in the "degree of mixing" does not change the polarity of optical signal.[19]

ACKNOWLEDGMENTS

The author would like to thank Dr. G. K. Walters for several interesting discussions regarding this work. The technical skill of F. D. Sinclair in the preparation of the sample cells is also appreciated.

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[19] The use of a He^3 lamp to optically orient the He^4 sample provides a strong source of D_3 only light because of the isotope shift of the spectral lines. In this case a signal reversal has been observed as expected by N. D. Stockwell and G. K. Walters (private communication).

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Electron-Detachment in Slow Collisions between Atoms and Negative Ions

A. Herzenberg*
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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The collision of a negative ion A^- and neutral atom B at a very low kinetic energy (a few eV or less) may lead to the release of an electron through the reaction $A^-+B\rightarrow(AB)+e$, known as "associative detachment." At higher energies, $A^-+B\rightarrow A+B+e$ also becomes possible. A theory of these processes is formulated by assuming that the electronic state is stable at large separations R of A^- and B, and changes adiabatically as R decreases; at very small R, of the order of 10^{-8} cm, the electronic state turns into an unstable compound state able to emit an electron. Expressions are derived for the total cross section for electron detachment, and for the cross sections for detachment leaving the nuclei in a single discrete final state. At thermal energies, the total cross section can become very large because of Langevin spiralling, arising from the long-range polarization between A^- and B. For example, in the reaction $H^-+H\rightarrow H_2+e$, the cross section is estimated to be of the order of 10^{-14} cm^2 at a relative kinetic energy of $k\times400$°K.

I. INTRODUCTION

UNSTABLE compound states of negative molecular ions which decay to neutral molecules by the emission of an electron are well known.[1–8] So far these states have usually been generated by the bombardment of neutral molecules with electrons, where they give rise to characteristic peaks in the cross sections as a function of energy. The existing theory[4–7] has been tailored for this case, and reasonable agreement with experiment has been obtained in those cases which have been treated in detail.[5,6]

In recent experiments,[9–11] similar unstable compound states have been generated by another method, the bombardment of neutral atoms or molecules by negative ions with kinetic energies up to a few electron volts. The object of this paper is to formulate a theory of this process, and to give expressions and estimates for the cross sections for the formation of different final states of the nuclei. We shall confine ourselves to the simplest case of a collision between a neutral atom and a negative atomic ion.

It might seem at first sight that no new theory is needed, because electron-molecule and ion-atom collisions are merely two different channels through which the same unstable compound states are formed; therefore it might seem that the expressions for the cross sections should differ only in the entry width which has

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* Permanent address: Theoretical Physics Department, University of Manchester, England.

[1] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950). Particularly, see Chaps. 2 and 3. For the reaction $O^-+O\rightarrow O_2+e$, see p. 119.

[2] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952), Chap. 4, Sec. 3.

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to be inserted in a Breit-Wigner formula.[12] That the problem *is* more complicated, and a new theory *is* required, comes from the fact that one is here dealing not with a single isolated unstable state—the case to which the Breit-Wigner formula applies—but with groups of such states. This in turn comes from the existence of two different time scales in molecular problems, related to the motion of the electrons and the very much slower motion of the nuclei. As a consequence, the compound states have to be defined adiabatically for fixed nuclei, and their effect on the motion of the nuclei treated in a second stage (as has always been done for *stable* electronic states in molecules). A single compound state for the electrons is the common element either of a set of many discrete vibration-rotation levels, if the compound electronic energy has a minimum, or of a continuous band of nuclear states, if the compound electronic energy is repulsive. These sets of states have to be treated together if the physical situation is to be seen in a proper perspective.

The basic idea of this paper is that the electronic state of the initial system A^-+B (where A^- is a negative ion and B a neutral atom) is stable at large separations R of the nuclei, and changes adiabatically as R decreases. When $R<R_s$, where R_s is a value characteristic of the system, the electronic state becomes unstable with respect to electron emission, but nevertheless continues to change adiabatically; its energy becomes complex:

$$W(R)=E(R)-\tfrac{1}{2}i\Gamma(R),$$

where E and Γ are real. The lifetime τ is given by $\tau=\hbar/\Gamma$. Electron detachment will be a probable outcome of a close collision between A^- and B if τ is short compared with the time the nuclei spend in the region $R<R_s$. The assumption that the electronic state continues adiabatically into the region of instability constitutes the main difference between the point of view of this paper and that in a discussion of the process (1.2) below given by Demkov.[13] Demkov supposes that the original electronic state is bound for $R>R_s$, merges with the continuum at $R=R_s$, and ceases to have any meaning when $R<R_s$.

The plan of the paper is as follows. A wave equation for the wave function describing the nuclear motion is derived in Sec. II and given in Eq. (2.12). The derivation is based on the assumption that in the region of configuration space where all the electrons are within a few angstrom units of the nuclei, the complete wave function may be approximated by $\xi(\mathbf{R})\psi(q,\mathbf{R})$, where ψ is the adiabatic electronic wave function calculated for fixed nuclei and belonging to energy $W(R)$. The nuclear coordinates are represented by $\mathbf{R}$, and the electronic coordinates by q. An important consequence of the presence of Γ is that ξ is a damped wave in $R<R_s$, the damping representing the loss of probability in the incident channel (A^-+B) due to electron emission. The total cross section for electronic detachment can be obtained directly from the difference of the incoming and outgoing probability fluxes. The relevant formulas are given in Sec. III.

The final state of the nuclei after an electron has been detached may be bound, yielding the reaction

$$A^-+B\rightarrow(AB)+e, \tag{1.1}$$

known as associative detachment, or unbound, giving the reaction

$$A^-+B\rightarrow A+B+e. \tag{1.2}$$

The partial cross section for the states of the residual molecule in (1.1) are derived in Sec. IV, the final formula being given in (4.17). For process (1.2), the cross section for leaving the nuclei in some small finite energy range is derived in Sec. V and given in (5.1). It is verified that the partial cross sections add up to the total detachment cross section of Sec. III. Process (1.1) is the inverse of dissociative attachment, which has been studied extensively.[3–7] The process will be exoergic—and therefore possible at zero initial kinetic energy—if the separation energy in the reaction $(AB)\rightarrow A+B$ exceeds the electron affinity of A. It may therefore be important in ionized gases at temperatures down to a few hundred degrees or less as the only mechanism for the detachment of electrons from negative ions by collisions without the participation of photons. Examples are the destruction of H^- ions in stellar envelopes through the reaction $\mathrm{H}^-+\mathrm{H}\rightarrow\mathrm{H}_2+e$, and the reaction $\mathrm{O}^-+\mathrm{O}\rightarrow\mathrm{O}_2+e$ which is thought to play a role in the maintenance of the electron density at night in the earth's upper atmosphere.[1] Process (1.2) can occur only if the initial relative kinetic energy of the nuclei exceeds the electron affinity of A, which may vary from a few electron volts down to a few tenths; this process is therefore not likely to be very important in ionized gases at temperatures less than some thousands of degrees K. (A theory of this process at kinetic energies of the order of hundreds of electron volts has been developed independently by Bardsley,[14] and compared by him with experiment.)

To calculate numerical values for the detachment cross section would in general require a detailed knowledge of Γ as a function of R. There is, however, a large class of compound states for which this is not necessary, at least for rough estimates. These are the states for which Γ is so large that the amplitude of the outgoing ξ wave is small compared with the incoming; then almost every close collision of A^- and B leads to detachment. The detachment cross section becomes independent of Γ and is determined solely by the maximum impact parameter for which the colliding

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[12] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons Inc., New York, 1952), Chap. VIII, Eq. (7.19).

[13] Yu. N. Demkov, Zh. Eksperim. i Teor. Fiz. **46**, 1126 (1964) [English transl.: Soviet Phys.—JETP **19**, 762 (1964)].

[14] J. N. Bardsley Proc. Phys. Soc. (London) **91**, 300 (1967).

atom and ion approach closely enough for Γ to be large. This maximum impact parameter is greatly affected by the long-range polarization attraction between the colliding atom and ion, which falls off with distance as R^{-4} and can lead to very large detachment cross sections at low energies ($\gg 10^{-15}$ cm^2). This effect is discussed in Sec. VI A. Section VI B deals with the question of whether sufficiently large values of Γ are likely to be attained.

The paper uses a number of simplifications and approximations, which could be removed without much difficulty. They are:

(1) As stated before, we have not considered the case where either A, or B, or both are polyatomic structures.

(2) All *spin*-dependent forces are neglected. (This makes the Hamiltonian *real.*)

(3) The electronic states are Σ states. (This implies that the rotational wave functions of the nuclei are spherical harmonics.)

(4) Only a single electronic state is available to the residual molecule. (This simplifies some formulas involving Γ.)

(5) The colliding atom and ion are supposed to be in their electronic ground states.

For the purpose of illustration, we shall repeatedly refer to the simple case H$^-$+H.

II. THE WAVE FUNCTION AND WAVE EQUATION

In this section we derive an approximate wave equation for the nuclei. As long as the velocities of the nuclei are small compared with those of the electrons, say at kinetic energies not exceeding a few hundred electron volts, one may approximate

$$\Psi(q,\mathbf{R})=\xi(\mathbf{R})\psi(q,\mathbf{R}), \tag{2.1}$$

where $\mathbf{R}$ is the vector separation of the nuclei, as before, and q the electronic coordinates. (We shall work in the center-of-mass frame.) The electronic wave function ψ is to satisfy the wave equation in the adiabatic approximation:

$$[H_{\mathrm{el}}(q,\mathbf{R})-W(R)]\psi=0. \tag{2.2}$$

Here

$$H_{\mathrm{el}}\equiv H-K, \tag{2.3}$$

H being the complete Hamiltonian and K the kinetic energy of the nuclei. The eigenvalue W is determined by the boundary condition that whenever any one of the electrons moves off to infinity either $\psi\to 0$ exponentially or $\psi\to$ outgoing wave with a wave number determined by the energy W. [See Appendix, Eq. (A13).] If the first case holds for all channels, ψ is a bound state and W is real; if the second is true for some channels, ψ is unstable with respect to electron emission, and W contains an imaginary part:

$$W(R)=E(R)-\tfrac{1}{2}i\Gamma(R). \tag{2.4}$$

The eigenvalue problem (2.2) for unstable states has been discussed in detail in two recent papers where further references will be found.[5] (These papers will be referred to as I and II.)

