electric field is applied to the target gas, the metastable 2s level will mix with the 2p level,[11] and an increase in the $2p \rightarrow 1s$ transition rate to 3.2% of the annihilation rate will occur, and should be observable.

IV. DISCUSSION

We have presented above a calculation of the energy-dependent annihilation rate of positrons incident on a helium target, as well as a prediction of the intensity of the He$^+$ ultraviolet radiation which is expected to follow the annihilation. In this work a simple model wave function describes both processes, as well as the elastic scattering. The predictions are thus not expected to be exact, but previous experience has given some cause for optimism.

Nevertheless, the results derived here must be used cautiously, as a guide only, until such time as more accurate solutions of the positron-helium scattering problem become available. As an example, we may note that the value of the parameter $\beta = 1.5992$ used throughout has been chosen to produce agreement with the long-range x^{-4} potential,[12] and thus does not necessarily represent well some of the other properties of the system. In a somewhat different context, Mittleman[9] has used a five-term exponential approximation to describe the helium atom wave function, and finds that a more accurate value of the 2s excitation probability is 2.23%, rather than our 2.00%. This agreement indicates that our qualitative results should be used as preliminary estimates in designing experiments, which may eventually test the future detailed theories.

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[11] W. E. Lamb, Jr., and M. Skinner, Phys. Rev. 78, 539 (1950). This paper contains a derivation of the dipole radiative lifetime of the metastable 2s state of He$^+$ in the presence of an electric field, $\tau = 1.6 \times 10^{-2} E^{-2}$, with E in V/cm. If this lifetime is shorter than that for collisional de-excitation, enhancement of the 304-Å line occurs. A measurement of the latter value could in principle be made this way.

[12] See Ref. 2, where another choice of β is made. As long as full monopole suppression is maintained, the results should be similar. The inclusion of short-range monopole parts in G will increase the effective electron number, and will reduce the relative excitation of the 2p state of the ion.

PHYSICAL REVIEW VOLUME 150, NUMBER 1 7 OCTOBER 1966

Theory of Dissociative Attachment*

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(Received 25 April 1966)

A fairly comprehensive theoretical treatment of the dissociative attachment (DA) of electrons to diatomic molecules ($AB+e \rightarrow A^- + B$) is given, going from general formalism to explicit cross-section formulas and comparison with experimental results. Using the Born-Oppenheimer separation, the process is understood as an electronic transition from a continuum to a discrete electronic state, which then dissociates. The final discrete state, being degenerate with a continuum, is necessarily a resonance. Accordingly, the theory is derived from a general rearrangement formalism which is based on projection operators onto this resonance state (defined along the lines of Feshbach) and uses the Born-Oppenheimer separation. This formalism, which is applicable to a fairly wide class of collision processes, is characterized by its extreme simplicity and practical usefulness. Exact transition matrix elements are derived for DA, together with its inverse and competing processes, in terms of the resonance and "potential scattering" wave functions. Finally, a certain adiabatic approximation is considered for the potential scattering function, which neglects the indirect influence of other inelastic processes on the resonance transition, treating them as higher order effects. After this approximation, the classical nature of the nuclear motion makes it possible to eliminate the nuclear wave functions in a fairly trivial way and to derive a simple explicit formula for the DA cross section from an arbitrary initial vibration-rotational state of the molecule. For the most interesting case, the ground vibrational and rotational state, this formula is in complete agreement with the previous result of Bardsley, Herzenberg, and Mandl. Later this adiabatic approximation is partly relaxed and more general formulas derived. Various implications of the results are also considered, such as the relation to experimentally observed isotope effects and temperature effects. The "vertical onset" threshold phenomenon which occurs when the resonance potential curve is attractive is also discussed.

1. INTRODUCTION

The theory of dissociative attachment (DA) of electrons to a diatomic molecule

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

is treated in a fairly comprehensive way. If we take the Born-Oppenheimer view of the process, there first occurs an electronic transition of the system to the state AB^{-*}, which state then dissociates into the end products $A^- + B$. This is illustrated in Fig. 1, which shows the potential-energy curves for a typical system.

Since the final state AB^{-*} can clearly auto-ionize, reverting back to the initial products $AB+e$, it is not

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* This work was supported by the Advanced Research Projects Agency.

a conventional bound state of the system but rather a resonance. (Thus the title "Resonant DA" given to a preliminary report on this work[1] is in a sense redundant.) Accordingly, a formalism is developed around this resonance state, starting with the very useful definition of a resonance given by Feshbach[2–4] generalized so as to be able to include the single-particle or potential-type resonance if necessary, and adapted to the special features of the molecular system. The elegant projection-operator decomposition, based on this resonance state, is then used to derive a very simple formulation of the problem of rearrangement collisions, which, it is hoped, will be useful for a wide class of rearrangements in which one of the states can be interpreted as a resonance state and the Born-Oppenheimer separation is appropriate. In addition to dissociative attachment and recombination together with their inverse processes, the type of formalism derived could prove to be the simplest way to treat many low-energy chemical kinetic processes, to the extent that these are not already adequately treated.

Using this formalism, exact expressions are derived for attachment as well as its inverse and competing processes (associative detachment, vibrational excitation, elastic scattering), and finally the explicit formulas (5.19) and (5.24) obtained after suitable approximations. These formulas, for the most interesting case, DA from the ground vibrational and rotational state, is in complete agreement with the result previously obtained by Bardsley, Herzenberg, and Mandl[5] (BHM), who started from the Kapur-Peierls formalism. It is believed that the present work goes beyond the BHM treatment in a number of ways—in the general rearrangement collision formalism used, in the obtaining of results for the inverse and competing processes, in the inclusion of excited vibrational and rotational states, in considering the effects of direct transitions on DA—and it is also hoped that the Feshbach definition of the resonance state may perhaps prove more useful than the earlier definitions.

The resonance state for the molecular system is briefly defined in Sec. 2; in particular the definition of Feshbach is given slightly generalized. In Sec. 3, the projection-operator formalism is used to derive the formal expression for the T-matrix elements for DA together with its competing and inverse reactions, vibrational excitation, associative detachment (AD), etc. In Sec. 4, the integral equations are solved, eliminating the exact wave functions in favor of the resonance and "potential scattering" wave functions. In Sec. 5, the complicated potential scattering function ϕ_p is approximated by an "adiabatic" approximation, slightly less restrictive than the exchange approximation. The Born-Oppenheimer approximation is also made. Then the semiclassical equations for nuclear motion are solved and explicit formulas are obtained. In Sec. 6, this approximation is relaxed somewhat and the effect of direct vibrational transitions on DA is considered.

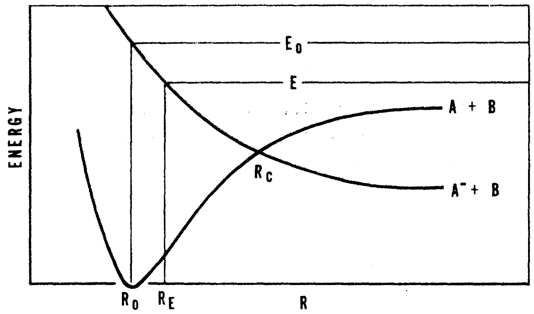

FIG. 1. Typical initial state (AB) and final resonance state (AB^{-*}) potential-energy curves for the dissociative attachment of electrons (with energy E) to molecule AB. R_E is the turning point for motion on the upper curve, determined by E. R_0 is the initial equilibrium distance. The negative-ion curve is considered relatively stable against auto-ionization for $R > R_C$.

A special feature (vertical onset) which occurs when the resonance potential curve is attractive, is considered in Sec. 7. Section 8 is devoted to a brief consideration of mass or isotope dependences. The influence of rotation on the results is made more explicit in Sec. 9. Section 10 is a summary and discussion. The semiclassical wave function for nuclear motion is analyzed in the Appendix.

2. THE RESONANCE STATE

The Hamiltonian for molecular systems is customarily broken up into an electronic part and a part for nuclear motion

$$H = H_{\mathrm{el}} + T_R, \tag{2.1}$$

where

$$H_{\mathrm{el}} = T_{\mathrm{el}} + V. \tag{2.2}$$

T_R and T_{el} are the kinetic-energy operators for nuclear and electronic motion; V is the sum of all the electrostatic potential interactions between pairs of particles.

The resonance state will be defined relative to the electronic motion only.[6] In a general way it is defined as an eigenstate of H_{el} with the lowest open electronic channel (or channels) projected out in some way. More specifically, the resonance wave function may be regarded as an eigenstate of a projection operator Q^0 onto a portion of Hilbert space,

$$Q^0 \phi_r = \phi_r, \tag{2.3}$$

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[1] T. F. O'Malley, in *Fourth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1964), p. 97.

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

[3] See also L. Fonda and R. G. Newton, Ann. Phys. (N.Y.) **10**, 490 (1960).

[4] Feshbach's resonance definition was first applied to molecular problems by J. C. Y. Chen, J. Chem. Phys. **40**, 3507 (1964); **40**, 3513 (1964); and to atomic systems by Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

[5] J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 415.

[6] This is also the procedure of Ref. 5.

which minimizes the Rayleigh-Ritz expression

$$(\phi_r H_{\text{el}} \phi_r) = V_f(R). \tag{2.4}$$

As is customary, the internuclear distance R is treated as a parameter, and the energy eigenvalue $V_f(R)$ then in turn serves as the potential for nuclear motion. We are directly interested here only in the *discrete* eigenvalue (or eigenvalues) of (2.4). [Equations (2.3) and (2.4) also have a continuous spectrum, and this can be made to play an important part in an alternate treatment for broad resonances.] For the present purpose, Q^0 will generally be taken to be Feshbach's[2] projection operator onto the excited states of the target,

$$Q^0 = 1 - \psi_g\rangle\langle\psi_g, \tag{2.5}$$

where ϕ_g is the target system's electronic ground state. Since the definition of projection operators is a matter of choice, we assume the same Q^0 for *all* R even when, e.g., $R > R_c$ in Fig. 1. The reason for this is both simplicity and the requirement of continuity. If one or more of the lowest excited states are projected out, we have a product of several factors like (2.5). To include the Pauli principle, if there are Z identical electrons, this may be generalized to[7]

$$Q^0 = \prod_{i=1}^{z} [1 - |\psi_g(-i)\rangle\langle\psi_g(-i)|], \tag{2.6}$$

where $(-i)$ denotes a state of all the electrons except the ith. The point is that Q^0 is identically orthogonal to the ψ_g of any $z-1$ electrons. This special definition of a resonance, corresponding to the compound-nucleus model, seems to include nearly all *atomic* resonances observed so far[8] and probably all those involved in processes such as dissociative recombination and attachment.[9] Another well-known kind of resonance is the single-particle or potential resonance, which occurs when a particle is effectively trapped for a time inside a Coulomb or a centrifugal barrier. Such resonances apparently are responsible for the vibrational excitation of N_2, CO, and H_2.[10] If there should be cases of DA for which the definition (2.5) is not appropriate, the more general definition implied in (2.3) and (2.4) may be assumed.

