

Dissociative Attachment in Rearrangement Electron Collision with Molecules

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A projection operator which is capable of decoupling the elastic channel and all the rearranged open channels from the rest of the Hilbert space is derived for dissociative attachment in rearrangement electron collision with molecules. This then leads to an exact description of the process by a finite set of coupled equations. Specialization of this method to account for resonance dissociative attachment is also carried out.

I. INTRODUCTION

THE problem of dissociative attachment in rearrangement electron collision with molecules has recently received considerable attention both theoretically^{1,2} and experimentally.^{3,4} Among the features associated with dissociative-attachment processes, the pronounced isotope effect recently observed³ in the electron-hydrogen system is most striking. Since the proposed expansion method¹ does not give a clear picture of auto-ionization, it is not convenient for dealing with dissociative attachment in the (e, H_2) system. To account for the competitive auto-ionization process, the problem of dissociative attachment was later reformulated by Bardsley *et al.*² using the Kapur-Peierls resonance theory.⁵ Their treatment, however, was confined within the adiabatic approximation. The purpose of this paper is to present an exact formalism for dissociative-attachment processes using projection-operator techniques.

Dissociative attachment of electrons to molecules may take place in different fashion. The most important dissociative-attachment processes for diatomic molecules are of the Franck-Condon type in which a transition takes place from a stable state of the molecule to a continuum (with respect to nuclear configuration) of the negative parent ion. Such direct capture of the incident electron into a repulsive state of the parent ion lying in the Franck-Condon region of the molecule would lead to a dissociation of the molecule under consideration in approximately a vibrational time of the constituent nuclei. Dissociative attachment, however, may also take place in an indirect way in which the incident electron is first captured into a discrete

state of the negative parent ion. There follows a radiationless intramolecular decomposition of the Auger type (this is known as predissociation⁶) as a result of the overlapping of this discrete state with continuum. There are also possibilities that dissociative attachment may take place indirectly as a result of ion-pair production followed by recombination of the electron with the positive ion.

For simplicity, we will confine our discussion to diatomic molecular systems and concern ourselves mainly with dissociative attachment of the Franck-Condon type. The description to be presented is, of course, applicable to dissociative recombination in rearrangement electron collision with molecular ions whenever it is appropriate.

The plan of the paper is as follows: In Sec. II, we show how a projection operator which is capable of decoupling the elastic channel and all the rearranged open-channels from the rest of the Hilbert space may be constructed for such a rearrangement collision. In terms of the derived projection operator, an exact description of dissociative-attachment processes by a finite set of coupled equations is then obtained. The size of the coupled equations is equal to one plus the total number of opened rearranged channels. We close this section by showing the simplifications that may result by neglecting the recoils in the rearranged channels. Specialization of this method to account for resonance dissociative attachment is carried out in Sec. III. The electronic scattering state involving resonance is solved for a fixed nuclear configuration, using Feshbach's treatment⁷ for resonance. We then construct the projection operator in terms of the scattering state by a straightforward application of the method derived in Sec. II. Finally, in Sec. IV, application of the formalism to the electron-hydrogen system is discussed. A comparison of the present formulation with that of Bardsley *et al.*² is also made.

II. COUPLED-EQUATION FORMALISM

The technique frequently used for describing rearrangement collision is to assume that the total wave

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² 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.

³ D. Rapp, T. E. Sharp, and D. D. Briglia, Phys. Rev. Letters **14**, 533 (1965).

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⁵ P. L. Kapur and R. E. Peierls, Proc. Roy. Soc. (London) **A166**, 277 (1938).

⁶ For further discussion, see G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (D. Van Nostrand Company, Inc., New York, 1950), p. 387.

⁷ H. Feshbach, Ann. Phys. (N. Y.) **19**, 287 (1962).

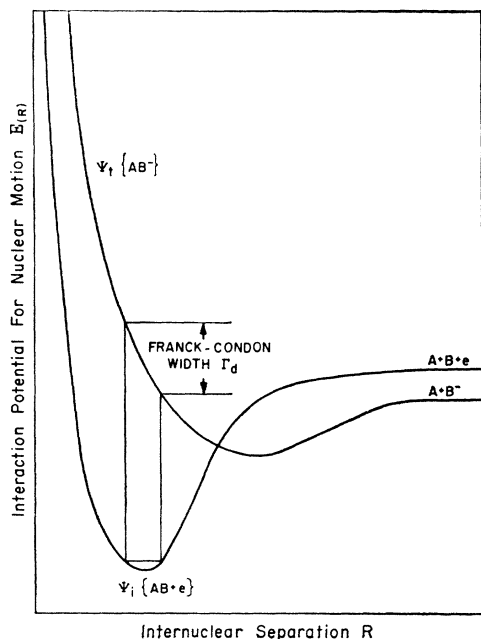


FIG. 1. Schematic diagram of interaction potentials for Franck-Condon type dissociative attachment.

function Υ is a linear combination of the initial and final states with unknown scattering and rearranged functions, respectively, in each. Thus for dissociative attachment $AB+e \rightarrow A+B^-$ (Fig. 1), one may start with the two-state approximation

$$\Upsilon(\mathbf{r}, \mathbf{R}) \cong \{\psi_n(\mathbf{r}', \mathbf{R})\chi_{nv}(\mathbf{R})\}F_{nv}^{(0)}(\mathbf{r}_0) + \mathcal{Q}\{\phi_m(\mathbf{r}_a)\phi_{m'}(\mathbf{r}_b)\}G_{mm'}^{(0)}(\varrho), \quad (2.1)$$

where $\psi_n(\mathbf{r}', \mathbf{R})$ and $\chi_{nv}(\mathbf{R})$ are, respectively, the initial electronic and nuclear wave functions of the target molecule AB , $\phi_m(\mathbf{r}_a)$ and $\phi_{m'}(\mathbf{r}_b)$ are the final electron wave functions of the atoms A and B^- , respectively, and \mathcal{Q} is the antisymmetrization operator operating only on the electrons. The coordinates of the system containing an incident electron and two heavy nuclei a and b are illustrated in Fig. 2. For simplicity the coordinates of the N_0 bound electrons are not included in Fig. 2.

