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by

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DISSOCIATIVE ATTACHMENT IN REARRANGEMENT ELECTRON COLLISION WITH MOLECULES

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ABSTRACT

The expansion method proposed for treating dissociative attachment in rearrangement electron collision with molecules is examined. It is shown that this method is useful only when the recoils in the rearranged channels can be neglected and when the intermediate negative ion states are stationary states. The latter limitation prevents the method from giving an adequate description of resonance dissociative attachment, since in this case the intermediate states are compound states with decaying widths. To account for these difficulties an alternative method is proposed. In this method, a projection operator is derived which is capable of decoupling the elastic channel and all the rearranged open-channels from the rest of the Hilbert space. This then leads to an exact description of the process by a finite set of coupled equations.

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Specialization of this method to account for resonance dissociative attachment is also carried out. It is then shown how the observed isotope effect for dissociative attachment in the electron-hydrogen system can be understood in terms of the present theory.

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 observed\(^3\) in the electron-hydrogen system for such dissociative attachment processes is most striking, and theoretical explanation of this observation is lacking. Although the proposal expansion method\(^1\) does provide us with mass-dependent interaction responsible for dissociative attachment processes, the approach is however not rigorously justifiable for the \((e,\text{H}_2)\) system, since for this system the intermediate electronic state is a resonance state (i.e., an autoionization state having a decaying width) so that it does not belong to the complete set used in the expansion. The adiabatic treatment later proposed\(^2\) using the Kapur-Peierls resonance formalism\(^5\) does not give a clear picture of the isotope effects.

The purpose of this paper is to present an exact formalism for dissociative attachment processes and to explain the pronounced isotope effect recently observed.

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 predisassociation) 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 recombinations in rearrangement electron collision with molecular ions whenever it is appropriate.

The plan of the paper is as follows: In Section II, the expansion method proposed for treating dissociative attachment is examined. It is shown that this method is useful only when the recoils in the rearranged channels can be neglected and when the intermediate negative ion states are stationary states. To account for these difficulties an alternative method is proposed in Section III. 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. 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 Section IV. The electronic scattering state involving
resonance is solved for a fixed nuclear configuration, using Feshbach's
treatment \(^7\) for resonance. We then construct the projection operator in
terms of the scattering state by a straightforward application of the method
derived in Section III. Finally in Section V, application of the formalism
to the electron-hydrogen system is carried out to explain the observed large
isotope effect.

II. THE EXPANSION METHOD

The Schrodinger equation for a system of \( N \) electrons and two
heavy nuclei \( a \) and \( b \) in the relative coordinates with the electron
coordinates referring to the center of mass of the nuclei is (in atomic units)

\[
\hbar \mathbf{T} = E \mathbf{T} = \left( -\frac{1}{2\mu} \nabla_R^2 + H_e \right) \mathbf{T}
\]

\[ (2.1) \]

with

\[
H_e (\mathbf{r}, \mathbf{R}) = \frac{1 + M_a + M_b}{2(M_a + M_b)} \sum_{i=1}^{N} \nabla_i^2 + V(\mathbf{r}, \mathbf{R})
\]

\[ (2.2) \]
\[ u = \frac{M_a M_b}{M_a + M_b} \quad (2.1) \]

where \( \nabla^2 \) is the Laplacian operator, \( V \) is the total potential energy, \( \mathbf{R} \) is the vector from \( b \) to \( a \), \( M_a \) and \( M_b \) are the masses of nuclei \( a \) and \( b \) respectively, and the cross terms \( \nabla_i \cdot \nabla_j \) which should appear in Eq. (2.2) for electrons are neglected. The total electronic Hamiltonian \( H_e \) for the incident electron and for the \( N_o \) molecular electrons has a set of antisymmetric eigenfunctions \( \psi_j(r, \mathbf{R}) \) for each fixed nuclear configuration \( \mathbf{R} \):

\[ H_e \psi_j(r, \mathbf{R}) = E_j(\mathbf{R}) \psi_j(r, \mathbf{R}) \quad (2.4) \]

where \( r = (r_0, r_1, \ldots, r_{N_o}) \) and \( j \) labels possible states of the \( N = N_o + 1 \) electron system. Thus, when the incident electron is not bound to the molecule, then \( j = (k_j, n) \) where \( k_j \)'s denote the wave numbers of the electron in the continuum and \( n \)'s label the residue bound electronic states.