In either case, we now define the projection operator Q onto this resonance state,

$$Q = \phi_r\rangle\langle\phi_r. \tag{2.7}$$

This projection operator and its complement

$$P = 1 - Q \tag{2.8}$$

form the basis for the general formalism for rearrangement collisions of the next section. Q clearly satisfies the definition of a projection operator, hence P also, so that

$$Q^2 = Q, \quad P^2 = P, \quad PQ = QP = 0. \tag{2.9}$$

Two properties of the operator Q as here defined should be pointed out. First Q, unlike Feshbach's operator Q^0, projects onto a single state only, the resonance state,[11] hence Q is a small operator included in the space Q^0 $(Q < Q^0)$. Secondly, Q projects onto the space of electronic wave functions only, containing the nuclear coordinate R only parametrically. The possibility of defining such an operator (in a useful way) is a consequence of the Born-Oppenheimer principle of the separation of electronic and nuclear motion. It is believed that it is these two properties of Q which are responsible for the extreme simplicity of the formalism developed in the next section.

Finally, the resonance state ϕ_r, the real part of whose energy is given by (2.4), develops a finite width (imaginary part) when coupled to the open (electronic) channel or channels excluded in its definition. This width is given by an expression of the form Eq. (4.11).

3. GENERAL REARRANGEMENT FORMALISM

Using the projection operators Q onto the resonance state and P, just defined in Eqs. (2.7) and (2.8), the solution of the Schrödinger equation is decomposed into its P and Q components;

$$\psi = P\psi + Q\psi. \tag{3.1}$$

When this is substituted into the full Schrödinger equation, and we multiply from the left first by P and then by Q, the following coupled equations for $P\psi$ and $Q\psi$ result:

$$\begin{aligned} P(H-E)P\psi &= -PHQ\psi, \\ Q(H-E)Q\psi &= -QHP\psi. \end{aligned} \tag{3.2}$$

The corresponding homogeneous equations

$$P(H-E)P\phi_P = 0, \quad Q(H-E)Q\phi_Q = 0, \tag{3.3}$$

define the full "potential scattering" and resonance states, for which $P\phi_P = \phi_P$ and $Q\phi_Q = \phi_Q$ as well. These states include nuclear as well as electronic motion. Since Q projects onto a single electronic state ϕ_r, the function ϕ_Q takes on a simple form

$$\phi_Q = \phi_r \xi_Q(R), \tag{3.4}$$

where from (3.3) and (2.4)

$$[T_R + T' + V_f(R) - E]\xi_Q(R) = (H_R - E)\xi_Q(R) = 0. \tag{3.5}$$

T' is the kinetic-energy term neglected in the Born-Oppenheimer approximation

$$T' = -(\hbar^2/2\mu)[(\phi_r \nabla_R^2 \phi_r) + 2(\phi_r \nabla_R \phi_r) \cdot \nabla_R] \tag{3.6}$$

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[7] See the second paper in Ref. 4.

[8] The high peaks in the electron cross sections for Ar, Kr, and Xe just above the Ramsauer minimum, although not generally spoken of as resonances, should probably be classified as D-wave potential-type resonances and therefore exceptions to the statement in the text.

[9] It seems that the 3.7-eV peak for H_2 is an exception to this. See G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965).

[10] G. J. Schulz, Phys. Rev. **135**, A988 (1964).

[11] Such a projection operator was previously used by B. A. Lippmann, Lockheed Technical Report NONR 3368(00), 1964 (unpublished).

and is generally negligible.[11a] The integral in (3.6) is over electron coordinates. The potential scattering wave function ϕ_P, on the other hand, is a many-channel wave function, including electronic, vibrational, and rotational excitation in addition to elastic scattering.

Now the coupled Eqs. (3.2) together with (3.3) will serve as the starting point for the derivation of the formalism in the same way that the Schrödinger equation, written alternately in post and prior form, has served as the starting point for other theories of rearrangement collisions.[12,13] Equation (3.2) has the desirable features that $P\psi$ asymptotically contains only the "direct" channels while $Q\psi$ contains only the rearranged channel, and further the homogeneous solutions ϕ_P and ϕ_Q already contain virtually all nonrearrangement scattering in both initial and final channels.

The solution of (3.2) may be written formally as an integral equation. First, if the incident channel is one of the channels α (characterized by rotational and vibrational as well as electronic state) included in P, the integral equations are

$$P\psi_{P\alpha}=\phi_{P\alpha}+G_PPHQ\psi_{P\alpha}, \tag{3.7a}$$

$$Q\psi_{P\alpha}=G_QQHP\psi_{P\alpha}, \tag{3.7b}$$

where

$$G_P=1/P(E-H+i\epsilon)P, \quad G_Q=1/Q(E-H+i\epsilon)Q. \tag{3.8}$$

The subscript P_α on ψ denotes the incident channel. If the incident channel is Q (physically this means that the heavy particles A^- and B collide), the integral form of Eq. (3.2) becomes

$$\begin{gathered} P\psi_Q=G_PPHQ\psi_Q, \\ Q\psi_Q=\phi_Q+G_QQHP\psi_Q. \end{gathered} \tag{3.9}$$

The idea of the resonance state being the incident channel, as opposed to its familiar role as intermediate state, may be a strange one. This possibility is opened up by the separation of electronic and nuclear motion in molecules. We have already defined the resonance state as being a closed channel (a discrete state) as far as electron motion is concerned in the space $Q^0>Q$. But there is an extra degree of freedom in the nuclear motion, and it is possible for the coordinate R to go to infinity while the electrons remain bound as in the AB^{-*} curve of Fig. 1. In this way the Q channel, though closed for motion of the electrons, is an open channel for nuclear motion.

The formal transition matrix elements T_{PP}, T_{PQ}, T_{QP}, and T_{QQ} follow immediately from the asymptotic behavior of (3.7) and (3.9), given that of the ϕ's and the G's. First the wave functions are assumed to be normalized to delta functions of the energy as in Feshbach's papers.[2] The asymptotic form of the full wave function ψ may then be written

$$\psi \xrightarrow[x_j\to\infty]{} \delta_{fi}\phi_i^{\text{pl}}+T_{fi}\phi_f^{\text{out}}, \tag{3.10}$$

where x_j is the coordinate in the jth channel (e.g., $j=Q$, P_α, $\cdots$) and i denotes the incident channel. The supplementary asymptotic functions ϕ_i^{pl} and ϕ_f^{out} with superscripts denoting plane and outgoing waves, respectively, are, in the P and Q channels,

$$\phi_Q^{\text{pl}}=N_Qe^{i\mathbf{K}\cdot\mathbf{R}}\xi_{A^-}\xi_B, \tag{3.11a}$$

$$\phi_Q^{\text{out}}=(\pi/K)N_QR^{-1}e^{iKR}\xi_{A^-}\xi_B, \tag{3.11b}$$

$$\phi_{P\beta}^{\text{pl}}=N_Pe^{i\mathbf{k}\cdot\mathbf{r}_\beta}\xi_{AB}(-r_\beta), \tag{3.11c}$$

$$\phi_{P\beta}^{\text{out}}=(\pi/k)N_Pr_\beta^{-1}e^{ik\beta}\xi_{AB}(-r_\beta), \tag{3.11d}$$

and

$$N_Q^2=2\mu K/\hbar^24\pi^2, \quad N_P^2=2m_ek/\hbar^24\pi^2. \tag{3.12}$$

ξ_{AB}, ξ_B, and ξ_{A^-} are the wave functions for molecule, atom, and ion, respectively. μ and $\mathbf{K}$ are the reduced mass and relative momentum for nuclear motion with $\mathbf{R}$ the corresponding space coordinate. m_e, $\mathbf{k}$, and $\mathbf{r}_\beta$ are the free-electron's mass, momentum, and space coordinate in the channel β. If Q were projecting onto a three-body channel, the appropriate generalizations of (3.11) would have to be used. For recombination, the replacement of the plane and outgoing waves by the corresponding Coulomb distorted waves would be necessary.

The T matrix as defined in (3.10), because of the delta function normalization assumed in Eqs. (3.10) through (3.12), differs from the more standard definition[14] of T by the factor N_PN_Q, and is the same as that used by Feshbach.[2] It is related to the differential cross section in general by

$$\sigma_{fi}(\Omega)=(\pi/k_i)^2|T_{fi}|^2. \tag{3.13}$$

The asymptotic form of the ϕ's and G's of Eqs. (3.7) and (3.9) in their respective channels are, in the Q channel,

$$\begin{gathered} \phi_Q \xrightarrow[R\to\infty]{} \phi_Q^{\text{pl}}+T_{QQ}^{(0)}\phi_Q^{\text{out}}, \\ G_Q \xrightarrow[R\to\infty]{} \phi_Q^{\text{out}}\langle\phi_Q^-, \end{gathered} \tag{3.14}$$

and for ϕ_p, assuming the electron is incident in channel α (referring to the initial vibrational, rotational, and electronic state), the asymptotic behavior in the β channel is given by

$$\begin{gathered} \phi_{P\alpha} \xrightarrow[r_\beta\to\infty]{} \delta_{\beta\alpha}\phi_{P\alpha}^{\text{pl}}+T_{\beta\alpha}^{(0)}\phi_{P\beta}^{\text{out}}, \\ G_P \xrightarrow[r_\beta\to\infty]{} \phi_{P\beta}^{\text{out}}\langle\phi_{P\beta}^-. \end{gathered} \tag{3.15}$$

The $T^{(0)}$ are determined by the homogeneous equations (3.3). The bras $\langle\phi^-$ are solutions of (3.3) with incoming

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[11a] *Footnote added in proof.* Note that the second term in (3.6) in the present form vanishes by symmetry.

[12] B. A. Lippmann, Phys. Rev. **102**, 264 (1956).

[13] See A. Dalgarno, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 609, for a review of rearrangement formalisms.

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

rather than outgoing boundary conditions. Using (3.14) and (3.15) in the asymptotic form of (3.7) and (3.9) and comparing with (3.10) we find all the T-matrix elements for the system. They are

$$T_{P\beta,P\alpha}=T_{\beta\alpha}{}^{(0)}+\langle\phi_{P\beta}{}^{-}PHQ\psi_{P\alpha}{}^{+}\rangle\,, \tag{3.16a}$$

$$T_{Q,P\alpha}=\langle\phi_{Q}{}^{-}QHP\psi_{P\alpha}{}^{+}\rangle\,, \tag{3.16b}$$

$$T_{P\beta,Q}=\langle\phi_{P\beta}{}^{-}PHQ\psi_{Q}{}^{+}\rangle\,, \tag{3.16c}$$

$$T_{Q,Q}=T_{Q}{}^{(0)}+\langle\phi_{Q}{}^{-}QHP\psi_{Q}{}^{+}\rangle\,. \tag{3.16d}$$

Equations (3.16) are the formal expressions for the T-matrix elements in the present rearrangement formalism. The ψ's can be eliminated by solving the integral equations (3.7) and (3.9), as will be done in Sec. 4. Equations (3.16) correspond very closely to the expressions previously derived[12,13] for rearrangement collisions. The only difference is that the homogeneous ϕ's here are already fully distorted by elastic scattering rather than being free waves, and the post and prior interactions H' and H'' are replaced by only the off-diagonal operators PHQ and QHP connecting the direct to the rearranged channels. It will be noticed that as a result of this, the matrix elements in (3.16) are always between mutually orthogonal functions. This feature was also present in Mittleman's[15] treatment of rearrangement collisions.

