamma K\mu)\,\sin(kR + N_\mu\pi/2)/R.$$

(82)

Comparing the coefficients of the general solution with the required asymptotic behavior, one readily obtains the result

$$C(n\Gamma K\mu) = (4\pi/2K+1)^{\frac{1}{2}}(2N_\mu+1)\,(N_\mu 0LM_L\,|\,N_\mu LKM_L)\,\exp(iN_\mu\pi/2 + i\delta_\mu).$$

(83)

The scattered wave may now be readily written in the basis X_μ as $R\to\infty$; it is,

$$[\exp(ikR)/R]\sum_{M_L'}f(M_L'; \theta, \psi)\phi'(n\Gamma M_L' M_s)$$

$$= \sum_N\sum_K[\exp(ikR)/kR](-1)^N(4\pi/2K+1)^{\frac{1}{2}}(2N+1)\,(N0LM_L\,|\,NLKM_L)[(e^{2i\delta_\mu}-1)/2i]X_\mu(n\Gamma K\mu).$$

(84)

The right-hand side of Eq. (81) is now expanded in appropriate functions; the scattered wave is

$$[\exp(ikR)/2ikR]\sum_{N_\mu}\sum_K(-1)^{N_\mu + M_N}(4\pi/2K+1)^{\frac{1}{2}}(2N_\mu+1)\,(e^{2i\delta_\mu}-1)\,(N_\mu 0LM_L\,|\,N_\mu LKM_L)$$

$$\times (N_\mu LKM_L\,|\,N_\mu M_N LM_L')\phi'(n\Gamma M_L' M_s)\,Y(NM_N; \theta, \psi).$$

(85)

The next step is to suddenly turn the spin-orbit interaction "on" again; wave functions $\phi'(n\Gamma M_L'M_s)$ are to be expanded in the eigenfunctions $\phi(n\Gamma J'M_{J'})$. The scattered wave then becomes

$$[\exp(ikR)/2ikR]\sum_{M_s}\sum_{N_\mu}\sum_{K}\sum_{J'}(LSJM_J\,|\,LM_LSM_s)(N_\mu 0LM_L\,|\,N_\mu LKM_L)(N_\mu LKM_L\,|\,N_\mu N_N LM_L')$$

$$\times(LM_L'SM_s\,|\,LSJ'M_{J'})(-1)^{N_\mu+M_N}(4\pi/2K+1)^{\frac{1}{2}}(2N_\mu+1)(e^{2i\delta_\mu}-1)\phi(n\Gamma J'M_{J'})\,Y(NM_N;\theta,\psi),\quad(86)$$

(note that the phase shift δ_μ depends on K as well as N_μ). This expression is set equal to the general expression for a final scattered wave:

$$[\exp(ikR)/R]\sum_{J',M_{J'}}f'(J'M_{J'};\theta,\psi)\phi(n\Gamma J'M_{J'});$$

$$M_{J'}+M_N=M_J.\quad(87)$$

Such a definition of f' yields the cross section for scattering as

$$\sigma(JM_J\rightarrow J'M_{J'})$$

$$=\int_0^\pi\int_0^{2\pi}\sin\theta d\theta d\psi\,|f'(J'M_{J'};\theta,\psi)|^2,\quad(88)$$

and the total inelastic cross section is

$$\sigma(J\rightarrow J')=(\tfrac{1}{2}J+1)\sum_{M_J}\sum_{M_{J'}}\sigma(JM_J\rightarrow J'M_{J'}).\quad(89)$$

C. Approximation (C)

This approximation is an obvious extension of approximations (A) and (B), and is an attempt to treat the case of slow passage through a region of competition between axial fields and spin-orbit interaction. Diagonalization of all perturbation terms, except those caused by radial motion, determines the electronic-rotational basis set.