Equation (2.1) is then substituted into a variational expression which is made stationary by an approximate choice of the two unknown functions, thus leading to a pair of coupled equations. These equations are then solved for the unknown functions with the following asymptotic boundary conditions

$$F_{nv}^{(0)}(\mathbf{r}_0) \xrightarrow{r_0 \rightarrow \infty} e^{ik_i \cdot r_0} + f_{\alpha}^{(0)}(\hat{k}_i, \hat{r}_0) \frac{e^{ik_i \alpha r_0}}{r_0}, \quad \alpha = (n, \nu), \quad (2.2)$$

$$G_{mm'}^{(0)}(\varrho) \xrightarrow{\rho \rightarrow \infty} g_{\nu}^{(0)}(\hat{k}_i, \hat{\rho}) \frac{e^{ik_i \nu \rho}}{\rho}, \quad \nu = (m, m'). \quad (2.3)$$

Recently, Feshbach⁷ has proposed a method which

is capable of improving the coupled-equation approach so that it becomes exact. The method involves construction of projection operators which project out from the total wave function the channels of immediate concern and treatment of the remaining channels as fields for generating effective optical potentials. The existence of a projection operator Π which can project out from the total wave function the two desired channels simultaneously has been demonstrated by Mittleman.⁸

$$\Pi \Upsilon(\mathbf{r}, \mathbf{R}) = \{\psi_n(\mathbf{r}', \mathbf{R})\chi_{nv}(\mathbf{R})\}F_{nv}(\mathbf{r}_0) + \mathcal{Q}\{\phi_m(\mathbf{r}_a)\phi_{m'}(\mathbf{r}_b)\}G_{mm'}(\varrho). \quad (2.4)$$

This then provides, except for the Pauli principle between the projectile and target molecular electrons, an exact description of the rearrangement collision by a pair of coupled equations. However, the projection operator Π which can decouple the two channels from the rest of the Hilbert space is a solution of an integral equation which could not be solved easily (if at all). The difficulties arise from the change in coordinates between the initial and the rearranged channels due to the rearrangement of the colliding system, thus resulting in equations which are intrinsically nonlocal.

An alternative method was later proposed by Chen and Mittleman⁹ which accomplishes the same purpose but is much simpler in constructing the projection operator. The technique used in this method is to constrain the coordinates in the two channels to be the same, thereby eliminating the intrinsically nonlocal aspect of the problem. In this section, we propose for dissociative attachment another method of constructing the projection operator which is exact and sufficiently simple to be numerically useful. The new method involves construction of the projection operator Π in terms of the elastic scattering channel which is assumed to be predetermined from the electronic Hamiltonian for a fixed nuclear configuration. The resulting coupled equations that are obtained from this method provide solutions for the rearranged scattering channels.

The total electronic Hamiltonian for the $N=N_0+1$ electron can be defined as

$$H_e = H + (1/2\mu)\nabla_{R^2}, \quad (2.5)$$

$$\mu = M_a M_b / (M_a + M_b), \quad (2.6)$$

where H is the total Hamiltonian of the system, ∇_{R^2} is the Laplacian operator associated with the relative

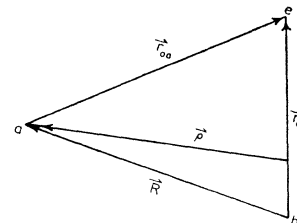


FIG. 2. Coordinate system for the one-electron model.

⁸ M. H. Mittleman, Ann. Phys. (N. Y.) 28, 430 (1964).

⁹ J. C. Y. Chen and M. H. Mittleman, Ann. Phys. (N. Y.) (to be published).

nuclear motion, and M_a and M_b are the masses of nuclei a and b , respectively. For each fixed nuclear configuration, we may solve the electronic Schrödinger equation

$$\{H_e - \mathcal{E}_i(\mathbf{R})\}\Psi_i(\mathbf{r}, \mathbf{R}) = 0, \quad i = (k_i, 0), \quad (2.7)$$

for the scattering state $\Psi_i(\mathbf{r}, \mathbf{R})$:

$$\Psi_i(\mathbf{r}, \mathbf{R}) \xrightarrow[r_0 \rightarrow \infty]{} \psi_0(\mathbf{r}_0', \mathbf{R}) \left\{ e^{i\mathbf{k}_i \cdot \mathbf{r}_0} + f_0(\hat{k}_i, \hat{r}_0) \frac{e^{i\mathbf{k}_i \cdot \mathbf{r}_0}}{r_0} \right\} \quad (2.8)$$

with

$$\mathcal{E}_i(\mathbf{R}) = \epsilon_0(\mathbf{R}) + \frac{1}{2}k_i^2, \quad (2.9)$$

where $\epsilon_0(\mathbf{R})$ is the electronic energy of the initial target state. The zero-point energy is set at the initial level of the nuclear state of the initial electronic state. Thus, at the equilibrium internuclear separation, R_e , $\mathcal{E}_i(\mathbf{R})$ is equal to the total energy E of the system; and at any other R , $\mathcal{E}_i(\mathbf{R})$ is equal to the E corrected by the energy stored in the nuclear motion which is governed by the relevant potential curve generated by the target electronic state.

To constrain the coordinate in the rearranged channel to be \mathbf{R} , we may use the relation (obtained from Fig. 2)

$$\boldsymbol{\rho} = \mathbf{R} - (1/M_b + 1)\mathbf{r}_{0b}. \quad (2.10)$$

Since, in Eq. (2.4), $\phi'_{m'}(\mathbf{r}_b)$ with $\mathbf{r}_b = (\mathbf{r}_{0b}, \mathbf{r}_{1b}, \dots)$ vanishes exponentially as its argument \mathbf{r}_{0b} becomes large, we may write for large R .

$$\boldsymbol{\rho} = |\boldsymbol{\rho}| = R - (1/M_b + 1)\hat{R} \cdot \mathbf{r}_{0b} + O(R^{-1}). \quad (2.11)$$

Substitution of (2.11) for $\boldsymbol{\rho}$ into Eq. (2.3) yields

$$G_{mm'}(\boldsymbol{\rho}) \xrightarrow[\rho \rightarrow \infty]{} \{g_\nu(\hat{k}_i, \hat{R})(e^{i\mathbf{k}_i \nu R/R})\} e^{-i\lambda \mathbf{k}_i \nu \cdot \mathbf{r}_{0b}} \quad (2.12)$$

with

$$\mathbf{k}_{i\nu} = \mathbf{k}_i \nu \hat{R}, \quad \lambda = 1/(M_b + 1). \quad (2.13)$$

This demonstrates that if one constrains the rearranged channel coordinate to be \mathbf{R} , one encounters a recoil factor $\exp(-i\lambda \mathbf{k}_i \nu \cdot \mathbf{r}_{0b})$ in the rearranged channel.