It is believed that a consequence of this orthogonality is that the matrix elements for rearrangements will generally be small (as compared with elastic scattering), and that first-order perturbation theory will frequently be accurate.[15a]

4. EXACT SOLUTION OF INTEGRAL EQUATIONS

The formal matrix elements for the process (1.1) and the related direct processes are given by Eqs. (3.16). As was just pointed out, it is expected that first-order perturbation theory, replaced ψ by ϕ, will frequently be accurate. However, it is not difficult to solve the coupled equations (3.7) and (3.9) exactly and eliminate the functions ψ in favor of the ϕ's and their associated Green's functions. This is analogous to what is done for simple resonant elastic scattering.[2]

To solve Eqs. (3.7), we note that ϕ_Q is given by Eq. (3.4) and similarly the full solution $Q\psi$ may be written

$$Q\psi=\phi_r\xi(R)\,. \tag{4.1}$$

Further

$$G_Q=\phi_r\rangle g\langle\phi_r\,, \tag{4.2}$$

where

$$g=(E+i\epsilon-H_R)^{-1} \tag{4.3}$$

and H_R is given by Eq. (3.5).

Using (4.2), Eq. (3.7b) becomes

$$Q\psi_P=\phi_r g a^{+}\,, \tag{4.4}$$

where

$$a^{+}=a^{+}(R)=\langle\phi_r HP\psi_P{}^{+}\rangle\,. \tag{4.5}$$

Now substituting (4.4) into (3.7a) produces

$$P\psi_P{}^{+}=\phi_P{}^{+}+G_P H\phi_r g a^{+}\,. \tag{4.6}$$

This is actually an integral equation for $P\psi_P{}^{+}$ by virtue of (4.5). It is solved for a^{+} by multiplying by $\langle\phi_r H$ on the left (the integration is again over electron coordinates), to produce a one-dimensional integral equation for a^{+}:

$$a^{+}=a_P{}^{+}+Fga^{+}\,, \tag{4.7}$$

or, writing the solution formally,

$$a^{+}=(1-Fg)^{-1}a_P{}^{+}\,, \tag{4.8}$$

where

$$a_P{}^{+}=a_P{}^{+}(R)=\langle\phi_r QHP\phi_P{}^{+}\rangle\,; \tag{4.9a}$$

and for later reference we also define

$$a_P{}^{-}=\langle\phi_P{}^{-}PHQ\phi_r\rangle\,; \tag{4.9b}$$

further

$$\begin{aligned}F&=\langle\phi_r QHPG_P PHQ\phi_r\rangle\\&=\Delta_a(R)-i\Gamma_a(R)/2\,.\end{aligned} \tag{4.10}$$

$F(R)$ has the form of the complex level shift[2] of the resonance-electron energy curve $V_f(R)$. The imaginary part Γ_a is the *total* width for auto-ionization (i.e., ejection of an electron), and Δ_a is the corresponding level shift. Γ_a is generally expanded as a sum over open channels in the form

$$\Gamma_a=2\pi\textstyle\sum_{\bar a}|\langle\phi_r QHP_{\bar a}\phi_{\bar a}\rangle|^2\,, \tag{4.11}$$

where the subscripts $\bar a$ stand for the open electronic channels.

Equation (4.8) together with (4.4) is essentially the desired solution of Eqs. (3.7) for ψ_P. Substituting (4.4), (4.9b), and (4.8) into Eq. (3.16a) for $T_{P\beta,P\alpha}$ and (3.4), (4.5), and (4.8) into (3.16b) for $T_{Q,P\alpha}$ gives

$$T_{P\beta,P\alpha}=T_{\beta,\alpha}{}^{(0)}+\langle a_{P\beta}{}^{-}g(1-Fg)^{-1}a_{P\alpha}{}^{+}\rangle \tag{4.12a}$$

and

$$T_{Q,P\alpha}=\langle\xi_Q{}^{-}(1-Fg)^{-1}a_P{}^{+}\rangle\,. \tag{4.12b}$$

Equations (3.9) for ψ_Q can similarly be solved and the results substituted into (3.16c) and (3.16d), with the result

$$T_{P\beta,Q}=\langle a_P{}^{-}(1-gF)^{-1}\xi_Q{}^{+}\rangle\,, \tag{4.12c}$$

$$T_{QQ}=T_{Q,Q}{}^{(0)}+\langle\xi_Q{}^{-}F(1-gF)^{-1}\xi_Q{}^{+}\rangle\,. \tag{4.12d}$$

Equations (4.12) can be reduced still further. If we define

$$\zeta=(1-gF)^{-1}\xi_Q\,, \tag{4.13}$$

ζ satisfies the equation

$$\zeta=\xi_Q+gF\zeta \tag{4.14}$$

or

$$[T_R+T'+V_f(R)+F(R)-E]\zeta=0\,, \tag{4.15}$$

where F, the complex level shift, is given by Eq. (4.10). It is clear that Eq. (4.15) represents the motion of the

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[15] M. Mittleman, Phys. Rev. **122**, 1930 (1961).

[15a] *Footnote added in proof.* This is in strong contrast with the standard formalism for which the perturbation expansion always diverges. See R. Aaron, R. D. Amato, and B. W. Lee, Phys. Rev. **121**, 319 (1961).

heavy particles under the influence of the *full* complex potential curve V_f+F. In terms of ζ and the associated Green's function

$$g_F=(E-T_R-T'-V_f-F+i\epsilon)^{-1}, \qquad (4.16)$$

Eqs. (4.12) may be rewritten

$$T_{P\beta,P\alpha}=T_{P\beta,P\alpha}{}^{(0)}+\langle a_P{}^- g_F a_P{}^+\rangle, \qquad (4.17a)$$

$$T_{Q,P\alpha}=\langle\zeta^-|a_P{}^+\rangle, \qquad (4.17b)$$

$$T_{P\beta,Q}=\langle a_P{}^-|\zeta^+\rangle, \qquad (4.17c)$$

$$T_{QQ}=T_{Q,Q}{}^{(0)}+\langle\xi_Q{}^- F\zeta^+\rangle, \qquad (4.17d)$$

with $a_P{}^{\pm}$ given by (4.9) in terms of the potential-scattering solution $\phi_P{}^{\pm}$. Equations (4.17) represent the desired exact T-matrix elements for the processes resulting from $e+AB$ and from A^-+B with the effects of the resonance state made explicit. They cannot be reduced any further without some approximations, except to note that the expression for the elastic process T_{QQ} is simply the exact expression for scattering by the 2-body potential $V(R)=V_f(R)+F(R)$ in Eq. (4.15), i.e., by the full complex resonance potential-energy curve. [See Eq. (5.9c).] This might have been guessed intuitively. The partial-wave solution of this problem is given in the Appendix. It has previously been treated by BHM.[5]

Equation (4.17a) gives the contribution of the dissociating resonance state to elastic scattering and vibrational excitation, in terms of ϕ_P and the Green's function constructed from the solutions of the semiclassical Eq. (4.15). It should be emphasized here that the situation treated in the present paper is essentially different from that considered by Mandl and Herzenberg[16] and by Chen[17] in their analyses of resonance vibrational excitation. These authors considered the resonance curve to be below the dissociation limit and found the effects of its discrete vibrational states. The result was found to be a very large cross section with sharp peaks. In the present paper, the resonance state is assumed to be a dissociating one, and so it is the continuum states of nuclear motion that contribute, as in the work of Chen and Magee.[18] A consequence of this is that Eq. (4.17a) has a Green's function in place of a resonance denominator. Therefore T_{PP} need never attain the maximum possible value, in contrast with the discrete case. In fact it may be seen from the next section that with reasonable approximations the resonance contribution to $T_{Pv',Pv}$ is proportional to the partial auto-ionization width $\Gamma_{\bar{a}}$, and so should be so small as to be unobservable, unless that width happens to be extraordinarily large.

The equality of the dissociative attachment matrix element $T_{Q,P}$ and the inverse associative detachment element $T_{P,Q}$ follows from general considerations and may easily be shown from Eqs. (4.17).

5. ADIABATIC APPROXIMATION FOR ϕ_P—EXPLICIT FORMULAS

The Eqs. (4.17) for DA and related processes are exact as they stand, assuming only the existence of a resonance state ϕ_r in the appropriate region. In order to make them more explicit, but not unduly complicated, some approximations are necessary. The T-matrix elements are expressed through Eqs. (4.17) and (4.9) in terms of ϕ_r, ζ, and g_F, and finally ϕ_P. The function ϕ_r presents no complications (in principle) and is considered known. Since ζ describes the motion of heavy particles, the semiclassical wave function should be considered exact. Similarly, g_F may be constructed from ζ and the corresponding irregular solution of (4.15), and so does not require any approximation.

This leaves the potential scattering function ϕ_P. As mentioned, ϕ_P is a complicated function which contains, in addition to elastic scattering, direct vibrational and rotational excitation and, for high enough energy, electronic excitation as well. To make ϕ_P more tractable, we consider the approximation of neglecting the effect of the "direct" transitions on ϕ_P. This approximation is suggested by the experimental results, which indicate that the matrix elements for direct vibrational excitation, for rotational transitions, and for electronic excitation are generally small quantities in contrast to that for elastic scattering. The wave function ϕ_P might accordingly be taken to be proportional to the target molecule's electronic, vibrational, and rotational wave functions ϕ_g, $\chi_v(R)$, and $Y_{J,M}(\hat{R})$, and so be written

$$\phi_P{}^+=PA\phi_g\chi_v(R)Y_{J,M}(\hat{R})f(r_e)/R.$$

This is called the exchange approximation and has been found very successful in predicting the total cross sections for electron-atom collisions.[19,20] It differs from the usual exchange approximation in that $\phi_P=P\phi_P$ must be orthogonal to ϕ_r. Here A is the electron antisymmetrization operator, and f is the wave function for the incident electron, determined in this approximation, i.e., by substituting the above expression into Eq. (3.3) and solving for f. A relaxation of this approximation would be to allow additional electronic terms proportional to the excited electronic states of the target, representing virtual (but not actual) excitation of these states, but without modifying the vibrational-rotational state. This is an adiabatic approximation and will be assumed in the remainder of the paper. The adiabatic wave function is written

$$\phi_P=P\phi_{\mathrm{ad}}\chi_v(R)Y_{J,M}(\hat{R})/R. \qquad (5.1)$$

The electronic function $P\phi_{\mathrm{ad}}$ results when the electronic problem in (3.3) is solved exactly, but as though nuclear

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[16] F. Mandl and A. Herzenberg, Proc. Roy. Soc. (London) **A270**, 277 (1962).

[17] See first paper in Ref. 4.

[18] J. C. Y. Chen and J. L. Magee, J. Chem. Phys. **36**, 1407 (1962).

[19] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), p. 219.

[20] P. G. Burke and K. Smith, Rev. Mod. Phys. **34**, 458 (1962).

motion were impossible. Note that at this stage the adiabatic approximation is made only in ϕ_P and not in the interaction Hamiltonian QHP.