To derive an equation for ξ, multiply the Schrödinger equation

$$(H-\epsilon)\Psi=0 \tag{2.5}$$

by ψ^* and integrate over the coordinates of all electrons while holding the nuclei fixed. (ϵ is the total energy.) For sufficiently large separations R, the state ψ is bound; the integration may then be carried over all space. For the range of R in which $\Gamma\neq 0$, $|\psi|$ increases exponentially as $r_i\to\infty$, where r_i is the radial coordinate of the ith electron. [See Eq. (A8).] However, there will be an inner region where all r_i are less than a few angstroms, and where the electron density falls to a minimum with increasing distance from the nuclei before starting to increase exponentially. (See Appendix, Fig. 6.) Therefore one can surround the negative ion by a spherical surface S with a radius near the density minimum, and integrate over the enclosed volume. If one now replaces Ψ by the approximation (2.1), and uses (2.2), one obtains

$$-\frac{\hbar^2}{2M}\nabla_R^2\xi+[W(R)-\epsilon]\xi =\left[\frac{\hbar^2}{2M}\left(2\nabla_R\xi\cdot\int dq\,\psi^*\nabla_R\psi+\xi\int dq\,\psi^*\nabla_R^2\psi\right)\Big/\int dq\,|\psi|^2\right]. \tag{2.6}$$

We have dropped some kinetic-energy terms of order (m/M) relative to those retained. (m = electronic mass, M = nuclear reduced mass.)

We next show that the right-hand side of (2.6) may be replaced by zero. The second term on the right in (2.6) will be smaller by a factor of order (m/M) than the kinetic energy term in H_{el}, and will be dropped. The remaining integral in the numerator on the right of (2.6) may be rewritten

$$\int dq\,\psi^*\nabla_R\psi=\tfrac{1}{2}\nabla_R\int dq\,|\psi|^2+\frac{1}{2}\int dq[\psi^*\nabla_R\psi-\psi\nabla_R\psi^*]. \tag{2.7}$$

To make the first term on the right of (2.7) vanish, we shall normalize ψ so that, for all $\mathbf{R}$,

$$\int dq\,|\psi|^2=1, \tag{2.8}$$

the integral being taken over the interior of S. The uncertainty in this integral due to the imprecise specification of S will be small, because ψ itself must be small on S if the notion of a compound state is to be physically meaningful. We shall consistently treat ψ on S as a small quantity, and drop terms of the first and higher order (see Appendix); the component added to the integral in (2.8) as a result of any change in S will be of the second order in the surface amplitude ψ. It may easily be verified that there exists a real function $\phi(\mathbf{R})$, such that the second term on the right in (2.7) vanishes if ψ is multiplied by the phase factor $\exp[i\phi(\mathbf{R})]$.

Equation (2.6) now becomes

$$-(\hbar^2/2M)\nabla_R^2\xi+[W(R)-\epsilon]\xi=0. \qquad (2.9)$$

It should be noted that this wave equation is homogeneous, in contrast to the wave equation which has to be used to describe the nuclear motion in a compound state generated by bombarding a neutral molecule by electrons. There one has a source term proportional to the initial state of the nuclei and to the amplitude of the wave function of the bombarding electrons. [See II, Eq. (2.26).] In the present problem, the sources are at infinity.

As an example, consider the collision of an H atom with an H^- ion. We shall denote the electronic wave functions for hydrogen atoms centered on the two nuclei by a and b, and the wave functions for negative ions by a^- and b^-. The possible functions ψ are then, as $R\rightarrow\infty$,

$$\begin{pmatrix}\psi_g\\ \psi_u\end{pmatrix}=[a(1)b^-(23)\pm b(1)a^-(23)] + \text{antisymmetrizing terms.} \qquad (2.10)$$

Here 1, 2, 3 stand for the coordinates of the three electrons. The suffix g or u on ψ distinguishes the two functions obtained by using the corresponding sign on the right. The two states in (2.10) are the asymptotic forms of the lowest ${}^2\Sigma_g$ and ${}^2\Sigma_u$ compound states of the H_2^- ion which account for most of the features of inelastic electron scattering at energies below 12 eV (II). The associated complex energies will be denoted by W_g and W_u. They have been calculated in I by a variational principle, and are reproduced in Figs. 1 and 2 together with the energy of the ground state of the H_2 molecule, which we shall need later. The calculations leading to the results in Figs. 1 and 2 were done with variational wave functions which go over into (2.10) as $R\rightarrow\infty$.

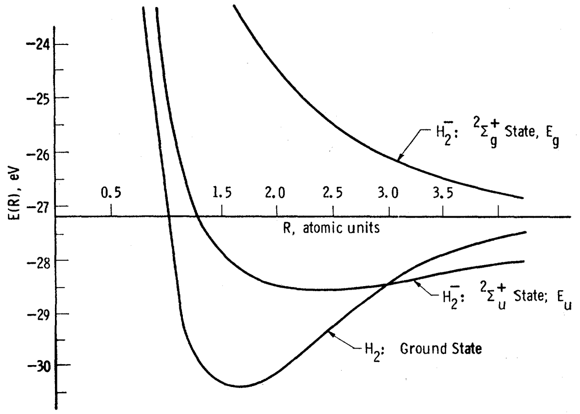

FIG. 1. The real parts E_g and E_u of the complex energies W_g and W_u of the lowest ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states of H_2^-, together with the energy of the electronic ground state of the H_2 molecule, all taken from variational calculations as explained in I. The numbers in this figure and Fig. 2 depend somewhat on the details of the wave functions used for the calculations (see I).

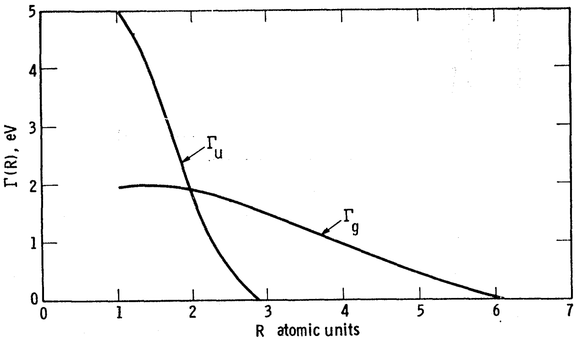

FIG. 2. Imaginary parts of the complex energies Γ_g and Γ_u for the lowest ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states of H_2^-.

Since $W(R)$ depends only on R, Eq. (2.9) is separable. We write

$$\xi(\mathbf{R})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{\xi_l(R)}{R}Y_{lm}(\hat{R})Y^*_{lm}(\hat{k}_0), \qquad (2.11)$$

where $\hat{R}$ denotes the angular coordinates in $\mathbf{R}$ and $\hat{k}_0$ the polar angles of the relative velocity before the collision. Equation (2.9) becomes

$$-(\hbar^2/2M)(\partial^2\xi_l/\partial R^2)+[W_l(R)-\epsilon]\xi_l(R)=0, \qquad (2.12)$$

where

$$\begin{aligned}W_l(R)&\equiv(\hbar^2/2M)[l(l+1)/R^2]+W(R)\\ &\equiv E_l(R)-\tfrac{1}{2}i\Gamma(R).\end{aligned} \qquad (2.13)$$

The angular dependence of ξ is more complicated if the electronic state ψ has angular momentum about the line joining the nuclei, unlike the states in (2.10).[15]

III. TOTAL CROSS SECTION FOR ELECTRON DETACHMENT

In this section we consider the total cross section for electron detachment, irrespective of the final state of the nuclei.

Following the notation of Ref. 16 we write

$$\xi_l(R)\rightarrow\frac{i^{l+1}}{k_0(2\pi)^{1/2}}\times[\exp(-i(k_0R-\tfrac{1}{2}l\pi))-\eta_l\exp(i(k_0R-\tfrac{1}{2}l\pi))], \qquad (3.1)$$

as $R\rightarrow\infty$; here k_0 is defined by

$$\hbar^2k_0^2/2M=\epsilon-W(\infty)\equiv\epsilon_0. \qquad (3.2)$$

The normalization of ξ_l has been chosen so that the

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[15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., London, 1959), Sec. 79.

[16] Reference 12, Chap. VIII, Eq. (2.8).

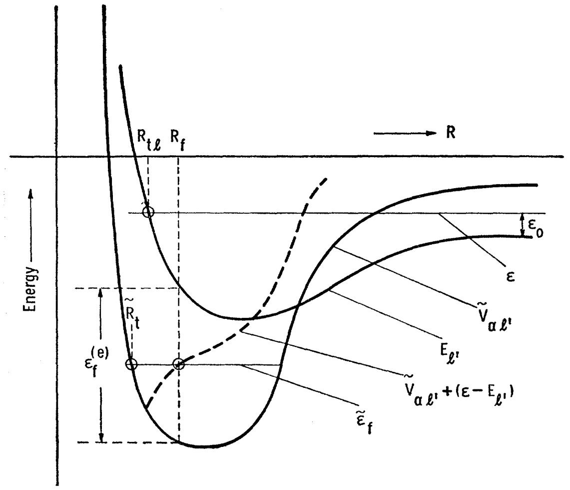

FIG. 3. Notation. The collision occurs with initial kinetic energy ϵ_0, and leads to a residual molecule with energy $\tilde{\epsilon}_f$. The total energy is ϵ. The transition takes place near the point R_f, determined by the intersection of the horizontal $\tilde{\epsilon}_f$ with the curve $\tilde{V}_{\alpha l'}+(\epsilon-E_{l'})$. An electron with energy $\epsilon_f^{(e)}$ is emitted. R_{tl} is the turning point in the initial channel A^-+B; $\tilde{R}_t$ is one of the turning points in the final state $\tilde{\epsilon}_f$. Physically important intersections are ringed.

incoming wave part is identical with that of a plane wave $\exp(i\mathbf{k}_0\cdot\mathbf{R})/(2\pi)^{3/2}$; the vector $\mathbf{k}_0$ has polar angles $\hat{k}_0$. In the case of H+H⁻,

$$W(\infty)=E_{\mathrm{H}}+E_{\mathrm{H}^-}, \qquad (3.3)$$

where E_{H} and E_{H^-} are, respectively, the electronic ground-state energies of the hydrogen atom and the negative hydrogen ion.