The procedure followed is the same as that of approximation (A), up to the development of the complete electronic-rotational Hamiltonian H_A. However, the *manifold* for approximation (C) is the direct sum of the manifolds of all possible J values and a fixed value of P for approximation (A). That is, a (C) manifold is designated only by the associated total angular momentum; it is of dimensionality $(2L+1)(2S+1)$ and is spanned by the complete set of electronic states for the Russell-Saunders term, multiplied by appropriate functions for angle dependence with total angular momentum P.

The zero-order electronic-rotational basis set for approximation (C) is obtained by diagonalizing H_A within each manifold. The resulting eigenfunctions we shall call $W(n\Gamma P\mu)$. They may be expressed in terms of the simple adiabatic functions:

$$W(n\Gamma P\mu;\mathbf{r},R,\theta,\psi)$$

$$=\sum_J\sum_\Omega C(n\Gamma P\mu;J\Omega;R)\phi[n\Gamma(J)\Omega;\mathbf{r},R]$$

$$\times\mathcal{K}(PM_p\Omega;\theta,\psi).\quad(90)$$

The eigenvalues are called $\rho(n\Gamma P\mu;R)$; the limiting

values are, for large R, weak axial fields,

$$\lim_{R\to\infty}\rho(n\Gamma P\mu;R)=\epsilon^0(n\Gamma J_\mu)$$

$$+[N_\mu(N_\mu+1)\hbar^2/2MR^2],\quad(91)$$

while for strong axial fields the energy is

$$\rho(n\Gamma P\mu;R)\to\epsilon[n\Gamma(J_\mu)\Omega_\mu;R]$$

$$+[P(P+1)-\Omega^2]\hbar^2/2MR^2.\quad(92)$$

The coefficients $C(n\Gamma P\mu;J\Omega;R)$ satisfy the unitary relations

$$\sum_{J,\Omega}C^*(n\Gamma P\mu';J\Omega;R)C(n\Gamma P\mu;J\Omega;R)=0,$$

$$\mu'\neq\mu;1,\mu'=\mu.\quad(93)$$

The basic zero-order eigenfunctions χ are of the form

$$\chi=(1/R)W_\mu(\mathbf{r},R,\theta,\psi)F_\mu(R),\quad(94)$$

where F_μ satisfies the equation

$$-(\hbar^2/2M)(d^2F_\mu/dR^2)+\rho_\mu(R)F_\mu(R)=EF_\mu,\quad(95)$$

is everywhere finite, and has the asymptotic property

$$\lim_{R\to\infty}F_\mu(R)=(1/k_\mu)\sin(k_\mu R+N_\mu\pi/2+\gamma_\mu).\quad(96)$$

When the Hamiltonian acts on a wave function composed of this zero-order set, the most significant perturbations arise from the terms

$$-(\hbar^2/M)[(dW_\mu/dR)\cdot(dF_\mu/dR)];$$

other terms come from $F_\mu(d^2W_\mu/dR^2)$, but we ignore these. The interaction integrals will all be of the form

$$H_I(\mu',\mu)$$

$$=(-\hbar^2/M)\iiiint dRF_{\mu'}{}^*W_{\mu'}{}^*(dW_\mu/dR)\cdot(dF_\mu/dR)d\tau_e$$

$$\times\sin\theta d\theta d\psi.\quad(97)$$

These elements are diagonal in P, M_p. We now find the explicit expressions for the electronic-rotational integrals:

$$\iiint W_{\mu'}{}^*(dW_\mu/dR)d\tau_e d(\cos\theta)d\psi$$

$$=\sum_{\Omega,J}C^*(n\Gamma P\mu';J\Omega)(d/dR)C(n\Gamma P\mu;J\Omega)$$

$$+\sum_{\Omega,J'\neq J}C^*(n\Gamma P\mu;J'\Omega)C(n\Gamma P\mu;J\Omega)A(J'J\Omega;R),\quad(98)$$

where

$$A(J'J\Omega; R) = \int d\tau_e \phi^*[n\Gamma(J')\Omega](d/dR)\phi[n\Gamma(J)\Omega].$$