In terms of perturbation theory, the adiabatic approximation (5.1) means that direct vibrational and rotational excitation, as well as actual electronic excitation at high enough energy, are treated as small first-order quantities and their indirect effect on DA is neglected as a higher order quantity. If DA itself is also treated as a first-order quantity, the present result reduces to a special distorted-wave treatment.[21] This is appropriate whenever Γ_a is sufficiently small, i.e., when $\rho \ll 1$ [see Eq. (5.2)].

With the approximate representation (5.1) for ϕ_P, the T-matrix elements in (4.17) may be made more explicit. In particular, Eq. (4.9) for a_P becomes

$$a_P{}^+ = V_{\bar{a}}(R)\chi_v(R)Y_{J,M}(\hat{R})/R\,, \qquad (5.2)$$

where

$$V_{\bar{a}}(R) = \langle \phi_r Q V_e P \phi_{\mathrm{ad}}{}^+ \rangle + T_{r,\mathrm{ad}}'\,,$$

and $a_p{}^- = (a_p{}^+)^*$. T', the non-Born-Oppenheimer term, is given by Eq. (3.6) with ϕ_{ad} replacing the second ϕ_r on the right. This term is written for the sake of generality. It is expected that it will always be negligible compared to the first term, except for $R_E > R_c$ (see Fig. 1), at which point the first term must vanish (by the conservation of energy). Since this region is generally far from the Franck-Condon region, it will rarely be of physical interest. This second term will therefore be neglected from this point on. This adds a second adiabatic approximation (and a more familiar one) to that already made. $V_{\bar{a}}$ now becomes

$$V_{\bar{a}} = \langle \phi_r Q V_e P \phi_{\mathrm{ad}}{}^+ \rangle\,. \qquad (5.3)$$

In standard fashion, $V_{\bar{a}}(R)$ is related to the partial width $\Gamma_{\bar{a}}$ for auto-ionization of the resonant state into the incident electronic channel defined by

$$\Gamma_{\bar{a}} = 2\pi |V_{\bar{a}}(R)|^2\,. \qquad (5.4)$$

When there is only the one electronic channel open, $\Gamma_{\bar{a}}$ is identical with the total auto-ionization width Γ_a of Eq. (4.11), given the present approximation. More generally, Γ_a is the sum of such partial widths.

The independence of $V_{\bar{a}}(R)$ of the angles follows from the adiabatic separation in (5.1). More generally there would be a small angular dependence which could change the rotational state by 2 units.[22] The fact that (aside from T') only V_e, the electron-molecule electrostatic interaction, survives in (5.3) follows from the fact that the remainder of H commutes with P and so vanishes by orthogonality.

The argument had formerly been proposed[23] that such cross sections as are here considered would vanish in the Born-Oppenheimer approximation ($T' = 0$). This was based on the incorrect assumption that the initial and final electronic wave functions were both eigenstates of H_{el}, from which it would follow that electronic matrix elements such as that in (5.3) must vanish. However, we have seen that the final electronic state ϕ_r, as an auto-ionizing state, cannot be an eigenstate of H_{el} in the ordinary sense[24] and so the electronic matrix element will in general be nonvanishing. A calculation done by Chen[25] was based on this assumption.

An interesting and related consequence of the definition (2.3) and (2.4) of the resonance state is that the *noncrossing rule*[26,27] for molecular states does not apply between this and any other state, since this rule also presupposes true eigenstates of H_{el}. Since many states of neutral molecules are interpretable as electrons bound to excited states of the target ion,[28] i.e., as resonances, there is no reason why such potential curves may not freely cross other curves of the same symmetry. It seems fair to say that the noncrossing rule is probably taken far more seriously than it should be. Many humps in molecular potential curves might properly be eliminated in favor of crossing curves.

Now, returning to the evaluation of the T matrix (4.17), since a_P in Eq. (5.2) is proportional to a single spherical harmonic Y_{JM} and since by assumption J is conserved, a partial-wave expansion of the function ζ for nuclear motion in the resonance state should be made. This expansion, agreeing with the normalization of Eq. (3.14), is

$$\zeta^+(R) = \sum_{J,M} i^J (4\pi)^{1/2} Y_{JM}{}^*(\Omega) Y_{JM}(\Omega_K) e^{i\delta} \chi(R)/R\,, \qquad (5.5)$$

where Ω_K is the solid angle in terms of the relative momentum vector K, and $\chi(R)$ is the regular solution of the partial-wave version of Eq. (4.15) with asymptotic form

$$\chi(R) \underset{R\to\infty}{\longrightarrow} (2\mu/\hbar^2\pi K)^{1/2} \sin(KR - J\pi/2 + \delta)\,. \qquad (5.6)$$

It should be noted that since the potential in (4.15) is complex, δ will also be complex and we may write

$$\delta = \bar{\delta} + i\rho/2\,. \qquad (5.7)$$

The imaginary part of δ has been emphasized by BHM[5] and is considered in the Appendix. The Green's func-

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[21] Reference 19, p. 144. See L. I. Poldubnyi, Zh. Eksperim. i Teor. Fiz. **47**, 558, [English transl.: Soviet Phys.—JETP **20**, 372 (1965)] for a related distorted-wave approach.

[22] J. C. Y. Chen, Phys. Rev. **146**, 61 (1966).

[23] R. E. Stanton, J. Chem. Phys. **32**, 1348 (1960).

[24] This point was also mentioned in Ref. 5.

[25] J. C. Y. Chen, Phys. Rev. **129**, 202 (1963).

[26] L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 262 ff.

[27] F. Mandl, Proc. Phys. Soc. (London) **87**, 871 (1966) has very recently derived a generalization of the noncrossing rule for complex Kapur-Peierls energy levels. His results do not change the present conclusion.

[28] This point is well illustrated in a recent very interesting paper by R. S. Mulliken, Phys. Rev. **136**, A962 (1964) on the He_2 system. The curves called B-core states are interpretable as resonances. It is clear from Fig. 1 of that paper that the B-core (resonance) curves have a tendency to cross the A-core (ordinary bound state) curves.

tion g_F also becomes diagonal in J and M and the kernel of its radial part becomes

$$g_F(R,R') = -\pi\chi(R_<)[\chi^{\text{ir}}(R_>)+i\chi(R_>)], \quad (5.8)$$

where χ^{ir} is the irregular solution of (4.15) defined by replacing sin by cos in (5.6). Note the absence of an $e^{i\delta}$ term in g_F. If $\rho \gg 0$, this results in a strong favoring of vibrational excitation over DA [see Eqs. (5.9)].

Now using Eqs. (5.2) through (5.7) in Eq. (4.17), the T matrix elements become

$$T_{v'J',vJ} = T_{v'J',vJ}{}^{(0)} + \delta_{J,J'}(\chi_{v'}V_{\bar{a}}g_F V_{\bar{a}}\chi_v), \quad (5.9\text{a})$$

$$T_{P,Q} = T_{Q,P} = i^J(\exp i\bar{\delta})(4\pi)^{1/2}Y_{J,M}(\theta_k,\phi_k) \times e^{-\rho/2}(\chi_v V_{\bar{a}}\chi), \quad (5.9\text{b})$$

$$T_{Q,Q} = -(2\pi i)^{-1}(e^{2i\delta}-1)(2J+1)P_J(\cos\theta), \quad (5.9\text{c})$$

where the parentheses indicate $\int_0^\infty dR$, and $V_{\bar{a}}$, χ, g_F, and δ are given by Eqs. (5.3), (5.6), (5.8), and (5.7), and the subscripts on T_{PP} have been made more explicit. It should be noted that the absence of resonance rotational excitation as indicated by $\delta_{J,J'}$ is a consequence of the approximations made in this section [Eq. (5.1)]. For the qualitatively different case of a nondissociating resonance state, this should be a more significant effect, as indicated by Chen.[22]

The vibrational excitation result will not be developed further at present, except to point out that, as a second-order quantity in $V_{\bar{a}}$, the resonance contribution to $T_{v',v}$ is essentially proportional to $\Gamma_{\bar{a}}$. So unless the resonance state is extraordinarily broad, this should be negligible. The result in[10] H_2 apparently corresponds to this latter case when the resonance must be very broad. It should be mentioned that there is no sharp dividing line distinguishing a broad resonance from a nonresonance, and some would prefer not to call such states resonances at all but would classify the process as a direct one.[29]

Evaluation of the Nuclear Overlap Integral

The remainder of the paper will be devoted entirely to the dissociative attachment process and the name T_{DA} will be substituted for T_{QP}. Accordingly, it now remains only to evaluate the integral in (5.9b). This is a standard problem. Aside from the slowly varying $V_{\bar{a}}(R)$, this is the Franck-Condon overlap integral between a discrete and a continuum vibrational state. It has long been known that, for a real potential curve at least, the continuum function such as χ is very well approximated by a δ function at its turning point R_E, provided that its potential curve has a slope V' perceptibly different from zero.

It is shown in the Appendix that the δ-function approximation is the leading term in an asymptotic expansion of the wave function in inverse powers of the large quantity

$$\lambda = 2\mu V'/\hbar^2\alpha^3,$$

where V' is the force acting to separate the final-state products at their turning point [see Eq. (A.2)]. α^{-1} is a distance over which the function appearing with χ in an integral varies significantly. For the present case, this is taken to be the initial oscillator's unit of length defined by[30]

$$\alpha = (\mu\omega/\hbar)^{1/2} = (\mu V_i''/\hbar^2)^{1/4}, \quad (5.10)$$

where ω is the oscillator's frequency and V_i'' its stiffness. In terms of this α, λ may be written

$$\lambda = \Gamma_d/\hbar\omega, \quad (5.11)$$

where

$$\tfrac{1}{2}\Gamma_d = V'/\alpha. \quad (5.12)$$

$\frac{1}{2}\Gamma_d$ is a partial half-width for dissociation, since $\hbar/\frac{1}{2}\Gamma_d$ is a measure of the time it takes the final products to move a distance from the turning point ($\sim 1/\lambda\alpha$) to where the approximate δ function begins to vanish, and so auto-ionization back to the initial vibrational state becomes impossible. (This should be distinguished from the much larger *total* dissociation time after which autoionization to *any* vibrational state becomes impossible.) Γ_d is also the physically observable width of the cross-section curve as is clear from Eq. (5.24).

We see from (5.11) and (5.10) that λ is proportional to $V'\mu^{1/4}$, and so the expansion in inverse powers of λ is, like the Born-Oppenheimer separation, an expansion in powers of $\mu^{-1/4}$. In addition, the limit of large λ corresponds to the classical limit ($\hbar \to 0$). Typical values of λ are 7 and 13 for the principal repulsive curves in H_2^- and O_2^-, respectively.

It is shown in the Appendix that in the limit of infinite λ, $\chi(R)$ becomes

$$\chi(R) = V'^{-1/2}\delta(R_E + i\Gamma_a/2V'), \quad (\lambda = \infty), \quad (5.13)$$

where Γ_a is the total width for auto-ionization. This differs from the standard δ-function approximation in that the turning point is displaced by an imaginary quantity due to the imaginary part of the resonance potential-energy curve. Effectively the same thing was found by BHM.[5]

The effect of the next term in the $1/\lambda$ expansion is shown in the Appendix to provide a slight distortion of the function operated on by the δ function. In particular, the vibrational function χ_v is modified to $\tilde{\chi}_v$ given by (A13).