The reaction cross section associated with the lth partial wave is [Ref. 16, Eq. (2.13)]

$$\sigma_{d,l}=\pi\lambda\!\!\!^{-2}(2l+1)(1-|\eta_l|^2), \qquad (3.4)$$

where $\lambda\!\!\!^{-}\equiv 1/k_0$. If η_l is calculated by solving (2.12), then $\sigma_{d,l}$ becomes the detachment cross section, because inelastic scattering enters only through the imaginary part $-\frac{1}{2}\Gamma$ of W, representing the decay of the negative ion by electron emission. We shall denote the complete cross section for detachment by σ_d, so that

$$\sigma_d=\sum_l \sigma_{d,l}. \qquad (3.5)$$

η_l may be calculated by solving Eq. (2.12) in WKB approximation. The WKB solution regular at $R=0$ was given in Eq. (2.47) of II. It is, when the coefficient of the incoming wave is made equal to that in (3.1),

$$\begin{aligned}\xi_l(R)=&[2k_0^{1/2}\exp(-i\pi(l+\tfrac{1}{12}))\exp(-iq_{l0})]^{-1}\\ &\times[q_l(R)/\kappa_l(R)]^{1/2}\\ &\times\{H_{1/3}^-(q_l(R))+\exp(i\pi/3)H_{1/3}^+(q_l(R))\},\end{aligned} \qquad (3.6)$$

where $H_{1/3}^+$ and $H_{1/3}^-$ are outgoing and ingoing wave Hankel functions of order $\frac{1}{3}$,

$$\kappa_l^2(R)\equiv(2M/\hbar^2)[\epsilon-W_l(R)], \qquad \kappa_l(\infty)=k_0, \qquad (3.7)$$

$$q_l(R)\equiv\int_{R_{0l}}^{R}\kappa_l(R')dR', \qquad q_{0l}\equiv\lim_{R\to\infty}[q_l(R)-k_0R]. \qquad (3.8)$$

To define the points R_{0l}, one has to continue $W_l(R)$ analytically off the real R axis and satisfy the equation

$$\epsilon-W_l(R_{0l})=0. \qquad (3.9)$$

Unless Γ is very large, R_{0l} will be close to the turning point R_{tl} defined by

$$\epsilon-E_l(R_{tl})=0. \qquad (3.10)$$

The physical significance of R_{tl} is illustrated on Fig. 3. If we make a linear approximation near R_{tl},

$$W_l(R)\cong E_l(R_{tl})-W_{1l}(R-R_{tl})-\tfrac{1}{2}i\Gamma(R_{tl}) \qquad (3.11)$$
$$[-W_{1l}\equiv(dW_l(R)/dR)_{R=R_{tl}}],$$

we get

$$R_{0l}-R_{tl}=-\tfrac{1}{2}i(\Gamma(R_{tl})/W_{1l}). \qquad (3.12)$$

It follows from a comparison with (3.1) that

$$\eta_l=\exp[i(2q_{0l}+l\pi+\tfrac{1}{2}\pi)],$$

so that

$$|\eta_l|=\exp\left[-2\,\mathrm{Im}\int_{R_{0l}}^{\infty}\kappa_l(R')dR'\right]. \qquad (3.13)$$

Whenever $\Gamma(R)\ll|(\epsilon-E_l(R))|$, the integrand may be rewritten

$$2\,\mathrm{Im}\kappa_l(R)\cong\Gamma(R)/\hbar v_l(R), \qquad (3.14)$$

where

$$v_l(R)\equiv[\epsilon-E_l(R)/\tfrac{1}{2}M]^{1/2} \qquad (3.15)$$

is the relative velocity of the nuclei at R. Since this approximation cannot be used near the turning point R_{tl}, it is convenient to split the range of integration in (3.13) into two sections, from R_{0l} to R_{1l}, and R_{1l} to infinity, R_{1l} being a real point chosen to be sufficiently close to R_{tl} for the approximation (3.11) to be valid, and yet sufficiently far out to satisfy the inequality $|\epsilon-E_l(R_{1l})|\gg\Gamma(R_{1l})$. For the first integral we use the linear approximation, obtaining

$$\mathrm{Im}\int_{R_{0l}}^{R_{1l}}dR'\kappa_l(R')=\mathrm{Im}\left(\frac{2M}{\hbar^2}\right)^{1/2}\frac{2}{3W_{1l}}[\epsilon-W_l(R_{1l})]^{3/2}. \qquad (3.16)$$

The second step is justified by the inequality governing the choice of R_{1l}. Thus if we suppose that Γ is sufficiently small to use (3.14) when $R_{1l}<R$, we get, using (3.13),

$$\sigma_{d,l}=\pi\lambda\!\!\!^{-2}(2l+1)\left\{1-\exp\left[-2\int_{R_{0l}}^{\infty}\frac{\Gamma(R')dR'}{\hbar v_l(R')}-2\left(\frac{M\Gamma^2(R_{1l})(R_{1l}-R_{tl})}{2\hbar^2W_{1l}}\right)^{1/2}\right]\right\}. \qquad (3.17)$$

This formula expresses the intimate relation between the damping of ξ and $\sigma_{d,l}$. The first term in the exponential gives the probability that the electron shall not be detached away from the turning point on either the inward or outward trajectories, $[\Gamma(R)/\hbar][dR/v(R)]$ being the probability of detachment in distance dR [covered in time $dR/v(R)$] when the decay rate is $\Gamma(R)/\hbar$. The second term gives the probability that electron should not be detached close to the turning point.

The formula (3.17) enables one to estimate a rough lower limit on Γ in order that $|\eta_l|^2 \ll 1$. It will clearly be sufficient that

$$\bar{\Gamma} a_B/\hbar\bar{v}_l \gtrsim 1,$$

where $\bar{\Gamma}$ and $\bar{v}_l$ are suitable representative values of $\Gamma(R)$ and $v_l(R)$, while the Bohr radius a_B is a measure of the distance over which the damping is important. If E_l is attractive, $\bar{v}_l$ will be of order $M^{-1/2}(\hbar^2/ma_B^2)^{1/2}$. Therefore one expects that $|\eta_l| \ll 1$ if

$$\bar{\Gamma} \gtrsim (m/M)^{1/2}(\hbar^2/ma_B^2) \approx 0.1 \text{ eV}. \tag{3.18}$$

This inequality is satisfied by a large margin by the lowest compound state of H_2^-(I). The lower limit (3.18) is sufficiently small for the approximation (3.14) on which the derivation was based, to be applicable. If Γ is larger, (3.14) may break down; but η will then be smaller because of the increased damping, so that (3.18) is sufficient to ensure that $|\eta_l| \ll 1$ for states with attractive E_l.

It is not easy to make a similar estimate for an ionic state for which E_l is repulsive, because here the distance through which the nuclei can penetrate into the unstable region will be strongly determined by the energy.

An instructive formula for $\sigma_{d,l}$ may be obtained by multiplying (2.12) by ξ^*_l, subtracting the complex-conjugate equation, and integrating from $R=0$ to $R=\infty$. Using (3.14), and the asymptotic form (3.1), one obtains

$$\sigma_{d,l} = \frac{2\pi^2(2l+1)}{v_0\hbar} \int_0^\infty dR\, \Gamma(R)\, |\xi_l(R)|^2, \tag{3.19}$$

where v_0 is the initial relative velocity of the atom and ion at large separations. Since $\sigma_{d,l}$ is proportional to the fraction of the probability flux lost from the channel (atom + ion) during the encounter, (3.19) relates this lost flux directly to the rate of loss in each interval dR.

IV. VIBRATIONAL STATES OF THE RESIDUAL MOLECULE IN ASSOCIATIVE DETACHMENT: REACTION $A^- + B \rightarrow (AB) + e$

In Sec. III we discussed the total cross section for electron detachment, irrespective of the final state of the nuclei. In this section we split this total cross section into partial cross sections for the formation of individual bound states of the residual molecule. (Such bound states of course exist only if the final electronic energy has a minimum as a function of R.) (The production of unbound states of the final molecule is treated in Sec. V.) An example is the reaction $H^- + H \rightarrow H_2 + e$, the final electronic state being the ground state of H_2, as shown in Fig. 1.

We need a notation for the final channel. The vibrational state will be denoted by a subscript v, the rotational quantum numbers of the molecule by (l', m'), the quantum numbers of the electronic state of the residual molecule by α, and of the emitted electron by β. It will often be convenient to use a single suffix f to stand for $(\alpha\beta l'v)$.

The cross section for detachment reaction leading to the final state fm' is given by

$$\sigma_{dfm'} = \frac{v_f}{v_0} \frac{(2\pi)^4 m^2}{\hbar^4} (Z+1) \left| \int \Phi^*_{fm'}(j)\, V_j \Psi(\hat{k}_0)\, dq d\mathbf{R} \right|^2. \tag{4.1}$$

Here $\Psi(\hat{k}_0)$ is the exact state, corresponding to a relative velocity vector with polar angles $\hat{k}_0$ before the collision, V_j is the interaction potential of the emitted electron—which we take to be the jth—with the other particles, and $\Phi_{fm'}(j)$ the final state calculated with neglect of V_j. The velocity of the outgoing electron is v_f, and the relative velocity of the colliding particles v_0. The factor $(Z+1)$ is the total number of electrons, and allows for the possibility that any one of them may be emitted.

We shall approximate Ψ by (2.1), calculating ξ from (2.12) and (3.1). For $\Phi_{fm'}(j)$ we have

$$\Phi_{fm'}(j) = \chi_f(R) S_\beta Y_{l'm'}(\hat{R}) \mu_\alpha(\text{not } j) \times [\exp(i\mathbf{k}_f \cdot \mathbf{r}_j)/(2\pi)^{3/2}]. \tag{4.2}$$

Here χ_f is the final vibrational and $Y_{l'm'}(\hat{R})$ the final rotational state of the nuclei. $\mu_\alpha(\text{not } j)$ is the electronic state of the residual molecule, which contains all electrons except the jth. $\hbar\mathbf{k}_f$ is the momentum of the outgoing electron. Its spin state is denoted by S_β. The normalization of Ψ is such that

$$\Psi \rightarrow \{\exp[i\mathbf{k}_0 \cdot \mathbf{R}]/(2\pi)^{3/2}\} \psi(q, \mathbf{R}) + \text{scattered wave} \tag{4.3}$$

as $R \rightarrow \infty$. The state ψ is supposed to be normalized as in (2.8), and is supposed to be completely antisymmetric.

The cross section $\sigma_{dfm'}$ will be integrated over all directions $\hat{k}_f$ of the outgoing electron, and summed over m' and the spin S_β; the result will be denoted by $\sigma_{l'v}$:

$$\sigma_{l'v} \equiv \sum_{S_\beta} \sum_{m'} \int d\hat{k}_f \sigma_{dfm'}. \tag{4.4}$$

Since this sum is independent of the direction $\hat{k}_0$ of the initial relative velocity, it remains unaltered if we average over $\hat{k}_0$, i.e.,

$$\sigma_{l'v} = (4\pi)^{-1} \int d\hat{k}_0 \int d\hat{k}_f \sum_{S_\beta} \sum_{m'} \sigma_{dfm'}. \tag{4.5}$$

Performing the integration over $\hat{k}_0$ and the summation over spins on (4.1), one gets

$$\sigma_{l'v}=\frac{4\pi^3m^2}{\hbar^4}(Z+1)\sum_{lm}\sum_{m'S_\beta}\frac{v_f}{v_0}\int d\hat{k}_f\left|\int d\hat{R}\,Y^*{}_{l'm'}(\hat{R})\,Y_{lm}(\hat{R})\int RdR\,\chi^*{}_f(R)\,\xi_l(R)\,\zeta_{\alpha\beta}(k_f,R,\hat{R})\right|^2, \qquad (4.6)$$

where

$$\zeta_{\alpha\beta}\equiv\int dq\,\frac{\exp(-i\mathbf{k}_f\cdot\mathbf{r}_j)}{(2\pi)^{3/2}}\,S^*{}_{\beta}\mu_{\alpha\beta}(\text{not}\,j)\,V_j(q,\mathbf{R})\psi(q,\mathbf{R}). \qquad (4.7)$$