In view of Eqs. (2.9) and (2.12), we introduce the notations

$$|i, 0\rangle = \Psi_i(\mathbf{r}, \mathbf{R}), \quad (2.14)$$

$$|f, \nu\rangle = \mathcal{G}\{\phi_m(\mathbf{r}_a)\phi_{m'}(\mathbf{r}_b)e^{-i\lambda \mathbf{k}_i \nu \cdot \mathbf{r}_b}\}, \quad (2.15)$$

and define a projection operator such that

$$\Pi\Upsilon(\mathbf{r}, \mathbf{R}) = |i, 0\rangle\chi_0(\mathbf{R}) + \sum_{\nu=1}^{p_0} |f, \nu\rangle G_\nu(\mathbf{R}), \quad (2.16)$$

where $\chi_0(\mathbf{R})$ is bounded in R and the $G_\nu(\mathbf{R})$'s have the boundary condition inferred from Eq. (2.12):

$$G_\nu(\mathbf{R}) \xrightarrow[R \rightarrow \infty]{} g_\nu(\hat{k}_i, \hat{R})(e^{i\mathbf{k}_i \nu R/R}). \quad (2.17)$$

We emphasize that the recoil states $|f, \nu\rangle$ are normalized but are not orthogonal, so that all the rearranged open channels must be included in the summation in Eq. (2.16). The asymptotic boundary condition for $r_0 \rightarrow \infty$ is satisfied by $\Pi\Upsilon$ due to $|i, 0\rangle$ [Eq. (2.8)].

The projection operator defined by Eq. (2.16) must satisfy the following equations:

$$\langle i, 0 | (1 - \Pi)\Upsilon = 0, \quad (2.18)$$

$$\langle f, \nu | (1 - \Pi)\Upsilon = 0, \quad \nu = 1, 2, \dots, p_0. \quad (2.19)$$

Equations (2.18) and (2.19) are just statements that the asymptotic forms of $\Pi\Upsilon$ and Υ should coincide for the elastic channel and all the rearranged channels. By defining

$$U_0(\mathbf{R}) = \langle i, 0 | \Upsilon, \quad (2.20)$$

$$V_\nu(\mathbf{R}) = \langle f, \nu | \Upsilon, \quad (2.21)$$

$$\Delta_{0\nu}(\mathbf{R}) = \langle i, 0 | f, \nu, \quad (2.22)$$

$$\eta_{\nu\nu'}(\mathbf{R}) = \langle f, \nu | f, \nu', \quad (2.23)$$

Eqs. (2.18) and (2.19) may be written as

$$\chi_0(\mathbf{R}) + \sum_{\nu=1}^{p_0} \Delta_{0\nu}(\mathbf{R})G_\nu(\mathbf{R}) = U_0(\mathbf{R}), \quad (2.24)$$

$$\sum_{\nu=1}^{p_0} \eta_{\nu\nu'}G_{\nu'}(\mathbf{R}) + \Delta_{0\nu}^*(\mathbf{R})\chi_0(\mathbf{R}) = V_\nu(\mathbf{R}). \quad (2.25)$$

Functions $\chi_0(\mathbf{R})$ and $G_\nu(\mathbf{R})$ are now solved from Eqs. (2.24) and (2.25) in terms of matrix notations

$$\chi_0(\mathbf{R}) = (1 + \mathbf{D}\mathbf{D}\mathbf{A}^*)U_0 - \mathbf{D}\mathbf{D}\mathbf{V}, \quad (2.26)$$

$$\mathbf{G}(\mathbf{R}) = \mathbf{D}(\mathbf{V} - \mathbf{A}^*U_0), \quad (2.27)$$

where

$$\mathbf{D} = \{\boldsymbol{\eta} - \mathbf{A}^*\mathbf{A}\}^{-1} = (d_{\nu\nu'}). \quad (2.28)$$

Now substituting Eqs. (2.26) and (2.27) into Eqs. (2.16) and using the definitions for U_0 and the V_ν 's [i.e., Eqs. (2.20) and (2.21)], we obtain

$$\begin{aligned} \Pi = \delta(R, R') \left\{ |i, 0\rangle \left[1 + \sum_{\nu=1}^{p_0} \sum_{\nu'=1}^{p_0} \Delta_{0\nu} d_{\nu\nu'} \Delta_{0\nu'}^* \right] \langle i, 0| \right. \\ \left. + \sum_{\nu=1}^{p_0} \sum_{\nu'=1}^{p_0} |f, \nu\rangle d_{\nu\nu'} \langle f, \nu'| \right. \\ \left. - \sum_{\nu=1}^{p_0} \sum_{\nu'=1}^{p_0} |f, \nu\rangle d_{\nu\nu'} \Delta_{0\nu'}^* \langle i, 0| \right. \\ \left. - \sum_{\nu=1}^{p_0} \sum_{\nu'=1}^{p_0} |i, 0\rangle \Delta_{0\nu'} d_{\nu\nu'} \langle f, \nu'| \right\}. \quad (2.29) \end{aligned}$$

It may easily be shown that Π is Hermitian and idempotent $\Pi^2 = \Pi$, so that it is a projection operator.

Since Π projects out from Υ , the complete elastic channel, it then follows that $\Omega\Upsilon$ with $\Omega = 1 - \Pi$ does not contain any incident wave [Eq. (2.18)]. Thus, the Schrödinger equation for the colliding system

$$H\Upsilon = E\Upsilon \quad (2.30)$$

may be solved for $\Pi\Upsilon$ in terms of Ω , yielding

$$(E - \mathcal{H}\mathcal{C})\Pi\Upsilon = 0, \quad (2.31)$$

with

$$\mathcal{H} = \Pi \left\{ H + H\Omega \frac{1}{E - \Omega H\Omega + i\eta} \Omega H \right\} \Pi, \quad (2.32)$$

where $\eta \rightarrow 0^+$ is introduced because Π does not include all the scattered open channels. From Eq. (2.31), the desired coupled equations are then obtained:

$$\{E - \mathcal{H}_{00}\} \chi_0(\mathbf{R}) = \sum_{\nu} \{\mathcal{H}_{0\nu} - E\Delta_{0\nu}\} G_{\nu}(\mathbf{R}), \quad (2.33a)$$

$$\{E - \mathcal{H}_{\nu\nu}\} G_{\nu}(\mathbf{R}) = \sum_{\nu' \neq \nu} \{\mathcal{H}_{\nu\nu'} - E\eta_{\nu\nu'}\} G_{\nu'}(\mathbf{R}) \\ + \{\mathcal{H}_{\nu 0} - E\Delta_{0\nu}^*\} \chi_0(\mathbf{R}) \quad (2.33b)$$

with

$$\mathcal{H}_{00} = \langle i, 0 | H + H\Omega \frac{1}{E - \Omega H\Omega + i\eta} \Omega H | i, 0 \rangle, \quad (2.34)$$

$$\mathcal{H}_{\nu\nu'} = \langle f, \nu | H + H\Omega \frac{1}{E - \Omega H\Omega + i\eta} \Omega H | f, \nu' \rangle, \text{ etc.,}$$

where we have used the relation $\Pi |i, 0\rangle = |i, 0\rangle$, and $\Pi |f, \nu\rangle = |f, \nu\rangle$, for $\nu = 1, \dots, \nu_0$.