Utilizing the fact that the \( \psi_j \)'s form a complete set in the space of electronic variables, the total wave function \( \chi(r, \mathbf{R}) \) may be then expanded in terms of them:

\[ \chi(r, \mathbf{R}) = \sum_j \int x_j(r) \psi_j(r, \mathbf{R}) \quad (2.5) \]

Substituting this expansion into Eq. (2.1) and forming matrix elements in the electronic variables, we obtain the following set of coupled equations...
for the expansion coefficients:

\[
\{ \frac{\nabla^2}{R} + 2v[E - V_j(R)] \} \chi_j(R) = - \sum_{j', j} C_{jj'}(R, \nu, R) \chi_{j'}(R) \tag{2.6}
\]

with

\[
V_j(R) = \varepsilon_j(R) + C_{jj}(R, \nu, R) \tag{2.7}
\]

\[
C_{jj'}(R, \nu, R) = 2A_{jj'}(R) \cdot V_{R} + B_{jj'}(R) \tag{2.8}
\]

\[
A_{jj'}(R) = \langle \psi_j(R, R) | \psi_{j'}(R, R) \rangle \tag{2.9}
\]

\[
B_{jj'}(R) = \langle \psi_j(R, R) | \psi_{j'}(R, R) \rangle \tag{2.10}
\]

where \( E \) is the total energy, \( V_j \) is the effective potential energy for nuclear motion, and the \( C_{jj} \)'s are the Born-Oppenheimer coupling terms.

In principle Eq. (2.6) is exact and would provide us with all the desired information.

For dissociative electron attachment by molecules \( AB + e \rightarrow A + B^- \), we want to solve \( \mathcal{T} \) for the asymptotic boundary conditions

\[
\mathcal{T}(\xi, R) \xrightarrow{R \rightarrow \infty} \sum_{\alpha=0}^{\infty} \psi_{\alpha}(r_1, \cdots, r_n) \chi_{\alpha}(R) \left[ \delta_{\alpha_0} e^{i k_1 \cdot R_0} + f_{\alpha} e^{i k_1 \cdot k_1} \right] \tag{2.11}
\]

\[
\mathcal{T}(\xi, R) \xrightarrow{R \rightarrow \infty} \sum_{\nu=(m, m')} \phi_{\nu}(r_a) \phi_{\nu}^*(r_b) \chi_{\nu}(r_i) \frac{e^{i k_1 \cdot r_0}}{r_0} \tag{2.12}
\]
where $\psi_n$, $\phi_m$ and $\phi'_m$ are the electronic wave functions for molecule $AB$, atoms $A$ and $B^-$ respectively, $\chi_{nv}(R)$ is the nuclear wave for $AB$, $f_n$ and $g_v$ are the scattered and rearranged amplitudes, $\rho$ is the distance between mass centers of $A$ and $B^-$, and finally the summations are summed over all the scattered and rearranged open channels.

We show here that the expansion method in practice does not yield the exact rearranged amplitudes. For simplicity, we confine the discussion to situations in which only the elastic and the lowest rearranged channels are open; then the summations in Eqs. (2.11) and (2.12) each reduce to one term. The rearranged asymptotic expression becomes

$$i'(\mathbf{r}, \mathbf{R}) \xrightarrow{R \to \infty} \phi_o(\mathbf{r}_a) \phi'_o(\mathbf{r}_b) g_o(\hat{k}_i, \rho) \frac{i^{N^0}}{\rho}.$$  \hspace{1cm} (2.13)

Let $\Psi_i(\mathbf{r}, \mathbf{R})$ and $\Psi_f(\mathbf{r}, \mathbf{R})$ which are eigenstates of Eq. (2.4) denote respectively the elastic scattering state $AB + e$ and a bound state $AB^-$ with unstable nuclear configuration within and near by the Franck-Condon region of $\Psi_i$ (Fig. 1). Once the reacting system is localized into the $\Psi_f$ state, dissociation $AB^- \rightarrow A + B^-$ may occur.