To do the sum over l and m one notes that $Y^*{}_{l'm'}$ and Y_{lm} oscillate rapidly with respect to angle. For example, in a collision of two oxygen atoms at thermal energies, say 0.03 eV, and at an impact parameter of 1 Å, one has $l\approx30$; therefore a typical wavelength in angle is $2\pi/30$. On the other hand, the factor ζ varies slowly with angle, so that only terms with $(l, m)\approx(l', m')$ weigh appreciably in (4.6). We can therefore replace $\xi_l(R)$ by $\xi_{l'}(R)$, so that the sufficies (l, m) appear only in $Y_{l,m}$. The completeness relation

$$\sum_{l,m}Y^*{}_{lm}(\hat{R})\,Y_{lm}(\hat{R}')=\delta(\hat{R}-\hat{R}') \qquad (4.8)$$

then reduces the two integrations over $\hat{R}$ in the two factors in the square in (4.6) to a single one. The integration $\int d\hat{k}_f$ makes the product of the two factors independent of $\hat{R}$, so that the remaining integral over $\hat{R}$ can be done by using the normalization of $Y_{l'm'}$. The sum $\sum_{m'}$ then yields a factor $(2l'+1)$. One gets

$$\sigma_{l'v}=(4\pi^3m^2/\hbar^4)\,(Z+1)\,(v_f/v_0)\,(2l'+1)$$
$$\times\sum_{S_\beta}\int d\hat{k}_f\left|\int dR\,R\chi^*{}_f(R)\,\xi_{l'}(R)\,\zeta_{\alpha\beta}(\mathbf{k}_f,R,\hat{R})\right|^2. \qquad (4.9)$$

This expression can be simplified further by noting that the main contribution to the integral must come from limited regions determined by the Franck-Condon principle. To show this, note that the factor ζ varies slowly, with a characteristic distance of order 10^{-8} cm, coming from the electronic wave functions in (4.7). The nuclear wave functions have reduced wavelengths of order $(m/M)^{1/2}\times10^{-8}$ cm, where m is an electronic and M a typical nuclear mass. Therefore most of the contribution to (4.9) will come from points where the wavelengths of χ_f and $\xi_{l'}$ are equal, since the rapid oscillations of the product $\chi^*{}_f\xi_{l'}$ make the contribution to the integral from other points small. To evaluate the integral in (4.9), we shall replace χ_f by the WKB approximation

$$R\chi_f(R)=(2M\omega/\pi\hbar)^{1/2}$$
$$\times\{\cos[\tilde{q}_f(R)-\tfrac{1}{4}\pi]/[\tilde{\kappa}_f(R)]^{1/2}\}, \qquad (4.10)$$

where

$$\tilde{q}(R_f)\equiv\int_{R_t}^{R}\tilde{\kappa}_f(R')\,dR',$$
$$\tilde{\kappa}_f(R)\equiv(2M/\hbar^2)^{1/2}[\tilde{\epsilon}_f-\tilde{V}_{\alpha l'}(\tilde{R}_t)]^{1/2}; \qquad (4.11)$$

$\tilde{R}_t$ is the smaller root of the equation $\tilde{\epsilon}_f-\tilde{V}_{\alpha l'}(\tilde{R}_t)=0$, $\tilde{\epsilon}_f$ is the energy of the residual molecule in state $\alpha l'v$, $\tilde{V}_{\alpha l'}$ the corresponding electronic energy, and ω the vibrational frequency. The normalization constant in (4.10) has been calculated by assuming $\tilde{V}$ to be parabolic, and chosen so that

$$\int R^2\,|\,\chi_f(R)\,|^2\,dR=1.$$

We then substitute (3.6) and (4.10) into (4.9), replacing the Hankel functions in (3.6) by their asymptotic forms [this will be justified because it turns out that the main contribution to (4.9) does not come from the neighborhood of turning points]. The integral in (4.9) then becomes, up to a constant factor,

$$\int_0^\infty dR\{\exp(i[q_{l'}(R)-\tilde{q}_f(R)])$$
$$+\exp(-i[q_{l'}(R)-\tilde{q}_f(R)])\}\zeta(R), \qquad (4.12)$$

where

$$\zeta(R)\equiv\zeta_{\alpha\beta}(\mathbf{k}_f,R,\hat{R}),$$

and where only those products of oscillating exponentials have been retained which have a point where the phase is stationary. Since in (4.12), ζ will be slowly varying in comparison with the exponentials, the main contribution will come from the neighborhood of points R_f defined by

$$\{(\partial/\partial R)[q_{l'}(R)-\tilde{q}_f(R)]\}_{R=R_f}=0,$$

i.e.,

$$\epsilon-W_{l'}(R_f)=\tilde{\epsilon}_f-\tilde{V}_{\alpha l'}(R_f). \qquad (4.13a)$$

Although the solution of this equation will in general be complex, we shall simplify the discussion by assuming that Γ is sufficiently small for the imaginary part of R_f to be neglected. [There would be no great difficulty in removing this restriction by introducing linear approximations for $W_{l'}$ and $\tilde{V}_{\alpha l'}(R)$ near R_f.] Equation (4.13a) is an expression of the Franck-Condon principle. The left- and right-hand sides are the kinetic energies of the nuclei before and after the emission of an electron. Therefore (4.13a) says that an electron can be emitted only near a point R_f at which the velocity of the nuclei remains unchanged.

Introducing the energy $\epsilon_f{}^{(e)}$ of the emitted electron, then since

$$\epsilon_f{}^{(e)}=\epsilon-\tilde{\epsilon}_f,$$
$$\epsilon_f{}^{(e)}=W_{l'}(R_f)-\tilde{V}_{\alpha l'}(R_f). \qquad (4.13b)$$

This relation is illustrated in Fig. 3.

The slowly varying function $\zeta(R)$ in (4.12) will be approximated by $\zeta(R_f)$, taken outside the integral, and written in terms of $\Gamma(R_f)$ by the formula

$$\frac{\Gamma(R)}{2\pi\hbar} \cong (Z+1)\,\frac{m^2 v_f}{\hbar^4} \sum_{S_\beta} \int d\hat{k}_f \,|\, \zeta_{\alpha\beta}(\mathbf{k}_f, R, \hat{R}) \,|^2, \qquad (4.14)$$

which is derived in the Appendix. The remaining integral in (4.12) may be evaluated by the saddle-point method, using the notation

$$(-)\{(\partial^2/\partial R^2)[q_{l'}(R)-\tilde{q}_f(R)]\}_{R=R_f} \equiv M\Delta_f/\hbar^2 \kappa_{l'}(R_f), \qquad (4.15)$$

where

$$\Delta_f \equiv \{(\partial/\partial R)[W_{l'}(R)-\tilde{V}_{\alpha l'}(R)]\}_{R=R_f}\,. \qquad (4.16)$$

The formula (4.9) finally becomes

$$\sigma_{l'v} = (2l'+1)\pi\lambdabar^2 \tau_f (\Gamma(R_f)/\hbar) \,|\, A_{f-}e^{-i\mu_f/2} + A_{f+}e^{i\mu_f/2} \,|^2, \qquad (4.17)$$

where

$$\mu_f/2 \equiv -\tfrac{1}{4}\pi + \mathrm{Re}(q_{l'} - \tilde{q}_f)_{R=R_f}\,, \qquad (4.18)$$

and

$$\tau_f \equiv \hbar\omega / v_{l'}(R_f)\Delta_f\,. \qquad (4.19)$$

$$A_{f+} \equiv \exp\left\{-\,\mathrm{Im}\left[\int_{R_{0l}}^{\infty} \kappa_{l'}(R')dR' + \int_{R_{0l}}^{R_f} \kappa_{l'}(R')dR'\right]\right\}, \qquad (4.20a)$$

$$A_{f-} \equiv \exp\left\{-\,\mathrm{Im}\left[\int_{R_f}^{\infty} \kappa_{l'}(R')dR'\right]\right\}. \qquad (4.20b)$$

Formula (4.17) is the final expression for the cross section for associative detachment. The various factors have simple physical interpretations:

(i) $(2l'+1)\pi\lambdabar^2$ is the geometrical cross section for the collision of atom and ion with relative angular momentum $\hbar l'$ and linear momentum $\hbar/\lambdabar$.

(ii) τ_f is the time a classical particle moving with velocity $v_{l'}(R_f)$ would spend traversing the region $\delta R_f \equiv R_f(\alpha l'v+1) - R_f(\alpha l'v)$ separating the point sR_f corresponding to two adjacent vibrational levels of the final molecule. To see this, we note from (4.13) and (4.16) that $|\,\Delta_f\,|\,|\,\delta R_f\,| = |\,\tilde{\epsilon}_{\alpha l'v+1} - \tilde{\epsilon}_{\alpha l'v}\,| = \hbar\omega$; therefore $\tau_f = \delta R_f / v_{l'}(R_f) = \hbar\omega/[v_{l'}(R_f)\Delta_f]$, in agreement with (4.19). This physical interpretation of τ_f must *not* be taken to mean that the R axis may be divided into intervals δR_f in each of which there is autoionization to only one final vibrational level. The range of R contributing to a single level v is the range near the point R_f in which the phases of the exponentials in (4.12) are slowly varying; from (4.15), it follows that this is of order

$$|\,2\hbar^2\kappa_{l'}(R_f)/M\Delta_f\,|^{1/2} = (\delta R_f)^{1/2}(2v_{l'}(R_f)/\omega)^{1/2},$$

which will generally differ from δR_f.

(iii) $\Gamma(R_f)/\hbar$ is the decay rate in the region where autoionization to the level v occurs.

(iv) The factor $|\cdots|^2$ is the square of the sum of the probability amplitudes for the oscillating nuclei to be at the point R_f during the inward and reflected motions, multiplied by phase factors depending on the final state. In the first term, the factor A_{f-} contains the damping of the incident wave from $R=\infty$ to $R=R_f$, while the factor $\exp(-i\mu_f/2)$ contains the corresponding phase. In the second terms, the factor A_{f+} is the modulus of the reflected wave, damped from $R=\infty$ to the reflection point near R_{0l} on the way in, and again from the reflection point to R_f on the way out. The factor $\exp(i\mu_f/2)$ contains the phase of the outgoing wave.

The presence of the two terms in $|\cdots|^2$ in (4.17) gives rise to oscillations in $\sigma_{l'v}$ as a function of ϵ. One has

$$|\,A_{f-}e^{-i\mu_f/2} + A_{f+}e^{i\mu_f/2}\,|^2 = A_{f-}{}^2 + A_{f+}{}^2 + 2A_{f+}A_{f-}\cos\mu_f. \qquad (4.21)$$

To estimate the period of the oscillations, we note that from (4.18) and (4.13) and neglecting Γ,

$$d\mu_f/d\epsilon = 2\,\mathrm{Re}(d/d\epsilon)q_{l'}(R_f;\epsilon) = \frac{2}{\hbar}\int_{R_{0l}}^{R_f} \frac{dR'}{v_{l'}(R')} \equiv \frac{\tau_f(\epsilon)}{\hbar}\,. \qquad (4.22)$$

$\tau_f(\epsilon)$ is the time a classical particle would take to move from R_f to the turning point and back in the potential $E_{l'}(R)$. Replacing $\tau_f(\epsilon)$ by a typical value $\bar{\tau}$, we have as a rough estimate for the period $\delta\epsilon$ of the oscillations

$$\delta\epsilon \approx 2\pi\hbar/\bar{\tau}. \qquad (4.23)$$

This will be of the order of a typical vibrational spacing, say about a tenth of an eV. The oscillations of the partial cross sections with different l' will not be quite in step because of the dependence of μ_f on l' [Eq. (4.18)].