The T-matrix element for DA given by Eqs. (5.9) may now be made more explicit still. If it is assumed, as is generally done, that the electronic matrix element $V_{\bar{a}}$ varies slowly compared to χ_v, the integral $(\chi V_{\bar{a}}\chi_v)$ appearing in (5.9) may be written in terms of the overlap integral $S = (\chi\chi_v)$, which is given in Eq. (A14) of

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[29] This is discussed by R. G. Newton, Ann. Phys. (N. Y.) 4, 29 (1958).

[30] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 61.

the Appendix. Through first order in $1/\lambda$, this is

$$(\chi V_{\bar{a}}\chi_v)=V_{\bar{a}}(\chi\chi_v)=V_{\bar{a}}(\tfrac{1}{2}\Gamma_d)^{-1/2}\tilde{\chi}_v(x_E-ig)\,, \tag{5.14}$$

where

$$\tilde{\chi}_v(x)=\chi_v(x)-(1/3\lambda)\chi_v'''(x) \tag{5.15}$$

and

$$g=\Gamma_a/\Gamma_d\,. \tag{5.16}$$

The function χ_v for the vth vibrational state is assumed to be normalized to unity by

$$\int_0^\infty \chi_v^2(x)dx=1\,, \tag{5.17}$$

where $x=\alpha R$. All quantities $V_{\bar{a}}$, Γ_a, and Γ_d are assumed to be evaluated at the turning point R_E of final-state motion. It should be noticed that Γ_a is the *total* width for auto-ionization, while $V_{\bar{a}}$ is connected through Eq. (5.4) with the partial width for auto-ionization to the initial electronic state. Where two or more electronic channels are open, the two will not be the same.

Substituting (5.14) into (5.9b) the T-matrix element for dissociative attachment becomes

$$T_{\mathrm{DA}}=i^J(4\pi)^{1/2}Y_{JM}(\Omega_k)(\exp i\bar{\delta})e^{-\frac{1}{2}\rho(E)}V_{\bar{a}}(R_E)$$
$$\times(\tfrac{1}{2}\Gamma_d)^{-1/2}\tilde{\chi}_v(x_E-ig)\,. \tag{5.18}$$

The energy dependence of ρ is now emphasized. The differential cross section is given by Eq. (3.13). Now unless the rotational magnetic substates are unequally populated, substitution of (5.18) into (3.13) gives a spherically symmetric result when M is summed over. Multiplying then by 4π, the general expression for the total cross section for DA becomes at last

$$\sigma_{\mathrm{DA}}=\frac{4\pi^2}{k_i^2}\bar{g}\frac{\Gamma_{\bar{a}}}{\Gamma_d}|\tilde{\chi}_v(x_E-ig)|^2e^{-\rho(E)}\,, \tag{5.19}$$

where k_i is the incident electron's wave number; $\bar{g}$ is a statistical factor into which are lumped the weight factors for rotational and electronic angular momentum as well as the relative spin multiplicity; $\Gamma_{\bar{a}}$ is the partial auto-ionization width, given by (5.4); χ_v is the initial vibrational wave function, normalized according to (5.17), i.e., with α^{-1} as the unit of length; x_E is the turning point of the final-state motion in the same units ($x=\alpha R$), and is of course determined by the electron energy E; g is the imaginary shift in x_E caused by the imaginary part Γ_a of the resonance energy and given by Eq. (A6). All quantities are evaluated at R_E. Finally the last factor is the survival probability, first employed by Holstein[30a] and derived by BHM.[5] In Ref. 1, it was reasoned that this factor would ***never*** differ appreciably from unity. Although this is true for sharp resonance states of the compound-ion type, it would not be so for broad resonances. Using the generally good approximation (A15) for ρ, the survival probability is

$$e^{-\rho(E)}=\exp\left[-\int_{R_E}^{R_C}\frac{\Gamma_a(R)dR}{\hbar v(R)}\right]$$
$$=\exp\left[-\hbar^{-1}\int_{R_E}^{R_C}\Gamma_a(R)dt(R)\right], \tag{5.20}$$

where $v(R)$ is the classical velocity of the dissociating particles, t is the time it takes them to dissociate to the point R.[31] If R_C is very large or infinite, the integral in (5.20) will still converge due to the decrease of Γ_a with R.

Equation (5.19) is the principal result of this section, the general expression for electron attachment from a vibrational state v. The case $v=0$ deserves special consideration, since at ordinary temperatures it is the only state of interest. Because of the relative compactness of the $v=0$ wave function, the harmonic-oscillator wave function is accurate for χ_0, and the function $\tilde{\chi}_0$ takes on the simple form given by Eq. (A20′). For the same reason, a linear approximation for the real part of the resonance potential curve $V_f+\Delta$, as given by (A2), is appropriate in the Franck-Condon region, i.e.,

$$V_f(R_E)+\Delta(R_E)$$
$$=V_f(R_0)+\Delta(R_0)-V'(R_E-R_0)\,. \tag{5.21}$$

From this it follows that, in terms of the electron energy,

$$x_E-x_0\equiv\alpha(R_E-R_0)=(E_0-E)/\tfrac{1}{2}\Gamma_d\,, \tag{5.22}$$

where R_0 is the oscillator's equilibrium distance, and E is the electron energy, i.e.,

$$E=V_f(R_E)+\Delta(R_E)-V_i(R_0)-(v+\tfrac{1}{2})\hbar\omega\,.$$

The wave function $\tilde{\chi}_0$ given by (A20′) and (A19), incorporating both the imaginary and real shifts, becomes in terms of (5.22)

$$\tilde{\chi}_0=\pi^{-1/4}\exp\left[-\frac{1}{2}\left(\frac{E_0-E+\frac{1}{2}\hbar\omega-\frac{1}{2}i\Gamma_a}{\frac{1}{2}\Gamma_d}\right)^2\right]. \tag{5.23}$$

Hence the cross section for $v=0$ becomes

$$\sigma_{\mathrm{DA}}(v=0)$$
$$=\frac{4\pi^{3/2}}{k_i^2}\bar{g}\frac{\Gamma_{\bar{a}}}{\Gamma_d}\exp\left[\frac{(\frac{1}{2}\Gamma_a)^2-(\bar{E}_0-E)^2}{\frac{1}{2}(\Gamma_d)^2}\right]e^{-\rho(E)}\,, \tag{5.24}$$

where $\bar{E}_0$ is defined as

$$\bar{E}_0=E_0+\tfrac{1}{2}h\omega=V_f(R_0)+\Delta(R_0)-V_i(R_0)\,. \tag{5.25}$$

Equation (5.24) reduces to the result of Ref. 1 for Γ_a sufficiently small. It is identical with the result of BHM.[5] The apparent difference of a factor of 3 may be due to an assumption about the statistical factor

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[30a] T. Holstein, Phys. Rev. 84, 1073 (1951).

[31] Some use of the expression (5.20) has been made by Y. N. Demkov, Phys. Letters **15**, 235 (1965). Demkov's formula seems to differ by a factor of 2 in the exponent.

made in that paper for the particular case of H_2 which was considered. Note that the real energy shift $\frac{1}{2}\hbar\omega$ added to E_0 exactly cancels a like term in the energy of the initial molecule, so that effectively vibrational kinetic energy is conserved in the vertical transitions[32] just as is rotational energy.

Note finally that the phenomenological peak in the cross section (5.24) will not occur at $\bar{E}_0$ because of the other energy-dependent factors, especially $\rho(E)$, and also $k_i^2=(2m/\hbar^2)E$. If $\rho(E)$ is not varying too rapidly, the peak energy $(d\sigma/dE=0)$ will be given approximately by

$$E_{\text{peak}}=\bar{E}_0-\tfrac{1}{8}\Gamma_d^2(\rho'+1/E), \tag{5.26}$$

where $\rho'=d\rho/dE$ is easily shown from (5.20) to be always positive. Because of (5.26) it could be treacherous to attempt to draw precise estimates of the location of the upper potential curve from the location of E_{peak}, unless something is known of ρ'. For example, the principal resonance curve in H_2^- might lie at 11 or 12 eV above the ground state at R_0, rather than at 10.4 eV.

6. INFLUENCE OF DIRECT-TRANSITION TERMS IN ϕ_P

The principal approximation made in the last section was the neglect of all "direct" transitions, vibrational, rotational, and also, in a sense, electronic transitions (to the extent that these change the state of nuclear motion). To these was added the Born-Oppenheimer approximation in (5.3). In order to investigate the implications of the neglect of direct transitions and the effect of relaxing this approximation, we shall briefly consider in this section the effect of allowing a direct vibrational transition to be included in ϕ_P. For definiteness let $v=0$, and assume that there is some "direct" excitation of other vibrational states. This excitation might either be direct in the usual sense, or in a special case it might be resonance vibrational excitation, proceeding through *another* resonance state. In either case, the appropriate generalization of Eq. (5.1) can then be written

$$\phi_P=P\phi_{\text{nad}}Y_{J,M}(\hat{R})R^{-1}[\chi_0+\textstyle\sum_v T_{v0}^{(0)}\chi_v]. \tag{6.1}$$

In the above, the subscript on ϕ_{nad} indicates that it is not quite adiabatic in the sense of Sec. 5. Actually each χ_v should have its own electronic function ϕ, differing slightly from ϕ_{nad} for energetic reasons, but for moderate v this difference is not important and may be neglected (provided one remembers that the electron's energy is diminished by $\hbar\omega v$). Equation (6.1) differs from (5.11) only in the substitution

$$\chi_v\rightarrow\chi_0+\textstyle\sum_v T_{v0}^{(0)}\chi_v. \tag{6.2}$$

The entire analysis of Sec. 5 may then be repeated and the only change is that, wherever χ_v appears, it is replaced by the substitution (6.2). We finally arrive at the cross-section formula (5.19) which becomes

$$\sigma=\frac{4\pi^2}{k_i^2}\bar{g}\frac{\Gamma_{\bar{a}}}{\Gamma_d}|\tilde{\chi}_0(x_E-ig)+\sum_v T_{v0}^{(0)}\tilde{\chi}_v(x_E-ig)|^2e^{-\rho(E)}. \tag{6.3}$$

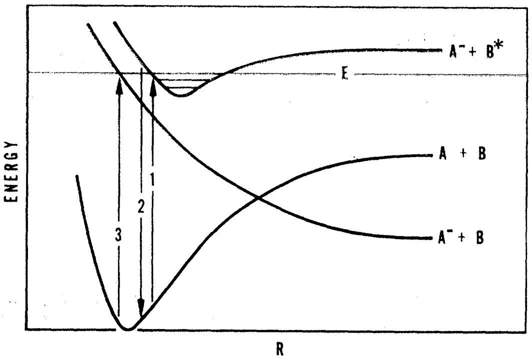

FIG. 2. Illustrates the "nonadiabatic" process described in the text, which is possible if the electron energy E matches one of the discrete vibrational states of the higher resonance state curve. Steps 1 and 2 correspond to resonant elastic scattering or vibrational excitation. This is followed in step 3 by ordinary DA, which consequently has the extra energy dependence of steps 1, 2 built into it.