For reacting systems where only the lowest rearranged channel ν is open, we have for Π the simple expression from Eq. (2.29)

$$\Pi = \delta(R - R') \{ |i, 0\rangle \langle i, 0| + |f, \nu\rangle \langle f, \nu| \\ - \Delta_{0\nu}^* |f, \nu\rangle \langle i, 0| - \Delta_{0\nu} |i, 0\rangle \langle f, \nu| \} / (1 - |\Delta_{0\nu}|^2). \quad (2.35)$$

The coupled equations (2.33) then reduce to a pair of coupled equations. In order to discuss the nature of the coupling, we approximate \mathcal{H} by its first term $\Pi H \Pi$. The pair of coupled equations becomes

$$\{\nabla_{\mathbf{R}}^2 + 2\mu[E - \mathcal{U}_0(\mathbf{R})]\} \chi_0(\mathbf{R}) \\ = \{\mathcal{U}_{0\nu}(\mathbf{R}) + 2\mu\mathcal{V}_{0\nu}(\mathbf{R})\} G_{\nu}(\mathbf{R}), \quad (2.36a)$$

$$\{\nabla_{\mathbf{R}}^2 + 2\mu[E - \mathcal{V}_{\nu}(\mathbf{R})]\} G_{\nu}(\mathbf{R}) \\ = \{\mathcal{U}_{\nu 0}(\mathbf{R}) - C_{\nu 0}(\mathbf{R}, \nabla_{\mathbf{R}})\} \chi_0(\mathbf{R}) \quad (2.36b)$$

with

$$\mathcal{U}_0(\mathbf{R}) = \mathcal{E}_i(\mathbf{R}) - (2\mu)^{-1} C_{ii}(\mathbf{R}, \nabla_{\mathbf{R}}), \\ \mathcal{U}_{\nu}(\mathbf{R}) = \langle f, \nu | H_e | f, \nu \rangle, \\ \mathcal{U}_{0\nu}(\mathbf{R}) = \langle i, 0 | H_e | f, \nu \rangle, \\ \mathcal{U}_{\nu 0}(\mathbf{R}) = -\Delta_{0\nu}(\mathbf{R}) [2\mu E + \nabla_{\mathbf{R}}^2], \\ \mathcal{V}_{\nu 0}(\mathbf{R}) = \Delta_{0\nu}^* \{2\mu[\mathcal{E}_i(\mathbf{R}) - E] - \nabla_{\mathbf{R}}^2\}, \\ C_{ii}(\mathbf{R}, \nabla_{\mathbf{R}}) = 2\langle \Psi_i | \langle \nabla_{\mathbf{R}} \Psi_i \rangle \cdot \nabla_{\mathbf{R}} + \langle \Psi_i | (\nabla_{\mathbf{R}}^2 \Psi_i) \rangle, \quad (2.37)$$

where the C_{ij} 's are the Born-Oppenheimer coupling terms between the electronic and nuclear motions.

The important thing to notice in Eqs. (2.36) is that the coupling potentials contain the nonadiabatic terms which are also contained in the coupled equations derived from the expansion method.¹ Examining Eq. (2.36b) we notice that if the overlapping between the electronic states is small, i.e., $\Delta_{0\nu}^* \approx 0$, the coupling potential responsible for transitions from $\chi_0(\mathbf{R})$ to $G_{\nu}(\mathbf{R})$

is solely due to those nonadiabatic coupling terms in the "static" approximation (i.e., $\mathcal{H} \cong \Pi H \Pi$).

We close this section with some remarks concerning the recoil factors in the rearranged channels. Since for most practical cases of interest the criterion $\kappa_f \nu \ll \lambda^{-1}$ is often satisfied for dissociative attachment because of the favorable mass ratio [see Eqs. (2.12) and (2.13)], the recoil in the rearranged channels may then be neglected. In this approximation we need not include in ΠT all the rearranged open channels, but only the desired ones because of the orthonormality properties of the atomic wave functions. We, thus, may want

$$\Pi T(\mathbf{r}, \mathbf{R}) = |i, 0\rangle \chi_0(\mathbf{R}) + |f, \nu\rangle G_{\nu}(\mathbf{R}) \quad (2.38)$$

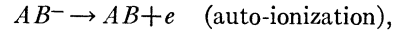
with

$$|f, \nu\rangle = \mathcal{A} \{ \phi_m(\mathbf{r}_a) \phi_{m'}(\mathbf{r}_b) \}. \quad (2.39)$$

From Eqs. (2.29) and (2.33), we obtain immediately the simple expression [Eq. (2.35)] for the projection operator and the corresponding pair of coupled equations.

III. RESONANCE DISSOCIATIVE ATTACHMENT

The negative ion AB^- which acts as an intermediate for the process of dissociative attachment (Fig. 1) may in some cases be unstable with respect to the configuration of the incident electron. Once the reacting system is localized into this state, two competitive processes



may take place within the nuclear configuration $R \leq R_c$ (Fig. 3). The attachment process is then complicated by the possibilities of auto-ionization of the intermediate AB^- , thus leaving the system to decay back to various possible nuclear states of Ψ_i and populating nuclear excitation of AB molecule. Here we show how the situation may be accounted for by the projection-operator techniques discussed in Sec. II. For simplicity we confine our discussions to cases where at a given energy region only one compound negative ion state is of importance for dissociative attachment (i.e., isolated resonance).