The expansion equation (2.5) may be truncated to two states, so that to an approximation we have

$$\chi(\mathbf{r}, \mathbf{R}) \xrightarrow{R \to \infty} \chi'_i(\mathbf{R}) \Psi_i(\mathbf{r}, \mathbf{R}) + \chi'_f(\mathbf{R}) \Psi_f(\mathbf{r}, \mathbf{R}) \hspace{1cm} ;$$  \hspace{1cm} (2.14)

and Eq. (2.6) reduces to
\[ \{ \psi_{i} \} (R) = -C_{i}^{f}(R, \psi_{i}) \psi_{i}^{*}(R) \quad \text{and} \quad \{ \psi_{f} \} (R) = -C_{f}^{i}(R, \psi_{f}) \psi_{f}^{*}(R) \]

In approximation Eq. (2.14), no difficulty arises for the scattered asymptotic expression since \( \psi_{f} \xrightarrow{R \to \infty} 0 \) and

\[ \psi_{i}(r, R) \xrightarrow{R \to \infty} \phi_{0}(r_{1}, \ldots, r_{N}) \left\{ e^{ik_{0}r_{0}} + f_{0}(k_{0}, r_{0}) e^{ik_{0}r_{0}} \right\} . \quad (2.16) \]

For the rearranged asymptotic expression, we find, however,

\[ \Phi(r, R) \xrightarrow{R \to \infty} \phi_{0}(r_{a}) \phi_{0}^{*}(r_{b}) g_{0}(k_{0}, \hat{r}) e^{ik_{0}r_{0}} . \quad (2.17) \]

Comparison of Eq. (2.17) with Eq. (2.13) reveals that \( \Phi(r, R) \) approximated by Eq. (2.14) is in the wrong asymptotic form.

The error involved in approximating the correct asymptotic expression [Eq. (2.13)] by that of Eq. (2.17) is however not serious for most practical purposes. To qualify this remark, we consider a one-electron model as illustrated in Fig. 2. We have

\[ \rho = R - \frac{1}{M_{b} + 1} R_{ob} . \quad (2.18) \]

Since \( \phi_{0}(r_{ob}) \) which appeared in Eq. (2.13) vanishes exponentially as its argument \( r_{ob} \) becomes large, we may write for large \( R \):
\[ \rho = |\rho| = R - \frac{1}{M_b + 1} \hat{R} \cdot \hat{r}_{ob} + O\left(\frac{1}{R}\right). \tag{2.19} \]

Substitution of (2.19) for \( \rho \) into (2.13) yields

\[ \Phi(r, R) e^{iK_{fo} \hat{R}} \Phi'(r, R) \{ \kappa_o(\hat{k}, R) e^{\frac{iK_{fo} \hat{R}}{R}} \} e^{i\lambda \hat{k} \cdot \hat{r}_{ob}} \tag{2.20} \]

with

\[ \kappa_{fo} = K_{fo} \hat{R}, \quad \lambda = 1/(M_b + 1) \tag{2.21} \]

Thus for cases in which the recoil factor \( \exp(i\lambda \hat{k} \cdot \hat{r}_{ob}) \) approaches unity in the rearranged channel, i.e.

\[ K_{fo} \ll \lambda^{-1} \tag{2.22} \]

Eq. (2.17) is an adequate approximation of the asymptotic expression [Eq. (2.13)]. This criterion [Eq. (2.22)] is satisfied for most incident electron energies of interest due to the favorable mass ratio \( 1/(M_b + 1) \).

The expansion method however suffers from another drawback in that it does not give a proper description of resonance dissociative attachment. In this case the intermediate state for \( AB^- \) is not a stationary state but a resonance state with a decay width; thus it does not belong to the complete set. To account for these difficulties, an exact coupled-equation description of dissociative attachment in rearrangement electron collision with molecules is presented in the next section.
III. COUPLED-EQUATION FORMALISM

The technique frequently used for describing rearrangement collision is to assume that the total wave function is a linear combination of the initial and final channels with unknown scattering and rearranged functions respectively in each. Thus, for dissociative attachment one may start with the approximation

$$\Psi (r, R) = \sum_{n_1, \ldots, n_N} \chi_{n_1, \ldots, n_N, 0} (r) \chi_{n_1, \ldots, n_N, 0} (R) F^{(o)}_{n_1, \ldots, n_N, 0} (r)$$

where

$$A \chi_{n_1, \ldots, n_N, 0} (r) \chi_{n_1, \ldots, n_N, 0} (R) G^{(e)}_{n_1, \ldots, n_N, 0} (r)$$

(3.1)

where $A$ is the antisymmetrization operator operating only on the atomic electrons. Equation (3.1) is then substituted into a variational expression which is made stationary by an appropriate choice of the two unknown functions, thus leading to a pair of coupled equations. These equations are then solved with the asymptotic boundary conditions inferred from Eqs. (2.11) and (2.12) for the two unknown functions.