Equation (6.3) represents the generalization of (5.19) when the approximation of neglecting "direct" vibrational excitation is relaxed. Comparison of Eq. (6.3) with the result of Bardsley, Herzenberg, and Mandl[5] which is identical with Eq. (5.24) makes it clear that these authors have in effect made the same adiabatic approximation, i.e., neglect of "direct" transitions, that was made in Sec. 5. This seems to be the one significant approximation of that paper.

It is interesting that, contrary to what one might guess, the presence of the higher vibrational states χ_v in (6.3) does not cause any structure at all to appear in the cross section for small or moderate T's. A simple numerical study shows that they produce only a shift and broadening plus a slight asymmetry for odd v.

However, there is one somewhat exceptional case in which (6.3) may introduce structure into the cross section. This occurs if there happens to exist another resonance state, a nondissociating one of the type responsible for the familiar resonance vibrational excitation and resonance elastic scattering,[10] and if further the trough of this other resonance state happens to lie in the energy range of interest for DA. A simple set of potential curves illustrating this situation is given in Fig. 2. The process described by Eq. (6.3) for the case shown in Fig. 2 may be thought of in time as first a resonant elastic scattering or vibrational excitation followed by DA either from the ground or excited vibrational state in the standard way.

The behavior of the wave function (6.1) for the situation of Fig. 2 in the appropriate energy range follows from the existing analysis of the resonance vibra-

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[32] This is in accord with the Franck-Condon principle in its general form, which states that neither position *nor* momentum of the nuclei should change in molecular transitions.

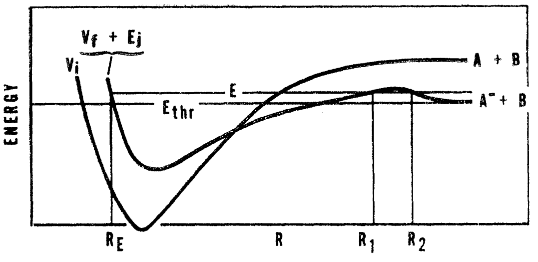

FIG. 3. Example of a final negative-ion resonance curve which is attractive, with the centrifugal energy E_J added. E_{thr} is the threshold energy for DA. The hump at large R due to E_J is greatly exaggerated. R_1 and R_2 are the two additional turning points for an energy E.

tional excitation problem.[16,17] ϕ_{nad} will contain a series of Breit-Wigner resonance factors, one for each vibrational state of the second resonance level, each with a width of the order of 0.1 eV or less. The $T_{v0}^{(0)}$ are then products of vibrational overlap integrals, some of them of order unity. The Breit-Wigner factors in ϕ_{nad} become incorporated in $\Gamma_{\bar{a}}$ of (6.3) and the cross section then has resonance peaks, broadened to the width of the electron beam used in an experiment. In addition, since the higher χ_v have their outermost peaks at $x \geq 1$, by (5.22) these are shifted from $\bar{E}_0$ by an amount of the order Γ_d. Thus a resonance term in ϕ_{nad} (i.e., in $\Gamma_{\bar{a}}$) at the proper energy could cause a large enhancement of the cross section displaced in energy by such an amount from the zero-order peak.

Now for the H_2 problem there does exist such a nondissociating resonance in the neighborhood of 12 eV as found by Kuyatt *et al.*[33] Further, the observed attachment cross sections[34,35] for H_2, HD, and D_2 do in fact show signs of structure in this energy region. It is possible that (6.3), with $\Gamma_{\bar{a}}(\phi_{\text{nad}})$ and $T_{v,0}^{(0)}$ modified as just described[17] by this additional resonance state, could be responsible for this structure. If this should be so, then experiments done with electrons of better energy resolution should show more detailed structure with sharper and larger peaks. There is also some structure in the observed cross section for NO.[34] In the absence of a better explanation, this could have a similar cause. Again if this is the case, using electrons with greater energy resolution should sharpen and magnify the structure and show additional peaks.

In a very similar way, the inclusion of direct electronic excitation might also be considered. To ϕ_P would then be added an additional sum just like that of (6.1) except that ϕ_{nad} is replaced by another electronic function representing the additional electronic channel. For the nuclear overlap integral of the form (5.14) to be nonvanishing in this case, a little consideration of the energetics shows that the potential curve V_f of our dissociating resonance state ϕ_r must lie or cross above the curve of the excited state of AB determining this electronically excited channel.

Finally, there is the kind of direct transition, mentioned but not emphasized, namely, direct DA. This is possible when E is small enough so that $R_E > R_c$ (Fig. 1). This transition, occurring between two true electronic states, could occur only through the T' term omitted in (5.3), as emphasized in Ref. 25. However, since R_c is always well outside the Franck-Condon region, the smallness of the overlap integral together with that of T' should make the cross section too small to be of much interest.

The mechanisms discussed in this section are certainly not meant to be exhaustive. The main purpose has been to show where the approximations of Sec. 5 may fail and to indicate the direction in which any needed improvements may be sought.

In the next three sections, certain consequences of the results of Sec. 5 are discussed in more detail, together with their experimental implications.

7. DISSOCIATIVE ATTACHMENT TO AN ATTRACTIVE POTENTIAL CURVE (VERTICAL ONSET)

It has been tacitly assumed that the resonance-state's potential curve is purely repulsive as in Fig. 1. It should be clear, however, that the analysis goes through in exactly the same way if the potential curve is attractive, as in Fig. 3, provided only that the electron energy is above the threshold energy E_t for the process to be energetically allowed. Below the threshold, the cross section must vanish. Above the threshold, the analysis leading to (5.19) and (5.24) is unchanged. Accordingly, Rapp and Briglia[34] recommended that the cross-section curve should be found in the same way as for the purely repulsive case and simply erased below the threshold energy E_t, resulting in the vertical onset of the cross section at that energy as shown in Fig. 4. This is undoubtedly the correct practical solution to the problem.

One might wonder how this is reconciled with the quantum-mechanical threshold laws, according to which the cross section for a given rotational state J should go to zero at E_{thr} according to the law[36]

$$\sigma_J \propto K^{2J+1}, \tag{7.1}$$

where K is the relative momentum of the heavy particles. Now any threshold behavior must come through the dissociating wave function $\chi(R)$. But Eq. (A11) of the Appendix for this function does not indicate any threshold behavior. The reason for this is that in using

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[33] C. E. Kuyatt, S. R. Mielczarek, and J. Arol Simpson, Phys. Rev. Letters **12**, 293 (1964).

[34] D. Rapp and D. D. Briglia, J. Chem. Phys. **43**, 1480 (1965); D. Rapp, T. E. Sharp, and D. D. Briglia, Phys. Rev. Letters **14**, 544 (1965).

[35] G. J. Schulz, Phys. Rev. **113**, 816 (1959).

[36] E. P. Wigner, Phys. Rev. **73**, 1002 (1948). Note that (7.1) refers to the threshold $K \to 0$. In the exceptional case where DA is exothermic, as for some of the halides, the quantum-mechanical threshold behavior in the *electron* energy is of course $\sigma \propto k^{2L-1}$, to the extent that this is not overwhelmed by the Gaussian in (5.19).

the JWKB approximation to trace the function out to $R \rightarrow \infty$, it was assumed that there exists only one turning point, R_E. However, for attractive potential curves, the centrifugal term E_J will produce a small hump in the potential curve V_f at the large R as shown in Fig. 3. Then if the electron energy lies above the threshold by an amount small compared with the centrifugal or rotational energy, there will develop two additional turning points at R_1 and R_2 as shown in Fig. 3. A more extended semiclassical treatment of the wave function at these turning points would then be needed in order to derive the threshold laws.

We shall content ourselves with finding an indication of the approximate range of energy (relative to the threshold) in which the threshold behavior would be relevant. To get an idea of this, assume that the long-range interaction between A^- and B is given by the polarization potential

$$V_f(R) \sim -e^2\alpha/2R^4, \tag{7.2}$$

where α is the polarizability of B. There will be turning points in the radial Schrödinger equation at large R if the momentum $K(R)$ vanishes, where asymptotically

$$K(R)^2 = \left(\frac{2\mu}{\hbar^2}\right)(E - V_f) \sim K^2 - \frac{(J+\frac{1}{2})^2}{R^2} + \frac{\mu e^2\alpha}{\hbar^2 R^4}.$$

The necessary condition for $K(R)^2$ to vanish at some R is that the discriminant of the quadratic in R^{-2} be positive, i.e.,

$$E - E_t = \frac{\hbar^2 K^2}{2\mu} \leq \frac{\hbar^4 (J+\frac{1}{2})^4}{8\mu^2 e^2 \alpha} = \frac{3.4(\text{eV})(J+\frac{1}{2})^4}{(\mu/m_e)^2 \alpha(\text{a.u.})}. \tag{7.3}$$

Now, since $\mu/m_e \simeq 920\bar{A}$, where $\bar{A}$ is the average atomic weight, it seems from (7.3) that the region of the quantum-mechanical threshold laws will always be negligibly small except for enormous values of the rotational quantum number J, and so the vertical onset approximation should be quite good. This is consistent with the expectation that the motion of the particles A^- and B is classical because of their large mass. Examples of this phenomenon have been pointed out by Rapp and Briglia.[34] They include the CO result at 9.7 eV in addition to that for H_2 at 14 eV. To these should be added the H_2 peak at 3.7 eV as well.

The vertical onset phenomenon should be especially significant for the inverse process, associative detachment, i.e., $A^- + B \rightarrow AB + e$. Since in this case the T-matrix element for either process is a maximum when $A^- + B$ have zero relative kinetic energy, the inverse process should therefore go with large cross section for thermal-energy particles, making it of practical importance.

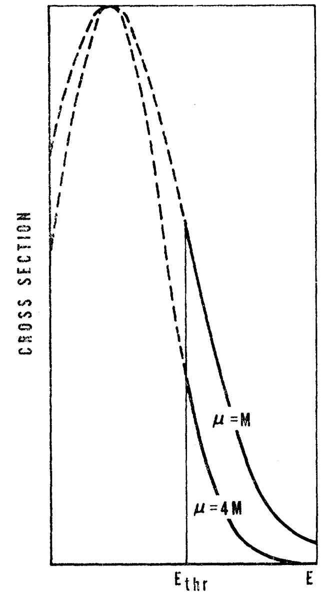

FIG. 4. Illustration of the vertical onset phenomenon. Only the portion of the curve to the right of the threshold energy E_{thr} represents an observable cross section. The lower curve is drawn for a hypothetical isotope with $\mu = 4M$, to illustrate the isotope effect associated with vertical onset.

8. MASS OR ISOTOPE DEPENDENCE

The isotope effect found by Rapp, Sharp, and Briglia[34] for hydrogen, makes the mass dependence of (5.19) and (5.24) of interest. Consider the more explicit Eq. (5.24). The only mass-dependent quantities are Γ_d (appearing in two places) and ρ. The mass dependence of both of these is trivial and follows from Eqs. (5.12), (5.10), and (5.20) together with (A15). It is

$$\Gamma_d \propto \mu^{-1/4}, \quad \rho \propto \mu^{1/2}, \tag{8.1}$$

where μ, of course, is the nuclear reduced mass. The Γ_d term in the denominator of (5.24) therefore gives σ a $\mu^{1/4}$ mass dependence which is always present. If $E \simeq \bar{E}_0$ and ρ is not large, this will be the only mass dependence.