The dependence of μ_f in (4.18) on the final vibrational state, through $\tilde{q}$, implies that the interference in (4.21) will make $\sigma_{l'v}$ fluctuate from one v to the next at a constant initial energy. This effect may be estimated by considering the change $\Delta\mu_f$ in μ_f as v changes by unity. One obtains from (4.13) and (4.18)

$$\Delta\mu_f = -2\omega\tilde{\tau}_v(\tilde{\epsilon}_f),$$

where $\tilde{\tau}_v(\tilde{\epsilon}_f)$ is the time a classical particle of energy $\tilde{\epsilon}_f$ would take to move from R_f to the inner turning point in the potential $\tilde{V}$. Since $2\tilde{\tau}_v(\tilde{\epsilon}_f)$ will usually be a sizable fraction of $(2\pi/\omega)$, there will generally be a change of order unity in the term containing $\cos\mu_f$ in (4.21) from one vibrational level to the next.

The expression (4.9) can be summed over all final states of the nuclei to verify consistency with (3.19). To do this, we take ζ outside the R integral, replace it by $\zeta(R_f)$ [as we did in treating (4.12)], and substitute for $|\,\zeta\,|^2$ from (4.14). The result is

$$\sigma_{l'v} = \frac{2\pi^2(2l'+1)}{v_0\hbar}\,\Gamma(R_f)\left|\int dR\,R\chi^*{}_f(R)\xi_{l'}(R)\right|^2. \qquad (4.24)$$

One can now use the slow variation of $\Gamma(R)$ with R to insert Γ back into one of the R integrals, replacing $\Gamma|\int\cdots|^2$ by

$$\Gamma\left|\int\cdots\right|^2\to\int RdR\,R'dR'\Gamma(R)\xi^*{}_{l'}(R)\xi_{l'}(R')$$
$$\times\chi_{l'v}(R)\chi^*{}_{l'v}(R').\quad(4.25)$$

Equation (4.24) can then be summed over v by using the completeness relation

$$\sum_v\chi_{l'v}(R)\chi^*{}_{l'v}(R')=\delta(R-R')/RR',\quad(4.26)$$

to recover (3.19). This argument is still valid if some of the final states of $(A+B)$ are unbound, since (4.26) remains true in that case.

If the individual levels v are not resolved, the interference term in (4.21) may be dropped because of the fluctuations of $\cos\mu_f$. One may then consider an interval $\tilde{\epsilon}_f$ to $\tilde{\epsilon}_f+\Delta\tilde{\epsilon}_f$ for the final energy of the nuclei, containing several levels (i.e., $\Delta\tilde{\epsilon}_f\gg\hbar\omega$). Denoting the cross section for all final levels of angular momentum l' in this interval by $\sigma_{l'}(\tilde{\epsilon}_f)\Delta\tilde{\epsilon}_f$, one finds that (4.17) is replaced by

$$\sigma_{l'}(\tilde{\epsilon}_f)\Delta\tilde{\epsilon}_f=(2l'+1)\pi\lambda\!\!\!^{-2}$$
$$\times\frac{\Gamma(R_f)}{\hbar}\left[\frac{\Delta\tilde{\epsilon}_f}{v_{l'}(R_f)\Delta_f}\right](A_{f-}{}^2+A_{f+}{}^2).\quad(4.27)$$

{The physical interpretation of the factor $[\cdots]$ is similar to that of Eq. (5.1) in the next section.} Equation (4.27) applies if the final levels are so close that the nuclei may be treated classically; the two contributions $A_{f-}{}^2$ and $A_{f+}{}^2$ then correspond to nuclei approaching and separating as they pass R_f.

V. NONASSOCIATIVE DETACHMENT: REACTION $A^-+B\to A+B+e$

After the emission of an electron, it may happen that the final state of the nuclei lies in a continuum, either because the final electronic state is repulsive, or because the electron carries away too little energy to leave the nuclei bound. The expression for the cross section for detachment in this case can still be obtained from (4.9) by taking the nuclear wave functions χ to be normalized within a box of radius L large compared with atomic dimensions. The cross section for leaving the system $A+B$ with energy between $\tilde{\epsilon}_f$ and $\tilde{\epsilon}_f+d\tilde{\epsilon}_f$ will be denoted by $\sigma_{l'}(\tilde{\epsilon}_f)d\tilde{\epsilon}_f$, as at the end of Sec. IV. The difference between (4.27) and the present case is that in (4.27) $\Delta\tilde{\epsilon}_f$ has to spread over many discrete final levels, whereas here we are dealing with a true continuum so that $d\tilde{\epsilon}_f$ can be infinitesimal. On letting L tend to infinity, one finds that $\sigma_{l'}(\tilde{\epsilon}_f)d\tilde{\epsilon}_f$ is given by (4.17) with τ_f replaced by

$$d\tau_f\equiv d\tilde{\epsilon}_f/v_{l'}(R_f)\Delta_f.\quad(5.1)$$

R_f is still defined by (4.13a) and Δ_f by (4.16). It follows, by an argument similar to that in point (ii) below Eqs. (4.20) that $d\tau_f$ is the time which a classical particle would need to traverse the distance δR_f between the points R_f corresponding to $\tilde{\epsilon}_f$ and $\tilde{\epsilon}_f+d\tilde{\epsilon}_f$.

VI. ESTIMATES OF THE CROSS SECTION FOR ELECTRON DETACHMENT

A. An Upper Limit on $\bar{\sigma}_d$

The expression (3.19) for the cross section for detachment depends on $\Gamma(R)$, so that exact calculations would require a knowledge of the complex energies of the compound states involved. However, the estimate (3.18) shows that it is easily possible for the contribution of the lth partial wave in the incident beam to reach the maximum attainable, according (3.4), when $|\eta_l|=0$. We shall calculate an upper limit to the cross section by assuming that all partial waves with l below some upper limit $l_{\max}(\epsilon)$ are completely absorbed by the process of electron detachment. We shall consider later to what extent this upper limit may be approached in practice.

If $\eta_l=0$ for $0\leq l\leq l_{\max}(\epsilon)$, the cross section for electron detachment will be denoted by $\bar{\sigma}_d$. It is

$$\bar{\sigma}_d(\epsilon)=\pi\lambda\!\!\!^{-2}\sum_{l=0}^{l_{\max}}(2l+1)=\pi\lambda\!\!\!^{-2}l_{\max}{}^2=\pi b_{\max}{}^2(\epsilon).\quad(6.1)$$

Here $\lambda\!\!\!^{-}$ is the reduced wavelength in the incident beam, and $b_{\max}(\epsilon)$ the classical impact parameter corresponding to an angular momentum $\hbar l_{\max}$. The values of l of interest will be so large that one always replace $(l+1)$ by l. In reality, if the partial waves with $l<l_{\max}$ have η_l small but finite, one has

$$\sigma_d<\bar{\sigma}_d(\epsilon).\quad(6.2)$$

We shall assume that there is a radius R_d such that detachment takes place with certainty whenever the nuclei approach to $R\leq R_d$. With a potential W having an attractive real part, R_d will be of the order of the separation at which the potential curve starts to slope down sharply as the nuclei approach. For the sake of illustrating orders of magnitude, we shall take $R_d=2\times10^{-8}$ cm. The quantity $\hbar l_{\max}$ is the highest angular momentum for which the particles can approach into $R\leq R_d$. In making the estimate, we shall neglect all barrier-penetration effects.

A knowledge of the interaction potential is needed only for $R>R_d$. To a good approximation this will be given by the polarization potential

$$-\alpha e^2/2R^4\quad(6.3)$$

between an ion of charge e, and an atom of polarizability α. Thus the complete effective potential for the lth partial wave is

$$W_l(R)=-(e^2\alpha/2R^4)+(\hbar^2l^2/2MR^2)+W(\infty)\quad(6.4)$$

when $R>R_d$. For the sake of illustration, we shall take for α the value

$$\alpha = 0.7 \times 10^{-24}\ \text{cm}^3 \tag{6.5}$$

for atomic hydrogen. Curves for W_l are shown in Fig. 4. Note that when l is small, $W_l(R)$ has a maximum in the region $R > R_d$; when l is large, there is no such maximum. The value of l marking the transition between the two regions will be denoted by l_c. It is determined by the condition $[\partial W_{l_c}/\partial R]_{R=R_d} = 0$ to be

$$l_c^2 = 2\alpha e^2 M/\hbar^2 R_d^2. \tag{6.6}$$

With the reduced mass of two hydrogen atoms for M, one gets $l_c \cong 24$. The curve for l_c is marked on Fig. 4. In calculating $l_{\max}(\epsilon)$, there are two different regimes to consider, depending on whether $\epsilon_0 > \epsilon_{0c}$ or $\epsilon_0 < \epsilon_{0c}$, where ϵ_0 is the initial kinetic energy introduced in (3.2) and

$$\epsilon_{0c} \equiv W_{l_c}(R_d) - W(\infty) = +\alpha e^2/2R_d^4, \tag{6.7}$$

ϵ_{0c} is marked on Fig. 4. With the numerical values quoted above, one gets $\epsilon_{0c} = 0.3$ eV.

(1) $\epsilon_0 > \epsilon_{0c}$. This case is illustrated by the line ϵ_1 in Fig. 4. Here

$$\epsilon = W_{l_{\max}}(R_d), \tag{6.8}$$

so that one gets from (6.4)

$$b_{\max}(\epsilon) = [\hbar l_{\max}/(2M\epsilon_0)^{1/2}] = R_d[1 + \alpha e^2/2\epsilon_0 R_d^4]^{1/2}. \tag{6.9}$$

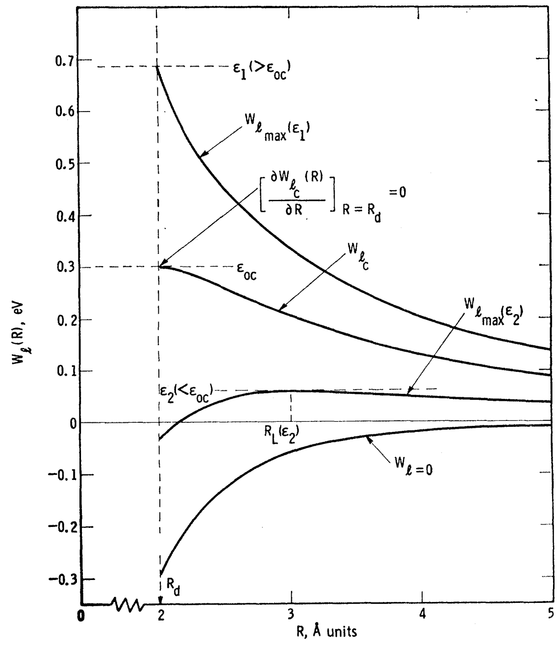

FIG. 4. The range $R > R_d$ outside the region where electron detachment becomes almost certain. A^- and B interact only through the polarization potential $-\alpha e^2/2R^4$. When $\epsilon_0 = \epsilon_2 < \epsilon_{0c}$, there is a finite gap between R_d and the distances of closest approach (which always exceed R_L) in collisions which do not lead to detachment. When $\epsilon_0 = \epsilon_1 > \epsilon_{0c}$, there is no such gap. $R_L(\epsilon_2)$ is the Langevin spiraling radius at which A^- and B can circle about one another if $\epsilon_2 < \epsilon_{0c}$.