We start with our discussion from the total electronic Hamiltonian Eq. (2.5) for a fixed nuclear configuration and consider the case illustrated in Fig. 3 in which only the elastic and the lowest rearranged channels are open. Thus,

$$H_e \Psi_i = \mathcal{E}_i(\mathbf{R}) \Psi_i = [\epsilon_0(\mathbf{R}) + \frac{1}{2} k_i^2] \Psi_i. \quad (3.1)$$

Following Feshbach's treatment of resonance,⁷ we construct a projection operator P such that

$$P \Psi_i(\mathbf{r}, \mathbf{R}) = \mathcal{A} \{ \Psi_0(\mathbf{r}_1 \cdots \mathbf{r}_{N_0} \mathbf{R}) F_0(\mathbf{r}_0) \} \quad R \leq R_c, \quad (3.2)$$

$$P \Psi_i(\mathbf{r}, \mathbf{R}) = \Psi_i(\mathbf{r}, \mathbf{R}) \quad R \geq R_c, \quad (3.3)$$

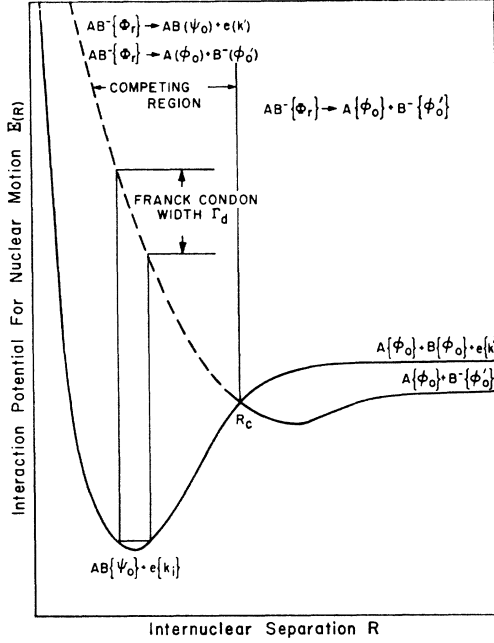


FIG. 3. Schematic diagram of interaction potentials for resonance dissociative attachment.

where \mathcal{Q} is the antisymmetrization operator operating only on electrons. The choice in Eq. (3.3) is made in order to account for the fact that after the crossing point R_c of the potential curves the negative ion state is no longer unstable with respect to the electronic configuration of the incident electron, so no auto-ionization may take place.

Solving the electronic Schrödinger equation (3.1) in terms of $Q=1-P$, we obtain

$$\{\mathcal{H}_e - \mathcal{E}_i(\mathbf{R})\}P\Psi_i = 0, \quad (3.4)$$

with

$$\mathcal{H}_e = P\{H_e + H_e Q(\mathcal{E}_i(\mathbf{R}) - QH_e Q)^{-1}QH_e\}P, \quad (3.5)$$

where \mathcal{H}_e is the effective electronic Hamiltonian for a fixed nuclear configuration. For nuclear configurations lying outside of the crossing point R_c , i.e. $R \geq R_c$, the effective electronic Hamiltonian \mathcal{H}_e reduces to H_e and $P\Psi_i$ to Ψ_i , since $P=1$ and $Q=0$. Thus, Eq. (3.4) reduces to Eq. (3.1) for $R \geq R_c$. For isolated resonance, Eq. (3.4) may be written as

$$\begin{aligned} &(\mathcal{E}_i(\mathbf{R}) - \mathcal{H}_e)P\Psi_i \\ &= P[H_e Q\Phi_r](\mathcal{E}_i(\mathbf{R}) - \mathcal{E}_r(\mathbf{R}))^{-1}\langle\Phi_r|QH_e\rangle P\Psi_i, \end{aligned} \quad (3.6)$$

with

$$\begin{aligned} \mathcal{H}_e' &= \mathcal{H}_e - P[H_e Q\Phi_r](\mathcal{E}_i(\mathbf{R}) - \mathcal{E}_r(\mathbf{R}))^{-1} \\ &\quad \times \langle\Phi_r|QH_e\rangle P\Psi_i, \end{aligned} \quad (3.7)$$

where Φ_r is the quasistationary representation of the auto-ionization state of AB^- and is obtained by solving the stationary state of the projected Hamiltonian $QH_e Q$.

$$(\mathcal{E}_r(\mathbf{R}) - QH_e Q)\Phi_r = 0. \quad (3.8)$$

The eigenvalue $\mathcal{E}_r(\mathbf{R})$ so obtained approximates the position of resonance. The shift in energy between $\mathcal{E}_r(\mathbf{R})$, and the exact resonance comes from the neglected coupling with the continuum in Eq. (3.8).

Equation (3.6) which contains the coupling can be solved exactly for isolated resonance yielding

$$\begin{aligned} P\Psi_i &= P\Psi_i^{(+)} \\ &\quad + (\mathcal{E}_i(\mathbf{R}) - \mathcal{H}_e' + i\eta)^{-1}\Lambda_r(\mathbf{R})PH_e Q|\Phi_r\rangle, \end{aligned} \quad (3.9)$$

with

$$(\mathcal{E}_i(\mathbf{R}) - \mathcal{H}_e')P\Psi_i^{(+)} = 0, \quad (3.10)$$

$$\begin{aligned} \Lambda_r(\mathbf{R}) &= \langle\Phi_r|QH_e P|\Psi_i^{(+)}\rangle/(\mathcal{E}_i(\mathbf{R}) - \mathcal{E}_r(\mathbf{R})) \\ &\quad - \langle\Phi_r|QH_e P[\mathcal{E}_i(\mathbf{R}) - \mathcal{H}_e' + i\eta]^{-1}PH_e Q\Phi_r\rangle, \end{aligned} \quad (3.11)$$

where $\Lambda(\mathbf{R})$ is the capture probability of the electron into the quasistationary state Φ_r . By defining the following quantities

$$\Delta_r(\mathbf{R}) = \langle\Phi_r|QH_e P\mathcal{O}(\mathcal{E}_i(\mathbf{R}) - \mathcal{H}_e')^{-1}PH_e Q\Phi_r\rangle, \quad (3.12)$$

$$\Gamma_r(\mathbf{R}) = 2\pi \int |\gamma_r(R)|^2 \zeta d\Omega_f, \quad (3.13)$$

$$\gamma_r(\mathbf{R}) = \langle\Phi_r|QH_e P|\Psi_i^{(+)}\rangle, \quad (3.14)$$

the capture probability may be rewritten as

$$\begin{aligned} \Lambda_r(\mathbf{R}) &= \gamma_r(\mathbf{R})/ \\ &\quad [\mathcal{E}_i(\mathbf{R}) - \mathcal{E}_r(\mathbf{R}) - \Delta_r(\mathbf{R}) + (i/2)\Gamma_r(\mathbf{R})], \end{aligned} \quad (3.15)$$

where $\Delta_r(\mathbf{R})$ is the energy shift in the position of resonance as approximated by $\mathcal{E}_r(\mathbf{R})$, the symbol \mathcal{O} is introduced to indicate that a principal value is to be taken when integrating across the singularity, $\Gamma_r(\mathbf{R})$ is the half-width of the resonance and $\gamma_r(\mathbf{R})$ is the partial capture width. In the expression for Γ_r , we have chosen to make the integration over the possible final angle Ω_f with ζ as the density of states.