Recently, Feshbach 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 $\Pi$ which can project out from the total wave function the two desired channels simultaneously has been demonstrated by Mittleman.
\[ \Pi \mathcal{Z}(r, R) = \{ \psi_n(r_1, \ldots, r_{N_0} R) \chi_{n_0}(R) \} F_{n_0}(r_0) + \sum \{ \phi_m(r_a) \phi'_m(r_b) \} G_{nm}(\varphi). \quad (3.2) \]

This then provides an exact description of the rearrangement collision by a pair of coupled equations. However, the projection operator \( \Pi \) 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 Mittleman\(^9\) 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 \( \Pi \) in terms of the elastic scattering channel which is assumed to be predetermined from the electronic Hamiltonian [Eq. (2.2)] for a fixed nuclear configuration. The resulting coupled equations that are obtained from this method provide solutions for the rearranged scattering channels.

In view of Eqs. (2.16) and (2.20), we introduce the notation

\[ |i, \sigma \rangle = \psi_i(r, R) \quad , \quad (3.3) \]
\[ |f,v\rangle = A_\beta \phi_m (\Sigma_a) \phi'_m (\Sigma_b) e^{i\lambda K_{f,m} \cdot r_b}, \ \nu = (m,m') \] (3.4)

where \( \lambda \) is the appropriate mass damping factor similar to that which appeared in Eq. (2.20), and \( \psi_i \) an antisymmetrized eigenstate of the total electronic Hamiltonian \( H_e \):

\[ H_e \psi_i (r,R) = \xi_i (R) \psi_i (r,R), \ \ i = (k,0) \] , (3.5)

\[ \xi_i (R) = \epsilon_o (R) + \frac{1}{2} k_i^2 \]

where \( \epsilon_o (R) \) is the electronic energy of the ground target state. The zero-point energy is set at the ground level of the nuclear state of the ground electronic target state. (We assume that the target is not initially excited.) Thus at the equilibrium internuclear separation \( R_e \), \( \xi_i (R_e) \) is equal to the total energy \( E \) of the system; and at any other \( R \), \( \xi_i (R) \) 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.

We want a projection operator such that

\[ \Pi \chi_{E,R} = |i,0 \rangle \chi_o (R) + \sum_{\nu=1}^{\nu_o} |f,v \rangle G_{\nu} (R) \] (3.6)

where \( \chi_o (R) \) is bounded in \( R \) and the \( G_{\nu} (R) \)'s have the boundary condition inferred from Eq. (2.20):
We emphasize that the 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. (3.6). The asymptotic boundary condition for $r \to \infty$ is satisfied by $\Pi \mathbf{T}$ due to $|i, o\rangle$ [Eq. (2.16)].

The projection operator defined by Eq. (3.6) must satisfy the following equations:

$$
\langle i, o \mid (1-\Pi) \mathbf{T} \rangle = 0 \quad ; \quad (3.8)
$$

$$
\langle f, \nu \mid (1-\Pi) \mathbf{T} \rangle = 0, \quad \nu = 1, 2, \ldots \nu_o \quad . \quad (3.9)
$$