The presence of Γ_d^2 in the first exponent of (5.24) makes the cross-section peak narrower for heavier isotopes without changing the peak value significantly. However, if the threshold for DA happens to lie at $E_{\text{thr}} \gg \bar{E}_0$ (this is the case of vertical onset discussed in the preceding section), then only the extreme tail of the Gaussian in Eq. (5.24) will be observable as in Fig. 4, and the peak value of the cross section, i.e., the value at E_{thr}, will be much larger for the lighter isotope. Quantitatively, we see from (8.1) that the exponent is proportional to $\mu^{1/2}$. This is the probable explanation for the isotope effect in the 14-eV peak for H_2,[34] which is clearly a case of vertical onset. The negative-ion resonance potential curve for this peak is probably the one calculated by Taylor and Williams.[37] The mass dependence of this peak was explained incorrectly by Demkov[31] as being due exclusively to the survival probability.

Finally there is the mass dependence of $e^{-\rho}$ which is of exactly the same nature as that of the Gaussian factor in (5.24) in that the exponent is again propor-

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[37] H. S. Taylor and J. K. Williams, J. Chem. Phys. 42, 4063 (1965).

tional to $\mu^{1/2}$ by virtue of (8.1). If ρ is small, as it probably is for many molecules, there will be a negligible mass dependence due to this factor. On the other hand, if ρ is very large, the cross section will be correspondingly small, and it will then be many times smaller for the heavier isotope, as the result of (8.1). It has been pointed out by BHM[38] that this is the probable explanation for the isotope effect in the 10-eV peak in H_2. This suggestion was also made by Demkov.[31]

The 3.7-eV peak in hydrogen[9] must be a combination of both the preceding effects. It is clearly a case of vertical onset, occurring right at the threshold, and further, as a potential-type resonance (as opposed to the compound resonance) Γ_a is broad,[9] making ρ large. The extreme isotope effect found by Schulz and Asundi[9] for this peak must be the result of both of these factors.

Finally, it is conceivable that ρ could be so large in a particular case that the cross section given by (5.24) would be smaller than that due to the relatively nonresonant process postulated in Ref. 1 to explain the H_2 results at 10 eV. A quantitative expression for this process is being derived and will be reported subsequently.

9. EFFECT OF ROTATIONAL STATES

The temperature effect found by Fite, Brackmann, and Henderson[39] for dissociative attachment in hot O_2 has raised the question of the effect of rotational states on DA.

Equations (5.19) and (5.24) already contain this effect implicitly. The only dynamical effect of rotational motion is to add the centrifugal energy term

$$E_J=(\hbar^2/2\mu)(J+\tfrac{1}{2})^2/R^2 \tag{9.1}$$

to both initial and final potential energy curves, V_i and V_f. The effect will be illustrated by considering the $v=0$ cross section (5.24) and expanding E_J about the equilibrium point, through the first derivative, i.e.,

$$E_J(R)=E_J(R_0)-(2/R_0)E_J(R_0)\quad(R-R_0)+\cdots. \tag{9.2}$$

$E_J(R_0)$ is the so-called rotational energy. Since this raises both V_i and V_f by the same amount, it has no effect (except to raise the threshold at which DA becomes possible). The effect of E_J's first derivative on V_i is to stretch the molecule[40] to the new equilibrium distance

$$R_1=R_0+(2/\mu\omega^2R_0)E_J. \tag{9.3}$$

E_J without an argument is used to mean $E_J(R_0)$. The effect of the first derivative on V_f is to increase the slope V' by the centrifugal force. The modified slope is

$$V_J'=V'[1+(2/R_0V')E_J]. \tag{9.4}$$

Because of (5.12), Γ_d is multiplied by the same factor.

$$\Gamma_{dJ}=\Gamma_d[1+(2/R_0V')E_J]. \tag{9.5}$$

The stretching given in Eq. (9.3), by changing the equilibrium distance R_0, thereby changes the equilibrium energy $\bar{E}_0$ by the amount

$$\bar{E}_{0J}-\bar{E}_0=-V'(R_1-R_0)=-(2V'/\mu\omega^2R_0)E_J. \tag{9.6}$$

Equations (9.6) and (9.5), which are to be substituted for Γ_d and $\bar{E}_0$ in (5.24), give the explicit effect of rotation on DA. Equation (9.6) shows a shift in the cross-section peak to lower energy while Eq. (9.5) produces a symmetrical broadening of the peak, in addition to a trivial reduction of the over-all magnitude of σ.

Although these effects could in principle explain the temperature effect in O_2,[39] a quantitative study shows that they fall far short and are in fact almost negligible. The quantities appearing in (9.5) and (9.6) are well known for O_2 except for V'. The observed DA cross-section width together with Eq. (5.12) shows that $V'\simeq 12$ eV$/a_0$, so that Eqs. (9.5) and (9.6) for O_2 become, for E_J in eV,

$$\Gamma_{dJ}=\Gamma_d(1+0.05E_J), \tag{9.5$'$}$$

$$\Delta\bar{E}_0=-0.5E_J. \tag{9.6$'$}$$

The broadening is almost entirely negligible, even for fairly high J, while (9.6′) implies that the shift due to a Maxwell distribution would be of the order of $\frac{1}{2}kT$, also almost negligible.

The effect of rotation on the survival probability $e^{-\rho(E)}$ follows from substituting Eq. (9.4) into (5.20). The exact expression would be sensitive to the details of the curve and the variation of Γ_a with R. However, it seems that the change in ρ is of the same order as that in Γ_d, as given by (9.5′) for O_2, and is therefore also negligible for this case.

One concludes then that rotational excitation does not seem to be the cause of the temperature shift[39] in O_2. On the other hand, a preliminary numerical study of the effects of vibrational states, using Eq. (5.19) with ρ constant, indicates that these account fairly well for the enhancement of the very low-E cross section *except* for the shift in the peak. A probable source of this shift is the energy variation of $\rho(E)$ in Eq. (5.19) for $v>0$. A conjecture along this line has been made by Demkov.[31]

10. SUMMARY AND DISCUSSION

To summarize, the principal features of the present paper are first the very simple general formalism of Sec. 3, appropriate to any rearrangement-type process where there is a resonance state involved and the Born-Oppenheimer separation is appropriate; second, the derivation of the exact expressions for resonance dis-

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[38] J. N. Bardsley, A. Herzenberg, and F. Mandl, *Fourth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1964), p. 359.

[39] W. L. Fite, R. T. Brackmann, and W. R. Henderson, *Fourth International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1964), p. 100.

[40] See Ref. 30, p. 305 ff.

sociative attachment together with its inverse and competing processes; and third, the formulas, Eqs. (5.19) and (5.24), resulting from the "adiabatic" approximation for ϕ_P as defined in Sec. 5. These latter are in complete agreement with the result of BHM[5] for the case ($v=J=0$) which they gave explicitly. The effect of relaxing this approximation is also studied in Sec. 6 and various practical conclusions are drawn in the succeeding sections.

An important qualitative distinction not emphasized in the paper is that between compound-ion-type resonance states, namely, an electron bound to an excited target, as defined by Feshbach, and the potential or single-particle-type resonance, i.e., an electron trapped by a centrifugal (or Coulomb) barrier in the neighborhood of the unexcited target. Calculations[41] and experiments[42] done so far indicate that the former are always very narrow ($\Gamma_a<0.1$ eV), while the potential resonances could be much broader. A good example of the latter seems to be the low-energy H_2^- resonance at about 2 eV above the ground state which has been observed through both vibrational excitation[10] and DA.[9] This seems to have a width of the order of a volt.[9] (See also Ref. 8.)

There is also a second kind of potential resonance which is illustrated in Fig. 5 for $R<R_{C1}$. This bears the same relation to a compound resonance as an ordinary potential resonance does to a true bound state, i.e., it is an electron trapped (with positive energy) by a centrifugal barrier in the neighborhood of an excited molecule. Such a state would auto-ionize to an excited target and a slow electron. This would correspond to a continuum solution of Feshbach's Q^0HQ^0 operator, while a discrete compound resonance is a bound state of the same operator. This second kind of potential resonance has been invoked[1] to explain the 10-eV peak in the DA results for H_2, postulating a potential curve as in Fig. 5 in analogy with the curves of Taylor and Harris[43] for the lowest state of H_2^-. The smallness of the cross section and the isotope effect indicate that this also must be very broad in the light of (5.24). A practical difference between the two kinds of resonance is the following. If all resonances were narrow compound-ion-type states, then the survival probability $e^{-\rho}$ in (5.20) would never differ much from unity. DA would then be a strictly first-order process of capture followed by dissociation. This was the assumption of Ref. 1. On the other hand, for broad potential-type resonances, $e^{-\rho}$ may be extremely small, and must therefore be carefully considered.

Another point about broad resonances is that when one becomes very broad, the advantage of treating it as a discrete state is reduced and it might be treated as profitably by continuum methods. This approach is presently being looked at, especially for the 10- and 3.7-eV peaks in H_2.

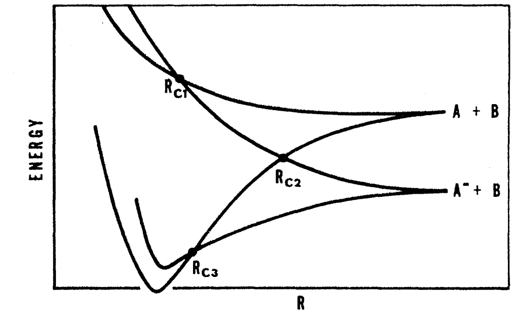

FIG. 5. Potential curves for a hypothetical negative molecular ion, illustrating three different kinds of resonance states. The lower negative-ion curve for $R<R_{C3}$ is an ordinary potential-type resonance. The upper negative-ion curve is a compound-ion-type resonance for $R_{C1}<R<\infty$, i.e., while it is *below* the excited-state curve for the target (AB), and a potential resonance of the second kind for $R<R_{C1}$. In the region $R>R_{C2}$, it does not differ significantly from an ordinary bound state.

All the experimental DA results[44] with the exception of hydrogen are consistent at least with the interpretation of compound-ion-type resonances with widths of the order of hundredths of volts. Although very small survival probabilities are ruled out by the magnitude of the cross sections, ρ's of the order of 1 or 2 or so are certainly not impossible. For the case of dissociative recombination, it is trusted that both Γ_a and ρ will be small in general, so that the process will be of the simple first-order variety just referred to.

Finally, although the present theory was derived only for diatomic molecules, the experiments show that the CO_2 and N_2O results are not greatly different in magnitude or energy variation from those for most diatomics, suggesting that the same theory may explain both. It has been pointed out[45] that if the nuclear motion of polyatomics is analyzed into normal modes, then each normal mode behaves like a diatomic molecule, so that the present theory would probably be applicable here also.

ACKNOWLEDGMENTS

The author would like to thank Dr. B. A. Lippmann and Dr. P. J. Redmond for very helpful discussions.

APPENDIX: ASYMPTOTIC EVALUATION OF NUCLEAR WAVE FUNCTION χ AND OF THE OVERLAP INTEGRAL

It is desired to evaluate the overlap integral

$$S=\int_0^\infty dR\,\chi(R)\chi_v(R) \tag{A1}$$

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[41] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962); P. G. Burke, D. D. McVicar, and K. Smith, Proc. Phys. Soc. (London) **84**, 749 (1964).