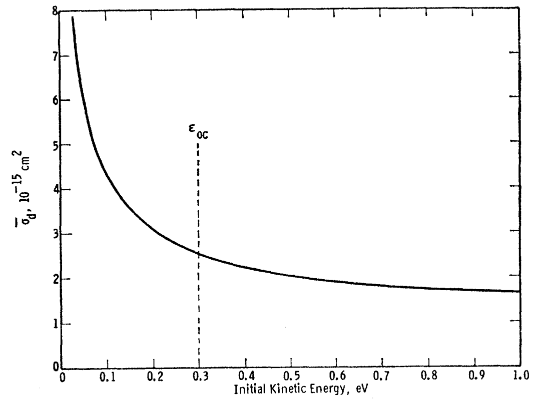

FIG. 5. Upper limit $\bar{\sigma}_d$ to the detachment cross section on the assumption that every collision in which the nuclei in A^- and B approach to within $R_d(=2\times10^{-8}$ cm) leads to detachment. When the initial kinetic energy ϵ_0 is less than $\epsilon_{0c}(=\alpha e^2/2R_d^4)$, the cross section is determined by Langevin spiraling and independent of R_d. When $\epsilon_0 \gg \epsilon_{0c}$, the cross section falls to πR_d^2. The curve is drawn for a polarizability $\alpha = 0.7\times10^{-24}$ cm^2.

(2) $\epsilon_0 < \epsilon_{0c}$. This case is illustrated by the line marked ϵ_2. The distance of closest approach at $l_{\max}$, which will be denoted by $R_L(\epsilon)$, and $l_{\max}$ itself are determined by

$$[\partial W_{l_{\max}}(R)/\partial R]_{R=R_L} = 0, \qquad W_{l_{\max}}(R_L) = \epsilon.$$

One gets

$$R_L(\epsilon) = (\alpha e^2/2\epsilon_0)^{1/4},$$

and

$$b_{\max}(\epsilon) = \sqrt{2} R_L(\epsilon).$$

With the value for α above, at $\epsilon_0 = 0.04$ eV, one obtains $R_L \cong 3.4\times10^{-8}$ cm, and $b_{\max} = 4.7\times10^{-8}$ cm. At the radius $R_L(\epsilon)$, the two particles can circle around each other steadily at energy ϵ. The classical orbits in a polarization potential (6.3) and the special role of $R_L(\epsilon)$ have been thoroughly discussed by Langevin.[17]

From $b_{\max}$ and (6.1) one can calculate $\bar{\sigma}_d$:

$$\text{for}\quad \epsilon_0 > \epsilon_{0c}, \qquad \bar{\sigma}_d = \pi R_d^2(1 + \epsilon_{0c}/\epsilon_0); \tag{6.10}$$

$$\text{for}\quad \epsilon_0 < \epsilon_{0c}, \qquad \bar{\sigma}_d = 2\pi(\alpha e^2/2\epsilon_0)^{1/2}. \tag{6.11}$$

Formulas (6.10) and (6.11) give the same values for $\bar{\sigma}_d$ and $d\bar{\sigma}_d/d\epsilon$ at $\epsilon_0 = \epsilon_{0c}$; Fig. 5 gives $\bar{\sigma}_d$ for the values or R_d and α quoted above. Note that $\bar{\sigma}_d$ can become very large at thermal energies; at $\epsilon_0 = 0.04$ eV (i.e., kT at 400°K) one gets $\sigma_d \cong 0.7\times10^{-14}$ cm^2. This large value arises from the pulling together of the colliding particles over large distances by the polarization potential.

B. The Order of Magnitude of $\bar{\sigma}_d$

We can now make rough estimates of the values of σ_d likely to be encountered in practice. Before doing this, we have to remove the restriction to a single electronic state on which the earlier sections were based. In general, there is not a single unique electronic state

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[17] P. Langevin, Ann. Chim. Phys. **5**, 245 (1905).

corresponding to the initial configuration

$$A^-+B,$$

even if A^- and B are in their ground states. Instead, if the ion A^- and the atom B have nonvanishing angular momenta, there will be a number of different states at large R which can be classified according to the spin and the orbital angular momentum along the internuclear axis. If the charges on the two nuclei are identical, there will be in addition a quantum number corresponding to reflection in the plane which bisects the internuclear axis and is normal to it. In the example of H+H$^-$, there are two such states, given by (2.13). Each has its own potential energy curve given in Fig. 1. The cross section σ_d may be written

$$\sigma_d=\sum_n g_n\sigma_{dn}, \tag{6.12}$$

where n runs over the initial electronic states with different sets of quantum numbers; σ_{dn} is the detachment cross section one would have if the system were prepared in the nth state initially, and g_n is the statistical weight of the nth state. The g_n must satisfy

$$\sum_n g_n=1. \tag{6.13}$$

In the example of H$^-$+H, the two states in (2.13) each have $g=\frac{1}{2}$. The σ_{dn} for different n have to be calculated along the lines discussed earlier in this paper. According to the estimate (3.18), any state n with a value of Γ exceeding about 0.1 eV will have a σ_{dn} approaching $\bar{\sigma}_d$. If any of the states n have detachment cross sections approaching $\bar{\sigma}_d$ they will dominate the sum (6.12).

There is a large class of compound negative-ion states of which many will satisfy condition (3.18) by a large margin; they are the states which give rise to shape resonances in electron scattering. The associated wave function ψ has approximately the form $\psi=\psi_0\varphi$, where ψ_0 is the ground state of a neutral molecule, and φ is the wave function of the additional electron. The reason for this large width can be seen from formula (A25) in the Appendix and the remarks following. We shall refer to these states as "shape compound." That some of the states n should be of this kind is probable for the following reason. Since we may assume A^- and B to be originally in their ground states, the initial electronic state of the configuration A^-+B has a wave function with a strong component of the form $\psi_A\psi_B\varphi$, where ψ_A and ψ_B are the ground states of the neutral atoms A and B, and φ is the wave function of the additional electron attached to A. As the nuclei move together, the product $\psi_A\psi_B$ will go over adiabatically into the ground state ψ_{AB} of the molecule AB, provided that the angular momentum and spin quantum numbers are those of ψ_{AB}; this will be the case with some states n. The state ψ will then either remain bound, or move up in energy relative to the ground state of (AB) to become a shape compound state. Which of these alternatives happens can only be settled by detailed calculations in a particular case; in the example of H$^-$+H, the lowest $^2\Sigma_u$ state turns into an unstable shape compound state.

There is another class of unstable negative ion states which should generally have much smaller widths. These are the states envisaged by Feshbach,[18] consisting of an additional electron bound to a neutral molecule in an excited electronic state. Here electron emission is inhibited by the need to change the state of the residual molecule at the same time. The widths of these states will vary widely from one case to another, and the corresponding values of σ_d should vary from $\bar{\sigma}_d$ downwards.

A high probability of electron detachment requires not only that Γ should be large, but also that the colliding nuclei should reach the region where this happens. If $E(R)$ is attractive, then this will certainly happen even at low energies if $l<l_{\max}(\epsilon)$. If $E(R)$ is repulsive at short distances, then the energy may have to exceed a threshold before the detaching region can be reached.

In the example of H+H$^-$, the lower state shown in Fig. 1 of paper II is attractive, and has a large Γ at small R. It should therefore have a detachment cross section very close to $\bar{\sigma}_d$. The upper state is repulsive so that more detailed calculations are needed before its contribution to σ_d can be estimated. According to (4.12) with $g=\frac{1}{2}$ for each state, we therefore get, for H+H$^-$,

$$\tfrac{1}{2}\bar{\sigma}_d<\sigma_d<\bar{\sigma}_d.$$

At low energies, the value of $\bar{\sigma}_d$ becomes the polarization limit given by Eq. (6.11), so that below about 0.5 eV, for H+H$^-$,

$$\frac{0.1\times10^{-14}\text{ cm}^2}{[\epsilon_0(\text{eV})]^{1/2}}<\sigma_d<\frac{0.2\times10^{-14}\text{ cm}^2}{[\epsilon_0(\text{eV})]^{1/2}}. \tag{6.14}$$

The figure of 0.5 eV is very uncertain owing to its dependence on the ill-defined parameter R_d. At higher energies where the upper states also contributes, the cross section will fall to πR_d^2; for $R_d\cong2$ Å, this is 10^{-15} cm^2.

VII. DISCUSSION

We have shown how a theory of electron detachment in the collision of a negative ion and a neutral atom can be founded on the assumption of a unique electronic state which changes adiabatically with the separation R of the nuclei, becoming autoionizing when R is of the order of 10^{-8} cm. Because the simplicity of the physical picture is somewhat obscured by the mathematical details, we shall now summarize the physical aspects.