Equations (3.8) and (3.9) are just statements that the asymptotic forms of $\Pi \mathbf{T}$ and $\mathbf{T}$ should coincide for the elastic channel and all the rearranged channels. By defining

$$
U_o(R) = \langle i, o \mid \mathbf{T} \rangle \quad , \quad (3.10)
$$

$$
V_{\nu}(R) = \langle f, \nu \mid \mathbf{T} \rangle \quad , \quad (3.11)
$$

$$
\Delta_{o, \nu}(R) = \langle i, o \mid f, \nu \rangle \quad , \quad (3.12)
$$

$$
\eta_{\nu, \nu'}(R) = \langle f, \nu \mid f, \nu' \rangle \quad , \quad (3.13)
$$
Eqs. (3.8) and (3.9) may be written as

\[ \chi_o(R) + \sum_{v=1}^{v'} \Delta_{ov}(R) G_v(R) = U_o(R) \]  \hspace{1cm} (3.14)

\[ \sum_{v'=1}^{v'} \eta_{vv'} G_{v'}(R) + \Delta^*_{ov}(R) \chi_o(R) = V_v(R) \]  \hspace{1cm} (3.15)

Functions \( \chi_o(R) \) and \( G_v(R) \) are now solved from Eqs. (3.14) and (3.15) in terms of matrix notations

\[ \chi_o(R) = (1 + \Delta \Delta^*) U_o - \Delta \Delta^* V \]  \hspace{1cm} (3.16)

\[ G_v(R) = D(\Delta^* U_o) \]  \hspace{1cm} (3.17)

where

\[ D = (\mathcal{R} - \Delta \Delta^*)^{-1} = (d_{vv'}) \]  \hspace{1cm} (3.18)

Now substituting Eqs. (3.16) and (3.17) into Eqs. (3.6) and using the definitions for \( U_o \) and the \( V_v \)'s [i.e., Eqs. (3.10) and (3.11)], we obtain

\[ \Pi = \delta(R,R')(|i,o\rangle[1 + \sum_{v=1}^{v'} \sum_{v'=1}^{v'} \Delta_{ov} d_{vv'} \Delta^*_{ov'}] \langle i,o | + \sum_{v=1}^{v'} \sum_{v'=1}^{v'} |f,v\rangle d_{vv'} \langle f,v'| - \sum_{v=1}^{v'} \sum_{v'=1}^{v'} |f,v\rangle d_{vv'} \Delta^*_{ov'} \langle i,o | - \sum_{v=1}^{v'} \sum_{v'=1}^{v'} |i,o\rangle \Delta_{ov} d_{vv'} \langle f,v|) \]  \hspace{1cm} (3.19)
It may easily be shown that $\Pi$ is Hermitian and idempotent $\Pi^2 = \Pi$, so that it is a projection operator.

Since $\Pi$ projects out from $\mathcal{T}$, the complete elastic channel, it then follows that $\Omega \mathcal{T}$ with $\Omega = 1 - \Pi$ does not contain any incident wave [Eq. (3.8)]. Thus, the Schrödinger equation (2.1) may be solved for $\Pi \mathcal{T}$ in terms of $\Omega$, yielding

$$ (E - \mathcal{H}) \Pi \mathcal{T} = 0 \quad (3.20) $$

with

$$ \mathcal{H} = \Pi \{ \mathcal{H} + \mathcal{H} \Omega \frac{1}{E - \Omega \Omega + i \eta} \Omega \mathcal{H} \} \Pi \quad (3.21) $$

where $\eta > 0^+$ is introduced because $\Pi$ does not include all the scattered open channels. From Eq. (3.20), the desired coupled equations are then obtained:

$$ \{E - \mathcal{H}_{oo}\} \chi_o(R) = \sum_v \{\mathcal{H}_{ov} - E\Delta_{ov}\} G_v(R), \quad (3.22a) $$

$$ \{E - \mathcal{H}_{vv}\} G_v(R) = \sum_{v', \neq v} \{\mathcal{H}_{vv'} - E_{vv'}\} G_{v'}(R) + \mathcal{H}_{vo} - E_{o}\} \chi_o(R) \quad (3.22b) $$

with

$$ \mathcal{H}_{oo} = \langle i, o | \mathcal{H} + \mathcal{H} \Omega \frac{1}{E - \Omega \Omega + i \eta} \Omega | i, o \rangle \quad (3.23) $$
\[ \Psi_\nu = \langle f, \nu | H + \frac{1}{E - \Omega \nu + i \eta} \Omega | f, \nu \rangle, \text{ etc.} \]  

(3.23)

where we have used the relation \( \Pi | i, o \rangle = | i, o \rangle \), and \( \Pi | f, \nu \rangle = | f, \nu \rangle \), for \( \nu = 1, \ldots, \nu_0 \).