(99)

The initial state of the system is, by analogy with approximation (A),

$$\Psi_i = (1/R) \sum_{N_\mu} \sum_P (4\pi/2P+1)^{\frac{1}{2}}(2N_\mu+1)$$

$$\times (N_\mu 0 J M_J | N_\mu J P M_J) \exp(iN_\mu\pi/2 + i\gamma_\mu) W_\mu F_\mu. \quad (100)$$

The transition matrix element is T_{fi},

$$T_{fi}(JM_J \rightarrow P\mu') = [\chi(P\mu'), H_I\Psi_i], \quad (101)$$

and the cross section is computed in a manner fully analogous to that of approximation (A), but with the new matrix elements $H_I(\mu', \mu)$ and phase shifts γ_μ, as well as new radial functions F_μ.

IV. METHODS OF CALCULATION

As was indicated in earlier discussion, the use of variational expressions based on the formal scattering theory, or of the explicit perturbation theory it provides, involves too much labor to be practical at present beyond the first approximation; therefore, we have devoted our attention to the development of useful electronic basis sets whose first or even zero-order approximations to inelastic scattering may be computed with no more labor than is common to all such calculations. This labor may be categorized into the following components:

(1) Determination of the effective "elastic scattering potential surfaces" for the approximation in question.

(2) Determination of the electronic-rotational basis associated with the eigenvalue surfaces [if a first-order theory with transition matrices be involved; in adiabatic approximation (B), for example, this is not necessary].

(3) Computation of the electronic-rotational parts of the transition matrix elements.

(4) Solutions for the radial functions $F_\mu(R)$, describing nuclear motion on each elastic surface, and the associated phase shifts, and computation of radial parts of the transition matrix elements.

(5) Summation of partial-wave cross sections. The present status of practical calculation on any of these component problems is rudimentary in the extreme. For example, most actual calculations on problem (4) have been based on the Born approximation or semiclassical approximations for the nuclear motion. Consequently, a large part of the necessary work is survey, concerned with merely studying the effect of assumptions or further approximations in the above five areas. Here we shall give only brief discussions of the situation in each at present, and of programs for further investigation. We hope to devote most of our future effort to pursuit of these programs.

(1) Effective "elastic scattering potential." Part of this problem, in fact the major part, is concerned with the classic problem of calculating or otherwise obtaining an accurate description of the interaction energy and wave function for the diatomic system. In the case of the high energy approximation, this problem is perhaps the simplest since there the elastic potential is defined in terms of the isolated atom wave functions, and one may hope that the Hartree-Fock wave functions for these will be sufficiently good to use for the most refined calculations. At present, our calculations employ a cruder estimate obtained with the simple "best atom exponent" Slater-type orbitals (STO) for the high energy approximation. In the adiabatic approximations, one must solve for the molecular electronic energies and wave functions, and we need not elaborate our commentary here by lamentation over conditions. One does the best he can, and perhaps should devote his energies to studying the effects of variation in the absolute value of the energy as a function of R, rather than of its shape, or investigate the perturbation splitting of spin-orbit interaction as a function of axial field strength. The other part of the eigenvalue problem, the diagonalization of the manifold matrices, we do not consider a real difficulty, since they are always of small dimensionality.

It might be proposed that experimental data be used to obtain the adiabatic potential energy curves. This data is nonexistent because present scattering measurements are all at far too high energies, and transport property measurements weight the attractive van der Waals region in a crude way, together with the repulsive region, while the only region of interest to us in most cases is the immediate vicinity of the classical turning point for given energy.

(2), (3) Electronic-rotational eigenfunctions and their transition matrix elements. The major part of this problem has already been discussed, i.e., the determination of adiabatic wave functions. The determination of the manifold eigenvectors is merely a computational operation, though perhaps a slightly tedious one.