It can be easily shown that $P\Psi_i$ asymptotically satisfies the boundary condition (2.8). A description of resonance dissociative attachment in terms of a pair of coupled equations can now be found by a straightforward application of the formalism described in Sec. II. We construct Π such that

$$\Pi T(\mathbf{r}, \mathbf{R}) = |P\Psi_i\rangle\chi_0(\mathbf{R}) + |f, \nu\rangle G_\nu(\mathbf{R}), \quad (3.16)$$

where $|f, \nu\rangle$ is defined by Eq. (2.15). This leads to the pair of coupled-equation description

$$\{E - \langle P\Psi_i|\mathcal{H}_e|P\Psi_i\rangle\}\chi_0(\mathbf{R}) = \langle P\Psi_i|\mathcal{H}_e - E|f, \nu\rangle G_\nu(\mathbf{R}), \quad (3.17a)$$

$$\{E - \langle f, \nu|\mathcal{H}_e|f, \nu\rangle\}G_\nu(\mathbf{R}) = \langle f, \nu|\mathcal{H}_e - E|P\Psi_i\rangle\chi_0(\mathbf{R}). \quad (3.17b)$$

The amplitude for dissociative attachment $g_\nu(\hat{k}_i, \hat{R})$ is then given by

$$g_\nu(\hat{k}_i, \hat{R}) = -(4\pi)^{-1}\langle G_\nu^{(0)}(\mathbf{R})|\mathcal{T}_e(\mathbf{R})|\chi_0(\mathbf{R})\rangle \quad (3.18)$$

with

$$\mathcal{T}_e(\mathbf{R}) = 2\mu\langle f, \nu|\mathcal{H}_e - E|P\Psi_i\rangle, \quad (3.19)$$

where $G_{\nu}^{(0)}(\mathbf{R})$ is the solution of the homogeneous part of Eq. (3.17b) and $\mathcal{T}_e(\mathbf{R})$ defined by Eq. (3.19) can be interpreted as the effective electronic transition matrix for a fixed nuclear configuration.

To examine \mathcal{T}_e qualitatively we make the "static" approximation $\mathcal{H}\mathcal{C}\cong\Pi H\Pi$. Equation (3.19) then reduces to

$$\mathcal{T}_e(\mathbf{R}) = B(\mathbf{R}) + \mathbf{A}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} \quad (3.20)$$

with

$$\mathbf{B}(\mathbf{R}) = \langle f, \nu | \mathcal{U}_e | P\Psi_i \rangle - \langle f, \nu | (\nabla_{\mathbf{R}}^2 P\Psi_i) \rangle, \quad (3.21)$$

$$\mathbf{A}(\mathbf{R}) = -2 \langle f, \nu | (\nabla_{\mathbf{R}} P\Psi_i) \rangle, \quad (3.22)$$

where the potential \mathcal{U}_e responsible for adiabatic electronic transition is defined in terms of $P\Psi_i$ and $\chi_0(\mathbf{R})$

$$[2\mu(H_e - E) - \mathcal{U}_e] P\Psi_i \chi_0(\mathbf{R}) = P\Psi_i (\nabla_{\mathbf{R}}^2 \chi_0(\mathbf{R})). \quad (3.23)$$

Again we observe the nonadiabatic coupling terms appearing in the transition matrix. Now if we assume that the electronic matrices are primarily determined at $\mathbf{R} = \mathbf{R}_e$, the equilibrium nuclear configuration of the ground target state, we obtained for dissociative-attachment amplitude the familiar expression

$$g_{\nu}(\hat{k}_0, \hat{R}) = -(4\pi)^{-1} \{ \mathbf{B}(\mathbf{R}_e) \langle G_{\nu}^{(0)}(\mathbf{R}) | \chi_0(\mathbf{R}) \rangle + \mathbf{A}(\mathbf{R}_e) \cdot \langle G_{\nu}^{(0)}(\mathbf{R}) | \nabla_{\mathbf{R}} \chi_0(\mathbf{R}) \rangle \}. \quad (3.24)$$

IV. APPLICATION TO THE ELECTRON-HYDROGEN SYSTEM

Calculation of the cross sections for dissociative attachment in the (e, H_2) system has been carried out using the expansion method.¹ This calculation was, however, overshadowed by the lack of accurate information concerning the intermediate state of H_2^- . After investigating all the available calculations in the literature for the ${}^2\Sigma_{\mu}^+$ state of H_2^- which was assumed to be responsible for the lowest resonance dissociative-attachment peak of the cross section in the (e, H_2) system,^{9a} it was suggested that the third electron in the ${}^2\Sigma_{\mu}^+$ state of H_2^- is not stationary at small nuclear configurations.¹⁰ This then violates the assumption of the distorted-wave approximation used to approximate the expansion method, since the neglected back coupling which accounts for the auto-ionization must now be treated explicitly by solving the coupled equations.

In order to account for the observation that the intermediate ${}^2\Sigma_{\mu}^+$ state of H_2^- for the dissociation attachment is a resonance state, Bardsley, Herzenberg, and Mandl² have later treated the problem in the adiabatic approximation using the Kapur-Peierls reso-

nance formalism. No calculation was reported in this treatment.¹¹ It can be shown however that their expression is equivalent to the "static" approximation equation (3.24) with the nonadiabatic terms and the recoil in the rearranged channel neglected. Unfortunately, a complete calculation using formulas derived in Sec. III for resonance dissociative attachment is not yet practical at the present stage. The difficulty still lies in the calculation of the resonance state Φ_r appearing in the expression for $P\Psi_i$ [Eqs. (3.9) and (3.11)].