The nuclear wave function ξ in the channel A^-+B satisfies the Schroedinger Eq. (2.9) in which the motion

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[18] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962).

of the electrons enters only through the adiabatic energy $W(R)$, which has an imaginary part $-i\Gamma/2$ arising from autoionization at small R. The function ξ can be separated into partial waves corresponding to definite orbital angular momentum $\hbar l$ of the nuclei [Eq. (2.11)]; each of these consists of an incoming wave and a wave reflected by the short-range repulsion. The damping of ξ by the term $(-i\Gamma/2)$ makes the amplitude of the reflected wave smaller than that of the incoming wave by the factor η_l in Eq. (3.1). The contribution of the lth partial wave to the total cross section for electron detachment is proportional to the loss of probability from the channel $A^- + B$ during reflection, i.e., to $(1- \mid \eta_l \mid^2)$; [see Eq. (3.57)]. For incident kinetic energies up to a few eV in the channel $A^- + B$, a value of Γ exceeding about 0.1 eV over a region of atomic dimensions will be sufficient to make electron detachment in a close collision so highly probable that the η_l are negligible in all partial waves affected (3.18). The total cross section for electron detachment is then determined by the largest impact parameter for which the colliding particles reach the detaching region and will be of the order of 10^{-15} cm^2 except at kinetic energies so low that the Langevin spiralling arising from the long-range polarization attraction can pull A^- and B together over distances much larger than the gas-kinetic diameters (Sec. VI); cross sections much larger than 10^{-15} are then possible. If one assumes that there exists a separation R_d such that detachment becomes virtually certain whenever the colliding particles approach to within R_d, the detachment cross section approaches πR_d^2 at high energies, and is proportional to (kinetic energy)$^{-1/2}$ at low energies; the transition occurs at the energy ϵ_{0c} determined by R_d and the polarizability and given by (6.7). As a consequence the rate constant for electron detachment is independent of temperature at low temperatures (less than a few thousand degrees in the case of $H^- + H$) and proportional to $T^{1/2}$ at high temperatures.[19]

The total cross section for electron detachment may be split into partial cross sections to individual states of the residual system $A+B$. All these cross sections may be calculated from the overlap integral of $\xi\psi$ with the states of the residual system [Eq. (4.1)]. Because of the rapid oscillation of both ξ and the nuclear wave functions of the final states, the major contribution to each overlap integral will come from the neighborhood of a point determined by the Franck-Condon principle, i.e., where the wavelengths of the two wave functions are equal. Since ξ consists of two separate components, the incident and reflected waves, each overlap integral consists of two terms, as shown by the last factor in (4.17) [this gives the cross section for a bound state of $A+B$, while (5.1) gives it for a continuum state]. The interference of these contributions leads to oscillations of each cross section as a function of energy [Eq. (4.23)], and to fluctuation in the cross sections from state to state. If the total detachment cross section is close to the upper limit $\bar{\sigma}_d$, the outgoing ξ wave will be small compared with the incoming, and may be ignored for a rough estimate of the partial cross sections. In this case, associative detachment should produce a highly inverted population of vibrational levels in the final molecule (AB), since detachment is more likely to occur just after entry into the autoionizing region at large separations than in the Franck-Condon domains of the lower vibrational levels where the ξ wave has a much reduced amplitude.

No experimental detachment cross sections at well-defined energies on which the theory could be tested have been published. The nearest available are measurements of the rate constant for electron detachment in drift tubes containing negative ions and neutral atoms or molecules[9–11] at laboratory temperatures. These rate constants correspond to average cross sections of the order of 10^{-14} cm^2 in many cases, i.e., greatly in excess of gas kinetic.[20] It should be noted that although this order of magnitude is in general agreement with the theory for the interaction of negative ions with neutral atoms, in the case of interaction with neutral diatomic molecules the polarization potential ($\propto R^{-4}$) may be dominated at large separations by the ion-dipole potential ($\propto R^{-2}$) for a heteronuclear molecule, or the ion-quadrupole potential ($\propto R^{-3}$) for a homonuclear molecule; in these cases the simple theory given in Sec. VI does not apply.

ACKNOWLEDGMENTS

The suggestion that the concept of unstable compound states should be applied to the electron-detachment problem was made by Professor Sir Harrie Massey, F.R.S. I am grateful to the Westinghouse Research Laboratory for its hospitality while this work was done, and to many of its members, especially P. J. Chantry, A. V. Phelps (who made me aware of Langevin spiraling), and G. J. Schulz for stimulating discussion. I am also grateful to Dr. J. N. Bardsley for informing me of his results (Ref. 14) before publication.

APPENDIX: DERIVATION OF EQUATION (4.14)

Equation (4.14) expresses the decay width of an unstable electronic state in terms of the volume integral (4.7). This relation has been derived before (see, e.g., Ref. 18) for Feshbach states—autoionizing states consisting of an electron bound to an excited target—but we need it under more general conditions. At no point have we made any restrictive assumption about the physical nature of the compound state of the electrons,

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[19] M. R. C. McDowell, Observatory **81**, 240 (1961). This paper predicts a $T^{1/2}$ dependence for $T < 10^6$ °K.

[20] The first interpretation of these large cross sections in terms of the Langevin spiralling process seems to have been given in two independent papers by E. Ferguson and the author at the Symposium on the Physics and Chemistry of the Lower Atmosphere, University of Colorado, Boulder, 1966 (unpublished).

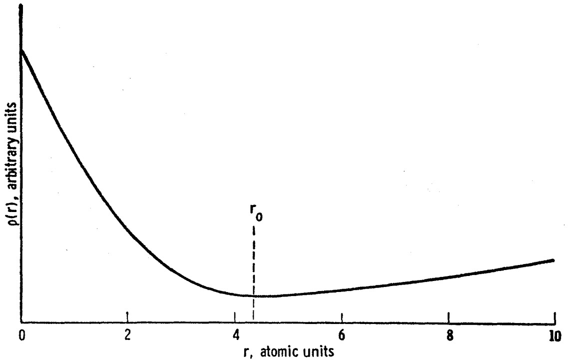

FIG. 6. Schematic electron density in an unstable compound state. There is a central peak falling to a minimum followed by a slowly growing exponential tail. The tail arises from the open channels [see Eq. (A9)]. The radius r_0 of the surface S is to be taken at the density minimum.

whether it be a Feshbach or a shape compound resonance. It is therefore desirable to derive (4.14) with the same degree of generality; that is the purpose of this Appendix.

The method we shall use to establish (4.14) is to imagine a spherical surface S surrounding the system A^-+B, and to express both sides of (4.14) in terms of amplitudes on S. (Only the case where the nuclei lie within a few Bohr radii of one another has to be considered, since only then is $\Gamma\neq 0$.) The radius of S will be denoted by r_0; its magnitude will be important in what follows and is discussed below.

The following definitions are needed:

$H_{\mathrm{el}}(\mathrm{not}\,j)$ is the electronic Hamiltonian with the jth electron omitted,
$\mu_\alpha(\mathrm{not}\,j)$ is one of its eigenfunctions belonging to the eigenvalue ϵ_α, so that

$$[H_{\mathrm{el}}(\mathrm{not}\,j)-\epsilon_\alpha]\mu_\alpha(\mathrm{not}\,j)=0. \tag{A1}$$

ϵ_α depends on the separation of the nuclei, i.e., $\epsilon_\alpha=\epsilon_\alpha(R)$; this dependence will mostly be left to be understood.
K_j is the kinetic energy of the jth electron, and
V_j its interaction with the rest of the system, so that the complete Hamiltonian is

$$H_{\mathrm{el}}=H_{\mathrm{el}}(\mathrm{not}\,j)+K_j+V_j. \tag{A2}$$

(There are as many such ways of splitting up H_{el} as there are electrons.)
$f_\beta(r_j,\epsilon')$ is the radial factor of an eigenfunction of K_j with energy ϵ', the suffix β standing for the spin- and orbital-momentum quantum numbers; thus

$$(K_j-\epsilon')f_\beta(r_j,\epsilon')Y_\beta(\hat{r}_j)=0. \tag{A3}$$

$Y_\beta(\hat{r}_j)$ is a spherical harmonic ($\hat{r}_j$ denoting the angular coordinates of the jth electron).
$S_\beta(j)$ is a spin function for the jth particle.

We expand ψ in a series

$$\psi=(-1)^j\sum_{\alpha\beta}\varphi_{\alpha\beta}(\mathrm{not}\,j)\psi_{\alpha\beta}(r_j), \tag{A4}$$

where

$$\varphi_{\alpha\beta}(\mathrm{not}\,j)\equiv\mu_\alpha(\mathrm{not}\,j)\,Y_\beta(\hat{r}_j)\,S_\beta(j), \tag{A5}$$

satisfying the orthogonality relation

$$\int d\hat{r}_j dq(\mathrm{not}\,j)\varphi^*{}_{\alpha\beta}(\mathrm{not}\,j)\varphi_{\alpha'\beta'}(\mathrm{not}\,j)=\delta_{\alpha\alpha'}\delta_{\beta\beta'}. \tag{A6}$$

[$\int dq(\mathrm{not}\,j)\cdots$ denotes integration over all coordinates except the spatial coordinates of the jth electron.] Clearly there are as many expansions of the form (A4) as there are electrons. The factor $(-1)^j$ ensures antisymmetry, provided that the coordinates in μ_α are written in ascending order, and μ_α is itself antisymmetric.

The electron density associated with ψ is, after averaging over angles,

$$\rho(r)=\text{constant}\times\sum_{\alpha\beta}|\psi_{\alpha\beta}(r)|^2, \tag{A7}$$

from Eqs. (A4) and (A6). If ψ were a bound state, all the functions $\psi_{\alpha\beta}(r)$ would decrease exponentially as $r\rightarrow\infty$. If ψ is an unstable compound state, most of the $\psi_{\alpha\beta}$ (the closed channels for which $E<\epsilon_\alpha$) will still fall off exponentially; however, in the open channels one has $E>\epsilon_\alpha$, so that

$$\psi_{\alpha\beta}(r)\rightarrow(\text{constant}/r)\times\exp\{ir[(2m/\hbar^2)(W-\epsilon_\alpha)]^{1/2}\}\quad\text{as } r\rightarrow\infty. \tag{A8}$$

If $\Gamma\ll(E-\epsilon_\alpha)$, then approximately

$$|\psi_{\alpha\beta}(r)|\rightarrow(\text{constant}/r)\times\exp[\Gamma r/2\hbar v_\alpha],\quad\text{as } r\rightarrow\infty, \tag{A9}$$

$$v_\alpha\equiv[(2/m)(E-\epsilon_\alpha)]^{1/2},$$

so that each open channel contributes an exponentially growing tail to $\rho(r)$ at large r. The function $\rho(r)$ in a well-defined compound state must look as in Fig. 6, with a central maximum falling to a relatively low minimum before the exponentially rising tails start to predominate. The tails make it necessary to cut off $\rho(r)$ at some arbitrary radius before it can be normalized; therefore ρ is defined only up to a constant. An example of a quasistationary state behaving as in Fig. 6 would be a particle confined to the neighborhood of a point by a high but nevertheless penetrable barrier; then the probability density is high in the space enclosed by the barrier, falls exponentially through the barrier, and rises again from the outer edge of the barrier to infinity. Another example is a compound state of Feshbach's type[18] consisting of an electron temporarily bound to an excited state of an atom; there the closed channels give the major portion of ρ close to the nucleus, while the open channels contribute exponentially growing tails at large distance.

We shall choose r_0 at the minimum in the electron density. If the compound state is to be physically meaningful, then $\rho(r_0)$ must be small compared with the order of magnitude of ρ in the central peak. Since the individual channels contribute additively to (A7), it follows that

$$r_0^3 \,|\, \psi_{\alpha\beta}(r_0) \,|^2 \Big/ \int dq \,|\, \psi(q) \,|^2 \ll 1 \tag{A10}$$

for each (α, β), the integral in the denominator being taken over the interior of S for all particles. In what follows, we shall treat the surface amplitudes $\psi_{\alpha\beta}(r_0)$ as small quantities and repeatedly drop terms above the lowest order.