One topic that is of interest here is whether it is a good idea to use independent procedures for elastic energy surfaces and for the associated electronic functions used to compute the transition matrix elements. This question has come into prominence because it is found that the transition matrix elements are almost always functions which decrease exponentially as R increases, in the interaction region, and mild displacements of the matrix element curve with respect to the potential energy curves lead to huge variations in the cross section. Our present feeling is that the two calculations should be strongly coupled, and further study will be made on the best way to do this.

(4) Solution of the radial equations for nuclear motion. The practical problem in this area is the question of machine time. Even the best methods of solving

the differential equations are time consuming when one considers that there are up to $(2L+1)(2S+1)$ radial equations for each partial wave, and as many as fifty of these may be needed.

Because, as has been stated, the major contribution to transition always comes from the classical turning point region, the WKB approximation is not very useful. On the other hand, a tremendous simplification is tempting, namely to use hard-sphere wave functions with hard-sphere radius equal to R_0, the classical turning point. This appears at present to be a good standard approximation, although its validity needs to be investigated later. Phase shifts are also easy to calculate in such a case, without an expensive additional integration.

(5) The last component problem does not appear difficult, except for the handling, generation, and processing of the large numbers of vector coupling coefficients, matrix elements, phase shifts, etc., needed for the final summations.

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Phase Transitions in the Ammonium Halides*

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High-pressure experiments, using the piston displacement technique have been performed at temperatures down to that of liquid nitrogen on NH_4I, NH_4Br, ND_4Br, and NH_4Cl. For the iodide two new phase transitions under pressure and a new triple point were observed. A new transition and a new triple point were observed in both the bromides; the existence of another transition was confirmed. The role of multipole interactions in causing the transitions is discussed, and on the basis of structural data and the present experiments a generalized phase diagram is presented which describes the gross behavior of the transitions in these substances.

I. INTRODUCTION

AMMONIUM chloride, bromide, and iodide exhibit at atmospheric pressure a number of phase transitions from one cubic structure to another. It is known from neutron diffraction studies (as will be discussed later) that in the various substances analagous phases appear. These modifications, labeled for convenience α, β, γ, and δ, involve some orientation or reorientation of the ammonium tetrahedron with respect to the halide ion. The temperatures at which the transitions occur under atmospheric pressure are given in Table I. Although identical structures appear from substance to substance, there is no evident correlation among the transition temperatures or any indication of why a particular phase should appear at the temperature it does. The purpose of the investigation reported here was to study the effect of pressure on the transitions, and to obtain some correlation among the phase diagrams.

II. EXPERIMENTAL TECHNIQUE

The method of the experiments is similar to that of Bridgman.[1] The polycrystalline substance to be studied is compressed into a coherent cylindrical mass, and wrapped in a 0.005-in.-thick sheet of indium metal. The indium acts as a lubricating agent and materially reduces friction in the apparatus. The wrapped sample is inserted into a thick-walled cylinder of hardened beryllium-copper. Beveled brass washers fit into each end of the cylinder to prevent extrusion of indium into the space between the compressing pistons and the cylinder walls. The cylinders used in these experiments had inner diameters of $\frac{1}{4}$ in. or $\frac{1}{2}$ in.; the former allowing a maximum pressure of 10 000 atm, the latter 2500 atm. The assembly of pistons and cylinder is placed in a hydraulic press similar to that of Stewart.[2]

The whole apparatus is set into a variable temperature cryostat which is of the design of Swenson and Stahl.[3] With liquid nitrogen in the cryostat, any temperatue between that and room temperature can be chosen and controlled to within about a tenth of a degree. The cryostat temperature is fixed and data accumulated as a series of readings of the piston displacement while the force on the piston is increased to a maximum and then decreased. In experiments with highly incompressible substances such as the ammonium

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[1] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **76**, 9 (1945).

[2] J. W. Stewart, Phys. Rev. **97**, 578 (1955).
[3] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).