For reacting systems where only the lowest rearranged channel \( \nu \) is open, we have for \( \Pi \) the simple expression from equation (3.19):

\[ \Pi = \frac{\delta(R-R')}{1-|\Delta_{ov}|^2} \left( |i, o\rangle \langle i, o| + |f, \nu\rangle \langle f, \nu| - \Delta_{ov} |i, o\rangle \langle f, \nu| - \Delta_{ov} |f, \nu\rangle \langle i, o| \right). \]  

(3.24)

The coupled Eqs. (3.22) then reduce to a pair of coupled equations. In order to discuss the nature of the coupling, we approximate \( \Psi_\nu \) by its first term \( \Pi \Pi \Pi \Pi \Pi \Pi \). The pair of coupled equations becomes

\[ \{v_R^2 + 2\mu[E - \nu_o(R)]\} \chi_o(R) = \{\mathcal{H}_{ov}(R) + 2\mu \mathcal{V}_{ov}(R)\} G_\nu(R), \]  

(3.25a)

\[ \{v_R^2 + 2\mu[E - \nu_o(R)]\} G_\nu(R) = \{\mathcal{V}_{vo}(R) - C_{vo}(R, v_R)\} \chi_o(R) \]  

(3.25b)

with

\[ \mathcal{V}_{vo}(R) = \mathcal{E}_i(R) - \frac{1}{2\mu} C_{ii}(R, v_R), \]

\[ \mathcal{V}_{\nu}(R) = \langle f, \nu | H_e | f, \nu \rangle, \]

\[ \mathcal{V}_{ov}(R) = \langle i, o | H_e | f, \nu \rangle \]  

(3.26)
\[ \mathcal{U}_{ov}(R) = - \Delta_{ov}(R) \{ 2 \mu E + \nabla^2_b \} \]

\[ \mathcal{V}_{vo}(R) = \Delta_{ov}^* \{ 2 \mu \mathcal{E}_1(R) - E \} - \nabla^2_b \]

where the \[ C_{ij} \] 's are defined by Eq. (2.8).

The important thing to notice in Eqs. (3.25) is that the coupling potentials contain the mass-dependent nonadiabatic terms which are also contained in the coupled equations derived from the expansion method (Section II). Examining Eq. (3.25b) we notice that if the overlapping between the electronic state is small, i.e. \[ \Delta_{ov}^* \sim 0 \], the coupling potential responsible for transitions from \[ \chi_0(R) \] to \[ \mathcal{G}_v(R) \] is solely due to those nonadiabatic coupling terms in the "static" approximation (i.e., \[ \mathcal{H} \sim \hat{H}\mathbf{W} \]). It would be of interest to see if the isotope effect observed for the dissociative attachment in the \( (e, \mathbf{H}_2) \) system is originated from these nonadiabatic coupling terms.

We close this section with some remarks concerning the recoil factors in the rearranged channels. Since for most practical cases of interest the criterion \[ K_{f_v} \ll \lambda^{-1} \] is often satisfied for dissociative attachment due to the favorable mass ratio, the recoil in the rearranged channels may then be neglected. In this approximation we need not include in \[ \mathbf{M} \] all the rearranged open channels, but only the desired ones because of the orthonormality properties of the atomic wave functions. Thus, we may want
\[ \mathcal{H}(r, R) = |i, o \rangle \chi_0(R) + |f, v \rangle G_v(R) \]  \hspace{1cm} (3.27)

with

\[ |f, v \rangle = \mathcal{A} \{ \phi_m(r_a) \phi'_m(r_b) \} \]  \hspace{1cm} (3.28)

From Eqs. (3.19) and (3.22) we obtain immediately the simple expression [Eq. (3.24)] for the projection operator and the corresponding pair of coupled equations.

IV. 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

\[ AB^- \rightarrow AB + e \quad \text{(autoionization)} \]

\[ AB^- \rightarrow A + B^- \quad \text{(dissociation)} \]

may take place within the nuclear configuration $R \leq R_c$ (Fig. 3). The attachment process is then complicated by the possibilities of autoionization of the intermediate $AB^-$, thus leaving the system to decay back to various
possible nuclear states of $\Psi_i$ and populating nuclear excitation of
AB molecule. Such an autoionization state is of course not a stationary
state, so the expansion method discussed in Section II does not rigorously
apply. Here we show how the situation may be accounted for by the projection-
operator techniques discussed in Section III. For simplicity we confine
our discussions to cases where only one such resonance negative ion state
is of importance for dissociative attachment (i.e., isolated resonance).