We start our discussion with the amplitude for dissociative attachment $g_{\nu}(\hat{k}_i, \hat{R})$ [Eq. (3.18)] in the "static" approximation $\mathcal{H}\mathcal{C}\cong\Pi H\Pi$. Substituting $P\Psi_i$ from Eq. (3.9) for a fixed nuclear configuration into \mathcal{T}_e , we may separate the electronic transition matrix into two terms

$$\mathcal{T}_e(\mathbf{R}) = \mathcal{T}_e^{(d)}(\mathbf{R}) + \mathcal{T}_e^{(r)}(\mathbf{R}). \quad (4.1)$$

The first term is simply the contribution due to direct potential scattering (including the broad potential resonance)

$$\mathcal{T}_e^{(d)}(\mathbf{R}) = \langle f, \nu | \mathcal{U}_e | P\Psi_i^{(+)} \rangle - \langle f, \nu | (\nabla_{\mathbf{R}}^2 P\Psi_i^{(+)}) \rangle - 2 \langle f, \nu | (\nabla_{\mathbf{R}} P\Psi_i^{(+)}) \rangle, \quad (4.2)$$

and the second term is the resonance electronic transition. We have for the latter term

$$\begin{aligned} \mathcal{T}_e^{(r)}(\mathbf{R}) = & \Lambda_r(\mathbf{R}) \langle f, \nu | \mathcal{U}_e (1/a) P H_e Q | \Phi_r \rangle \\ & - 2 \Lambda_r(\mathbf{R}) \langle f, \nu | (\nabla_{\mathbf{R}} (1/a) P H_e Q \Phi_r) \rangle \cdot \nabla_{\mathbf{R}} \\ & - 2 (\nabla_{\mathbf{R}} \Lambda_r(\mathbf{R})) \langle f, \nu | (1/a) P H_e Q | \Phi_r \rangle \cdot \nabla_{\mathbf{R}}, \end{aligned} \quad (4.3)$$

with

$$a^{-1} = (\mathcal{E}(\mathbf{R}) - \mathcal{H}_e' + i\eta)^{-1}, \quad (4.4)$$

where we have dropped the term involving $(\nabla_{\mathbf{R}}^2 P\Psi_i)$ in Eq. (4.3) because of its smallness in comparison with $\mathbf{A}(\mathbf{R}) \cdot \nabla_{\mathbf{R}}$.

It is not difficult to see that the direct transition matrix of the Born-type $\mathcal{T}_e^{(d)}$ is much smaller than the resonance transition matrix $\mathcal{T}_e^{(r)}$ in the region of the resonance energy, so that $\mathcal{T}_e^{(d)}$ can be neglected in this energy region. The cross section σ corresponding to resonance dissociative attachment is then given by

$$\sigma = \frac{1}{k_i} \int \left| \frac{1}{4\pi} \langle G_{\nu}^{(0)}(\mathbf{R}) | \mathcal{T}_e^{(r)}(\mathbf{R}) | \chi_0(\mathbf{R}) \rangle \right|^2 d(\hat{k}_i, \hat{R}), \quad (4.5)$$

where we have chosen to normalize $G_{\nu}^{(0)}$ in the $\kappa_{f\nu}$ scale, so that the wave number $\kappa_{f\nu}$ for the relative motion of

^{9a} Note added in proof. Recently a paper on measurement of H⁻ formation in the (e, H_2) system has appeared [G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965)] which reports that the lowest resonance dissociative attachment peak appears at about 3.75 eV very close to the theoretical threshold for H⁻ formation.

¹⁰ For a discussion, see footnotes 31 and 32 of Ref. 1, and H. S. Taylor and F. E. Harris, J. Chem. Phys. **39**, 1012 (1963).

¹¹ A single configuration calculation for the resonance state of H_2^- were recently presented by Bardsley, Herzenberg, and Mandl at the 1Vth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, August 1965. At the same conference the treatment of Bardsley *et al.* was discussed by T. F. O'Malley in terms of Feshbach's resonance formalism. See *Abstracts of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec 1965* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965).

the two nuclei in the final state is included in $G_v^{(0)}$. The three terms appearing in the expression for $\mathcal{T}_e^{(r)}$ [Eq. (4.3)] have simple physical interpretations. The first term gives, in the adiabatic sense, the product of probability of capturing the incident electron into the Φ_r state of H_2^- [i.e., $\Lambda_r(R)$] and the matrix element for propagating from the Φ_r state into the desired final state via a propagator a^{-1} . The second and third are the nonadiabatic terms which account for the coupling between the electronic and nuclear motions in the rearrangement collision process.

When the colliding system is localized into the resonance state Φ_r , dissociation of AB^- may take place with an acceleration depending on the steepness of the repulsive potential generated by Φ_r in the Franck-Condon region. This gives rise to a resonance peak in the cross section which is closely related to the broadness of the Franck-Condon region and to the steepness of the repulsive potential in this region. We refer to the width of such a resonance as the Franck-Condon width Γ_d (see also Figs. 1 and 3). The dissociative process is, however, damped because Φ_r is coupled with continuum states having a resonance width for auto-ionization. This results in a reduction in the magnitude of the cross section and constitutes a possible explanation of why the dissociative-attachment cross section for the (e, H_2) [Fig. 4] system is much smaller than for other systems.

Now we compare the present formalism with that of Bardsley *et al.*² and O'Malley.¹¹ If we neglect the nonadiabatic terms and the recoil effects in $\mathcal{T}_e^{(r)}$, and make the angular decomposition of the nuclear wave functions of Σ state

$$G_v^{(0)}(\mathbf{R}) = \sum_{l,m} \frac{1}{R} g_{vlm}^{(0)}(R) Y_l^m(\hat{R}), \quad (4.6)$$

$$\chi_0(\mathbf{R}) = \sum_{l,m} \frac{1}{R} X_{0lm}(R) Y_l^m(\hat{R}), \quad (4.7)$$

we obtain from Eq. (4.5) the adiabatic cross section

$$\sigma_a \cong \sigma_{el}(R_e) \left| \int g_v^{(0)*}(R) X_0(R) dR \right|^2, \quad (4.8)$$

$$\sigma_{el}(R_e) = \frac{1}{k_i} \int \left| \frac{1}{4\pi} \times \sum_{\substack{l,l' \\ m,m'}} c \langle Y_l^m(\hat{R}) | \mathcal{T}_e^{(r)}(\mathbf{R}) | Y_{l',m'}(\hat{R}) \rangle \right|^2 \times d(\hat{k}_i, \hat{R}), \quad (4.9)$$

$$\mathcal{T}_e^{(r)}(\mathbf{R}) \cong \Lambda_r(\mathbf{R}) \langle f, \nu | \mathcal{U}_e(1/a) PH_e Q | \Phi_r \rangle, \quad (4.10)$$

where we have taken $\sigma_{el}(R)$ outside of the R integral assuming that the electronic matrix are primarily