A relation between Γ and $\psi_{\alpha\beta}(r_0)$ may be obtained by multiplying (2.2) by ψ^*, subtracting the complex conjugate, and integrating all electron coordinates over the interior of S. The result is

$$\frac{\hbar^2}{2mi} \sum_j \left\{ \int_{r_i \leq r_0;\, i \neq j} r_j^2 d\hat{r}_j dq(\text{not } j) \left[\psi^* \frac{\partial \psi}{\partial r_j} - \psi \frac{\partial \psi^*}{\partial r_j} \right] \right\}_{r_j = r_0} = \Gamma \int dq \,|\, \psi \,|^2. \tag{A11}$$

Now substitute (A4), constructing the coefficients $\psi_{\alpha\beta}(r)$ so that the sum of the series vanishes whenever any one particle is outside S; this is permissible since the integrations in (A11) are carried only over the interior of S. Using the orthonormality relation (A6) and the identity of all electrons, one gets

$$(Z+1) \frac{\hbar^2}{2mi} \sum_{\alpha\beta} \left\{ r_0 \psi^*_{\alpha\beta}(r_0) \frac{\partial [r_0 \psi_{\alpha\beta}(r_0)]}{\partial r_0} - r_0 \psi_{\alpha\beta}(r_0) \frac{\partial}{\partial r_0} [r_0 \psi^*_{\alpha\beta}(r_0)] \right\} = \Gamma \int dq \,|\, \psi \,|^2. \tag{A12}$$

The derivatives in (A12) can be expressed in terms of $\psi_{\alpha\beta}(r_0)$ by means of the outgoing-wave boundary condition which, together with (2.2), defines ψ:

$$\begin{aligned} [1/\psi_{\alpha\beta}(r_0)](\partial/\partial r_0)[r_0 \psi_{\alpha\beta}(r_0)] &= F_\beta^{(+)}(r_0, W - \epsilon_\alpha) \\ &\equiv [h_\beta^{(+)}(r_0, W - \epsilon_\alpha)]^{-1} (\partial/\partial r_0) [r_0 h_\beta^{(+)}(r_0, W - \epsilon_\alpha)], \end{aligned} \tag{A13}$$

where $h_\beta^{(+)}(r_0, W)$ is an outgoing-wave spherical Hankel function, satisfying

$$\{r^{-1}(\partial^2/\partial r^2) r - [l_\beta(l_\beta+1)/r^2] + (2m/\hbar^2)(W - \epsilon_\alpha)\} \times h_\beta^{(+)}(r, W - \epsilon_\alpha) = 0. \tag{A14}$$

In applying the boundary condition (A13) at r_0 instead of at infinity, we are ignoring the interaction of any particle outside S with the rest. With the aid of (A13), Eq. (A12) becomes

$$\Gamma = (Z+1) \sum_{\alpha\beta} \Gamma_{\alpha\beta}, \tag{A15}$$

where

$$\Gamma_{\alpha\beta} \equiv \frac{\hbar^2}{2mr_0^2} \left(r_0^3 \,|\, \psi_{\alpha\beta}(r_0) \,|^2 \Big/ \int dq \,|\, \psi \,|^2 \right) \times (-i) [F_\beta^{(+)}(r_0, W - \epsilon_\alpha) - F_\beta^{(+)*}(r_0, W - \epsilon_\alpha)]. \tag{A16}$$

Equations (A15) and (A16) can be simplified by working with terms of lowest order in the $\psi_{\alpha\beta}(r_0)$. By writing $F_\beta^{(+)}(r_0, W - \epsilon_\alpha) = F_\beta^{(+)}(r_0, E - \epsilon_\alpha) +$ terms of order Γ, one can construct from (A15) and (A16) a series in powers of $|\, \psi_{\alpha\beta}(r_0) \,|^2$; the leading term is

$$\begin{aligned} \Gamma_{\alpha\beta} = {} & \frac{\hbar^2}{2mr_0^2} \left(r_0^3 \,|\, \psi_{\alpha\beta}(r_0) \,|^2 \Big/ \int dq \,|\, \psi \,|^2 \right) \\ & \times (-i) [F_\beta^{(+)}(r_0, E - \epsilon_\alpha) - F_\beta^{(+)*}(r_0, E - \epsilon_\alpha)] && \text{for open channels } (E > \epsilon_\alpha), && \text{(A17a)} \\ = {} & 0 && \text{for closed channels } (E < \epsilon_\alpha). && \text{(A17b)} \end{aligned}$$

Here we have used the fact that for closed channels

$$F_\beta^{(+)}(r_0, E - \epsilon_\alpha) - F_\beta^{(+)*}(r_0, E - \epsilon_\alpha) = 0.$$

Another expression for the $\psi_{\alpha\beta}(r_0)$ appearing in (A17) can be derived as follows. The product $\varphi_{\alpha\beta}(\text{not } i) f_\beta(r_j, E - \epsilon_\alpha)$ satisfies

$$[K_i + H_{\text{el}}(\text{not } i) - E] \varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E - \epsilon_\alpha) = 0. \tag{A18}$$

(We shall neglect all spin-dependent forces, so that $H^* = H$.) Multiply (A18) by ψ, (2.2) by $\varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta$

$(r_i, E-\epsilon_\alpha)$, subtract, and integrate all coordinates over the interior of S. The result is

$$\left(-\frac{\hbar^2}{2m}\right)\sum_j \left\{\int_{r_i<r_0;\, i\neq j} r_j^2 d\hat{r}_j dq(\text{not } j)\left[\psi \frac{\partial}{\partial r_j}\left(\varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E-\epsilon_\alpha)\right) - \varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E-\epsilon_\alpha)\frac{\partial\psi}{\partial r_j}\right]\right\}_{r_j=r_0}$$

$$-\int dq\, \varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E-\epsilon_\alpha) V_i\psi - \tfrac{1}{2}(i\Gamma)\int dq\, \varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E-\epsilon_\alpha)\psi = 0. \quad \text{(A19)}$$

We shall suppose that the states $\mu_\alpha(\text{not } i)$ corresponding to the open channels are bound, so that the magnitude of $\varphi_\alpha(\text{not } i)$ will be small whenever one of the Z particles whose coordinates appear in $\mu_\alpha(\text{not } i)$ is on or outside S. Therefore we shall drop all the terms except that with $j=i$ in the sum over j, the magnitude of the remaining term being determined by f_β.

To simplify the term containing $\partial f_\beta/\partial r_j$ in (A19), we decompose f_β into outgoing and ingoing wave components; i.e., for any energy ϵ' we write

$$f_\beta(r, \epsilon') = f_\beta^{(+)}(r, \epsilon') + f_\beta^{(-)}(r, \epsilon'), \quad \text{(A20)}$$

where

$$(\partial/\partial r)[r f_\beta^{(\pm)}(r, \epsilon')] = F_\beta^{(\pm)}(r, \epsilon') f_\beta^{(\pm)}(r, \epsilon'). \quad \text{(A21)}$$

[$F^{(-)}$ is defined by (A13) with $h^{(+)}$ replaced by $h^{(-)}$.]

Substituting (A21) into (A19) after dropping terms with $j\neq i$, expanding ψ according to (A4), and neglecting terms of second and higher order in $\psi_{\alpha\beta}(r_0)$, one gets finally

$$(\hbar^2/2m) r_0 \psi_{\alpha\beta}(r_0) f_\beta^{(+)*}(r_0, E-\epsilon_\alpha)$$
$$\times[F_\beta^{(+)}(r_0, E-\epsilon_\alpha) - F_\beta^{(-)}(r_0, E-\epsilon_\alpha)]$$
$$= \int dq\, \varphi^*_{\alpha\beta}(\text{not } i) f^*_\beta(r_i, E-\epsilon_\alpha) V_i\psi \quad \text{(A22)}$$

(using $F_\beta^{(+)*}=F_\beta^{(-)}$ for open channels). The factor $[F_\beta^{(+)}-F_\beta^{(-)}]$ may be expressed in terms of the Wronskian of the functions $f_\beta^{(-)}$ and $f_\beta^{(+)}$, leading to

$$|f_\beta^{(+)}(r_0, E-\epsilon_\alpha)|^2$$
$$\times[F_\beta^{(+)}(r_0, E-\epsilon_\alpha) - F_\beta^{(-)}(r_0, E-\epsilon_\alpha)] = i/\pi k_\alpha r_0, \quad \text{(A23)}$$

where $k_\alpha^2 = 2m(E-\epsilon_\alpha)/\hbar^2$. The functions f_β have been normalized so that

$$\frac{e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}}}{(2\pi)^{3/2}} = \sum_{l_\beta m_\beta} i^{-l} f_\beta^*\left(r_j, \frac{\hbar^2\kappa^2}{2m}\right) Y_\beta(\hat{\kappa}) Y_\beta^*(\hat{r}). \quad \text{(A24)}$$

Equation (4.14) is obtained by substituting (A24) into (4.7), setting $\hbar^2\kappa^2/2m = E-\epsilon_\alpha(R_f)$ [in accordance with (4.13b)], expressing $\int dq\cdots$ in terms of $\psi_{\alpha\beta}(r_0)$ from (A22), taking the squared modulus, integrating over the directions of $\mathbf{k}_f$, summing over l_β, s_β, and m_β, and using formula (A15).

Formula (A17) can be used to give a rough estimate of the widths of possible "shape resonances." These are compound negative-ion states with wave functions $\psi = \psi_0\varphi$, where ψ_0 is the electronic ground state of a neutral molecule, and φ the wave function of the additional electron. The choice of r_0 at the minimum in Fig. 6 implies that r_0 must lie outside any possible centrifugal barriers in important channels. We may therefore approximate $[F_\beta^{(+)}(r_0, E-\epsilon_\alpha) - F_\beta^{(+)*}(r_0, E-\epsilon_\alpha)] \cong 2ik_\alpha r_0$, where $\hbar^2 k_\alpha^2/2m \equiv E-\epsilon_\alpha$. The structure of ψ makes ψ_0 cancel out from (A17). Moreover, as stated in the Introduction, we are supposing that there is only a single decay channel in which the additional electron departs to leave the molecule in the state ψ_0 with energy ϵ_α. After summing over β, (A17) is replaced by

$$\Gamma = \left(\frac{\hbar^2}{2mr_0^2}\right)$$
$$\times\left\{r_0^3\int d\hat{r}\,|\varphi(r_0,\hat{r})|^2 \Big/ \int r^2 dr d\hat{r}\,|\varphi(r_0,\hat{r})|^2\right\} 2k_\alpha r_0. \quad \text{(A25)}$$

With $r_0 \cong 2$ Å, and $E-\epsilon_\alpha \approx 1$ eV, one gets $k_\alpha r_0 \approx 1$ and $(\hbar^2/2mr_0^2) \cong 1$ eV. The factor in the bracket is the ratio of the mean-square amplitude of $|\varphi|$ on S to the mean square within S, and must be substantially smaller than 1 for there to be a physically meaningful compound state at all. However, except for the possible centrifugal barriers, there is no mechanism to make $\{\cdots\}$ very small, so that a value of Γ of the order of 1 eV should be possible.