We start with our discussion from the total electronic Hamiltonian

$$H_e \Psi_i = \mathcal{E}_i(r) \Psi_i = (\varepsilon_0(R) + \frac{1}{2} k_i^2) \Psi_i.$$  \hspace{1cm} (4.1)

Following Feshbach's treatment of resonance, we construct a projection
operator $\mathcal{P}$ such that

$$\mathcal{P}^\dagger \Psi_i (r, R) = \mathcal{A}\{ \Psi_0 (r_1, ..., r_{N_0}, R) \mathcal{F}_0 (r_o) \} \quad R \leq R_c,$$ \hspace{1cm} (4.2)

$$\mathcal{P} \Psi_i (r, R) = \Psi_i (r, R) \quad R \geq R_c,$$ \hspace{1cm} (4.3)

where $\mathcal{A}$ is the antisymmetrization operator operating only on electrons.

The choice in Eq. (4.3) is made in order to account for the fact that after
the crossing point of the potential curve $R_c$, the negative ion state is no
longer unstable with respect to the electronic configuration of the incident
electron, so no autoionization may take place.

Solving the electronic Schrödinger equation (4.1) in terms of 

\[ Q = 1 - p, \]

we obtain

\[ (\hat{H}_e - \varepsilon_1(R)) \Psi_i = 0 \]  \hspace{1cm} (4.4)

with:

\[ \hat{H}_e = P \left( \frac{1}{\varepsilon_1(R) - Q \varepsilon_e} \right) P \hat{H} e \hspace{1cm} (4.5) \]

where \( \hat{H}_e \) 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 \( \hat{H}_e \) reduces to \( H_e \) and \( P \Psi_i \) to \( \Psi_i \), since \( p = 1 \) and \( Q = 0 \). Thus, Eq. (4.4) reduces to Eq. (4.1) for \( R \geq R_c \). For isolated resonance, Eq. (4.4) may be written as

\[ (\varepsilon_i(R) - \hat{H}_r) \Psi_i = P \frac{\varepsilon_1(R) - \varepsilon_r(R)}{\varepsilon_1(R) - \varepsilon_r(R)} \Psi_i \]  \hspace{1cm} (4.6)

with

\[ \hat{H}_e' = \hat{H}_e - P \frac{\varepsilon_1(R) - \varepsilon_r(R)}{\varepsilon_1(R) - \varepsilon_r(R)} \Psi_i \hspace{1cm} (4.7) \]

where \( \Phi_r \) is the quasi-stationary representation of the autoionization state of \( AB^- \) and is obtained by solving the stationary state of the projected
Hamiltonian \( Q_i \Omega \).

\[
(\mathcal{E}_r(R) - Q_i \Omega) \phi_r = 0
\]  

(4.8)

The eigenvalue \( \mathcal{E}_r(R) \) so obtained approximates the position of resonance. The shift in energy between \( \mathcal{E}_r(R) \), and the exact resonance comes from the neglected coupling with the continuum in Eq. (4.8).

Equation (4.6) which contains the coupling can be solved exactly for isolated resonance yielding

\[
P \psi_i = P \psi_i^{(+)} + \frac{1}{\mathcal{E}_i(R) - \mathcal{H}_e + i} \Lambda_r(R) P H e \Omega | \phi_r \rangle
\]  

(4.9)

with

\[
(\mathcal{E}_i(R) - \mathcal{H}_e') P \psi_i^{(+)} = 0
\]  

(4.10)

\[
\Lambda_r(R) = \frac{\langle \phi_r | Q H e P | \psi_i^{(+)} \rangle}{\mathcal{E}_i(R) - \mathcal{E}_r(R) - \langle \phi_r Q H e P \frac{1}{\mathcal{E}_i(R) - \mathcal{H}_e' + i} P H e \Omega | \phi_r \rangle}
\]  