determined at the equilibrium nuclear separation R_e of the initial nuclear target state. The cross section should then be averaged over the initial distribution of the rotational states l_0 according to the experimental conditions. Equation (4.8) has the familiar interpretation: $\sigma_{el}(R_e)$ is the electronic cross section for the process of dissociative attachment averaged over the nuclear rotational states and the second factor is simply the nuclear overlap integral. The electronic cross sections constitute two factors [see Eq. (4.10)]; one gives the probability of capture of the electron into the compound state, and the other gives the matrix element for propagating from the compound state to the desired final electronic state via a propagator a^{-1} . Now, if we assume that the distortion effects on the nuclear wave function χ_0 due to the field $\langle P\Psi_i | H_e | P\Psi_i \rangle$ (Eq. 3.17a) is negligible so that χ_0 may be approximated by the initial nuclear target state, then we obtain the expression derived by O'Malley using delta-function approximation¹² for the continuum nuclear wave function $g_v^{(0)}(R)$. This assumption for χ_0 is, however, not desirable, since the nuclear state χ_0 associated with the electronic state $P\Psi_i$ is strongly distorted as the electronic system going through a resonance.

The similarity between the present approach with that of Bardsley *et al.*² is however not as apparent. The reason for this comes from the differences in the definition of the electronic compound states. In the present approach, the compound states are defined as bound states in the excited field of the target molecule. This permits us to remove the energy dependence from the resonance energy \mathcal{E}_r . Instead, the energy dependence is carried in the Hamiltonian \mathcal{H}_e' [Eq. (3.7)]. In the approach of Bardsley *et al.*, the electronic configuration space is divided into two regions and the resonant states are then defined as solutions of the electronic Schrödinger equation in the internal region with homogeneous boundary conditions at the joining radius. This then leads to complex eigenvalues for the resonant states with energy-dependent boundary condition.

These two approaches are of course completely equivalent in their exact forms.⁷ This can be demonstrated as follows. If we eliminate the open channels in the absence of any incident wave, we obtain from Eq. (3.1) an effective electron Hamiltonian \mathcal{H}_e'' for the closed channels

$$(E - \mathcal{H}_e'') Q \Psi = Q H P \Psi^{(+)} \quad (4.11)$$

with

$$\mathcal{H}_e'' = Q \{ H_e + H_e P (E - P H_e P + i\eta)^{-1} P H_e \} Q, \quad (4.12)$$

$$(E - P H_e P) P \Psi^{(+)} = 0. \quad (4.13)$$

The solutions ξ_i of the effective electron Hamiltonian \mathcal{H}_e'' [Eq. (4.12)],

$$(\mathcal{H}_e'' - W_i) \xi_i = 0 \quad (4.14)$$

¹² E. U. Condon, Phys. Rev. **32**, 858 (1928); J. G. Winans and E. C. G. Stueckelberg, Proc. Natl. Acad. Sci. U.S.A. **14**, 867 (1928).

form a biorthogonal set. The eigenvalues W_i are complex whose imaginary part $\text{Im}W_i$ is

$$\text{Im}W_i = -\pi |\langle \psi^{(-)} | PH_e Q | \xi_i \rangle|^2 < 0. \quad (4.15)$$

This demonstrates that the functions ξ_i which are derived using the present approach are the Kapur-Peierls type resonance states.

Now instead of Eq. (3.9), we may express the scattering states $P\Psi_i$ in terms of the Kapur-Peierls state ξ_i

$$P\Psi_i = (E - PH_e P + i\eta)^{-1} PH_e Q \xi_i, \quad (4.16)$$

where $P\Psi_i$ contains no incident wave and satisfies the Kapur-Peierls type of boundary condition. This then permits us to derive complex potentials for the nuclear wave function χ_0 associated with $P\Psi_i$, and to derive the results of Bardsley *et al.* without evoking the concept of channel radius. It should be noted that the electromagnetic interactions present in the molecular system are of the long-range nature. Thus the treatment of Bardsley *et al.* on resonant states with a joining radius outside of which the interaction of the electron with the molecule is neglected is probably not as accurate. This may become even more critical for dissociative recombination. The importance of the long-range nature of the interaction potential which support the projectile electron in forming compound states has been demonstrated by Gailitis and Damburg.¹³

Returning now to Eq. (3.20) and examining the adiabatic electronic transition matrix $\langle f, \nu | \mathcal{U}_e | P\Psi_i \rangle$, we obtain with the help of Eq. (3.23) the approximation

$$\langle f, \nu | \mathcal{U}_e | P\Psi_i \rangle \cong \langle f, \nu | P\Psi_i \rangle \{ 2\mu(\mathcal{E}_i(\mathbf{R}) - E) - \nabla_R^2 \} + 2\mu \langle f, \nu | QH_e P | P\Psi_i \rangle. \quad (4.17)$$

¹³ M. Gailitis and R. Damburg, Proc. Phys. Soc. (London) **82**, 192 (1963).

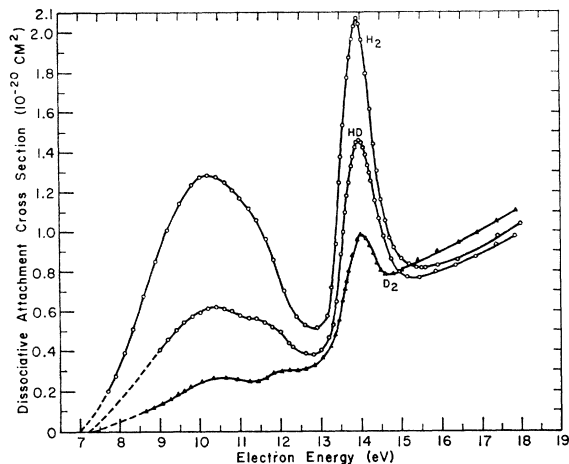


FIG. 4. The energy dependence of the total cross section for dissociative attachment of electrons in H_2 , HD , and D_2 as observed by Rapp, Sharp, and Briglia [Ref. 3].

This result is consistent with the coupling potentials derived in Eq. (2.36b). Thus again we notice that the magnitude of the adiabatic electronic transition matrix is linearly dependent on the overlapping integral $\langle f, \nu | P\Psi_i \rangle$, assuming the exchange integral is small. For the case where the electronic states $|f, \nu\rangle$ and $|P\Psi_i\rangle$ are almost orthogonal, the nonadiabatic terms in the electronic transition matrix may become the dominating terms.

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