[42] C. E. Kuyatt, J. Arol Simpson, and S. R. Mielczarek, Phys. Rev. **138**, A385 (1965). References to other measurements may also be found in this paper.

[43] H. S. Taylor and F. Harris, J. Chem. Phys. **39**, 1012 (1963).

[44] See first paper of Ref. 34 and other references given there.

[45] P. J. Redmond (private communication).

between the continuum function[46] χ determined by the partial-wave solution of Eq. (4.15) and the discrete vibrational wave function χ_v, and to look for an asymptotic expansion of the result in terms of some small parameter. The χ_v are considered known. To evaluate χ, we first expand the complex potential V_f+F+E about the "turning point" R_E of its real part $V_F+\Delta+E$, i.e.,

$$E-V-E_J=V'(R-R_E)+\tfrac{1}{2}i\Gamma_a(R_E)+\cdots, \qquad \text{(A2)}$$

where V' is the negative of the slope of $V_f+\Delta+E_J$, and E_J is the centrifugal energy (9.1). The variation of Γ_a with R has not been considered, nor have higher derivatives of V_f.

To produce a meaningful expansion, the wave function χ should be written in dimensionless form by choosing a unit of length. The only natural unit of length associated with the overlap integral (A1) is α^{-1}, the zero-point amplitude[30] of the oscillator χ_v, which is given by Eq. (5.10). This is the distance over which any χ_v changes by a significant fraction of itself. Accordingly, the dimensionless variable

$$x=\alpha R, \quad x_E=\alpha R_E \qquad \text{(A3)}$$

is defined. In terms of x, and using (A2), the dimensionless form of Eq. (4.15) is

$$[d^2/dx^2+\lambda(x-x_E+ig)]\chi(x)=0, \qquad \text{(A4)}$$

where

$$\lambda=2\mu V'/\hbar^2\alpha^3=\Gamma_d/\hbar\omega, \qquad \text{(A5)}$$

and

$$g=\mu\Gamma_a/\hbar^2\alpha^2\lambda=\Gamma_a/\Gamma_d. \qquad \text{(A6)}$$

Γ_d is given by Eq. (5.12).

We consider the quantity λ to be large and look for an expansion of χ and of the overlap integral S in powers of $1/\lambda$. For the purpose of finding the expansion, consider[45] the Fourier transform of χ, defined by

$$\chi(x)=\frac{1}{2}\int_{-\infty}^{\infty} e^{ip(x-x_E+ig)}f(p)dp. \qquad \text{(A7)}$$

Because the g term generates a real exponential, for convergence x must be restricted by the condition $\mathrm{Im}(x)=-ig$. This requires that the path of the overlap integral (A1) involving x be deformed accordingly. Substituting (A7) in (A4), $f(p)$ is easily found, giving

$$\chi(x)=\frac{1}{2}\int_{-\infty}^{\infty} \exp[ip(x-x_E+ig)]\exp(-ip^3/3\lambda)dp. \qquad \text{(A8)}$$

Equation (A8) is of course an Airy function.[47] Before proceeding with the expansion, we note that the Airy function defined by (A8) is equal for $x\geq x_E$, to

$$\chi(x)=\tfrac{1}{3}\pi[\lambda(x-x_E+ig)]^{1/2}[J_{1/3}(\xi)+J_{-1/3}(\xi)], \qquad \text{(A9)}$$

where $\xi=\tfrac{2}{3}\lambda^{1/2}(x-x_E+ig)^{3/2}$.

Now if $\lambda\to\infty$, we note that the second exponential in (A8) becomes equal to unity and $\chi(x)$ becomes equal to π times the familiar representation of the δ function.[48] Incidentally, from (A4) we see that the width of the approximate δ function is of the order $\Delta x\sim 1/\lambda$. This δ-function behavior of χ amply justifies the linear approximation made in (A2) for any reasonable λ.

To obtain higher terms in the expansion in $1/\lambda$, the second exponential in (A8) may be expanded. Further, it is recognized that the quantity p^3 is equal to $-id^3/dx_E^3$ operating on the first exponential. Expanding then, making this replacement, and exchanging orders of differentiation and integration, we find

$$\begin{aligned}\chi(x)&=\frac{1}{2}\int_{-\infty}^{\infty}[1-ip^3/3\lambda+O(1/\lambda^2)]e^{ip(x-x_E+ig)}dp\\ &=\pi[1-(1/3\lambda)d^3/dx_E^3]\delta(x-x_E+ig)\\ &\qquad\qquad+O(1/\lambda^2).\end{aligned} \qquad \text{(A10)}$$

(A10) is the desired expansion, through first order in $1/\lambda$, of the function χ, aside from normalization. The proper normalization of χ is given by Eq. (5.6). In order to make the connection, it is most convenient to start with the form (A9) and trace it out to $R=\infty$ by means of the JWKB approximation.[49] One then finds that χ as defined above must be multiplied by the factor $(2\alpha/\pi^2\Gamma_d)^{1/2}$ in order to agree with (5.6). Calling the properly normalized function $\chi^{(n)}$, we have

$$\chi^{(n)}=(\alpha/\tfrac{1}{2}\Gamma_d)^{1/2}[1-(1/3\lambda)d^3/dx_E^3]\delta(x-x_E+ig) \qquad \text{(A11)}$$

through order $1/\lambda$ for the properly normalized χ. Note that $\delta(R-R_E)=\alpha\delta(x-x_E)$. Substituting (A11) into the overlap integral (A1), and remembering (A3) gives

$$\begin{aligned}S=\int_0^{\infty}\chi^{(n)}\chi_v dR=\left(\frac{\Gamma_d}{2}\right)^{-1/2}&[1-(1/3\lambda)d^3/dx_E^3]\alpha^{-1/2}\\ &\times\chi_v(x_E-ig),\end{aligned} \qquad \text{(A12)}$$

again through $O(1/\lambda)$. Equation (A12) is the most general expression to first order for the desired overlap integral for all v and E. The quantity $\alpha^{-1/2}\chi_v$ is dimensionless. If χ_v is taken to be a normalized function of the dimensionless variable x rather than normalized in R space as has been assumed, the $\alpha^{-1/2}$ drops out. Normalization in x space will be assumed from here on and the $\alpha^{-1/2}$ dropped.

The first term in (A12) is the delta-function approximation, with the argument of the vibrational function χ_v shifted by the imaginary quantity $-ig$. The second term represents the small deviation from this δ function to first order in $1/\lambda$. If we define the function

$$\tilde{\chi}_v(x)=\chi_v(x)-(1/3\lambda)\chi_v'''(x), \qquad \text{(A13)}$$

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[46] χ corresponds to the function u_l of Ref. 5.

[47] E. C. Stueckelberg, Phys. Rev. **42**, 522 (1932).

[48] See Ref. 30, p. 51.

[49] Reference 30, p. 190.

then the overlap integral may be written

$$S=(\tfrac{1}{2}\Gamma_d)^{-1/2}\tilde{\chi}_v(x_E-ig)\,. \qquad \text{(A14)}$$

(A14) is the desired result.

The phase shift δ also follows by tracing the solution (A9) out to infinity via the JWKB approximation in the same way. This has previously been done by BHM.[5] The result is

$$\delta=\lim_{R\to\infty}\int_{R_E-ig/\alpha}^{R}\{2\mu[E-V_f-\Delta+\tfrac{1}{2}i\Gamma_a(R)]/\hbar^2 - (J+\tfrac{1}{2})^2/R^2\}^{1/2}dR-KR+(J+\tfrac{1}{2})\pi/2\,, \qquad \text{(A15)}$$

where $K=(2\mu E/\hbar^2)^{1/2}$. The imaginary part $\frac{1}{2}\rho$ of δ is of special interest. BHM have indicated that if Γ_a is not too large, the square root may be expanded to give

$$\tfrac{1}{2}\rho\sim\tfrac{1}{2}\hbar^{-1}\int_{R_E}^{R_c}\frac{\Gamma_a(R)dR}{v(R)}\,, \qquad \text{(A16)}$$

where $v(R)=[2(E-V_f-\Delta-E_J)/\mu]^{1/2}$ is the relative velocity. R_c is the distance where the width Γ_a goes to zero, generally where the resonance curve V_f crosses below the curve of the target state into which it autoionizes (see Fig. 5 or 1). Alternately, since the width Γ_a must fall to zero rapidly with large R, the integral in (A16) may converge before R_c is reached.

An analysis of (A15) shows that the approximation (A16) requires that $\Gamma_a/2$ be small compared to the difference $V_f(R_E)-V_f(R_c)$ in order to be valid. The latter quantity is typically a few eV.

Returning to the overlap integral, (A13) may be made more explicit if it is assumed that the χ_v are harmonic-oscillator functions satisfying the equation

$$d^2\chi_v/dy^2=(y^2-2v-1)\chi_v\,. \qquad \text{(A17)}$$

$\tilde{\chi}_v$ then becomes

$$\tilde{\chi}_v=\chi_v(y)-(1/3\lambda)[2y\chi_v(y)+(y^2-2v-1)\chi_v'(y)]\,, \qquad \text{(A18)}$$

where

$$y=x_E-x_0-ig\,, \qquad \text{(A19)}$$

and $x_0=\alpha R_0$ with R_0 the equilibrium distance.

For $v=0$, (A18) becomes

$$\tilde{\chi}_0=\pi^{-1/4}[1-(y-\tfrac{1}{3}y^3)/\lambda]\exp(-y^2/2) \qquad \text{(A20)}$$

$$\simeq\pi^{-1/4}\exp[-(y+1/\lambda)^2/2]+O(1/\lambda^2)\,, \qquad \text{(A20')}$$

where the latter approximation holds for $y^2\ll 3$, i.e., in the broad neighborhood of the peak at $y=0$. The deviation from the δ-function approximation in this case is purely an additional real shift $\Delta y=1/\lambda$ in the argument of the function $\chi_0(y)$.

For $v\neq 0$, χ_v has $v+1$ peaks and is symmetrical or antisymmetrical about $y=0$. There is no such simple expression as (A20′) for the general case. Each of the v peaks on either side of the origin is shifted by a different amount, and in addition the magnitude of the peak is generally altered to first order. The amount of the shift of a given peak from the complex δ-function approximation may be easily calculated by setting the first derivative of (A18) equal to zero, using (A17), writing $\chi_v'=\chi_v''\Delta x_E$, and keeping first-order terms in $1/\lambda$. The result is

$$\Delta y=-\frac{1}{3\lambda}\left[2v+1-y^2+\frac{2}{2v+1-y^2}\right], \qquad \text{(A21)}$$

where y is now the coordinate of a particular maximum or minimum in χ_v. In addition to being shifted, it is evident from (A18) that the magnitude of χ_v is altered by the factor $(1-2y/3\lambda)$. This equals unity only for the peaks centered (in zero order) at $y=0$, as in Eq. (A20′) for $v=0$. It is clear from (A21) [as from (A13)] that the deviation of $\tilde{\chi}_v$ from χ_v is approximately proportional to the local kinetic energy[32] of the function, and in fact an analysis of (A18) shows that this deviation vanishes very near to the classical turning points of χ_v.