(4.11)

where \( \Lambda(R) \) is the capture probability of the electron into the quasi-stationary state \( \phi_r \). By defining the following quantities

\[
\Lambda_r(R) = \langle \phi_r Q H e P \frac{1}{\mathcal{E}_i(R) - \mathcal{H}_e'} P H e \Omega | \phi_r \rangle
\]  

(4.12)
\[ \Gamma_r(R) = 2\pi \int |\gamma_r(R)|^2 \sin \Omega_r d\Omega_r \]  \quad \ldots \quad (4.13)

\[ \gamma_r(R) = \left\langle \Phi_r Fr | 0H | \psi_i^{(+)} \right\rangle \]  \quad \ldots \quad (4.14)

the capture probability may be rewritten as

\[ \Lambda_r(R) = \frac{\gamma_r(R)}{\left[ i\sqrt{\lambda_1}(R) - \sqrt{\lambda_2}(R) - \Lambda_r(R) + \frac{i}{2} \Gamma_r(R) \right]} \]  \quad \ldots \quad (4.15)

where \( \Lambda_r(R) \) is the energy shift in the position of resonance as approximated by \( \sqrt{\lambda_2}(R) \), the symbol \( \Phi \) is introduced to indicate that a principal value is to be taken when integrating across the singularity, \( \Gamma_r(R) \) is the half-width of the resonance and \( \gamma_r(R) \) is the partial capture width. In the expression for \( \Gamma_r \), we have chosen to make the integration over the possible final angle \( \Omega_f \) with \( \zeta \) as the density of states.

It can be easily shown that \( P_{\psi_i} \) asymptotically satisfies the boundary condition (2.16). 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 Section III. We construct \( \Pi \) such that

\[ \Pi \mathcal{T}(r, R) = \left| P_{\psi_i} \right| \chi_o(R) + \left| f, \nu \right\rangle G_v(R) \]  \quad \ldots \quad (4.16)

where \( \left| f, \nu \right\rangle \) is defined by Eq. (3.4). This leads to the pair of coupled-equation description
\[ \{ E - \langle \mathbf{P}_1 | \mathbf{H} | \mathbf{P}_1 \rangle \} \psi_0 (R) = \langle \mathbf{P}_1 | \mathbf{H} - E | f, u \rangle \phi_v (R), \quad (4.17a) \]

\[ \{ E - \langle f, u | \mathbf{H} | f, u \rangle \} \psi_v (R) = \langle f, u | \mathbf{H} - E | \mathbf{P}_1 \psi \rangle \psi_0 (R). \quad (4.17b) \]

The amplitude for dissociative attachment \( g_v (k_1, \hat{R}) \) is then given by

\[ g_v (k_1, \hat{R}) = \frac{1}{4\pi} \left\langle G_v^{(o)} (R) | \mathcal{J}_e (R) | \psi_0 (R) \right\rangle \quad (4.18) \]

with

\[ \mathcal{J}_e (R) = \langle f, u | \mathbf{H} - E | \mathbf{P}_1 \rangle \quad (4.19) \]

where \( G_v^{(o)} (R) \) is the solution of the homogeneous part of Eq. (4.17b) and \( \mathcal{J}_e (R) \) defined by Eq. (4.19) can be interpreted as the effective electronic transition matrix for a fixed nuclear configuration.

To examine \( \mathcal{J}_e \) qualitatively we make the "static" approximation \( \mathbf{H} \approx \mathbf{H}_e \mathbf{H}_s \). Equation (4.19) then reduces to

\[ \mathcal{J}_e (R) = B(R) + A(R) \cdot v_R \quad (4.20) \]

with

\[ B(R) = \langle f, u | \mathcal{J}_e | \mathbf{P}_1 \rangle - \frac{1}{2} \left\langle f, u | (v^2 R^2 | \mathbf{P}_1 \right\rangle, \quad (4.21) \]
\[ A(R) = -\frac{1}{\mu} \langle f, \nu | (F_R P_{\nu}) \rangle \]  \hspace{1cm} (4.22)

where the potential \( V_e \) responsible for adiabatic electronic transition is defined in terms of \( P_{\nu} \) and \( \chi_0(R) \):

\[ (H_e - V_e - E)P_{\nu} \chi_0(R) = \frac{1}{2\mu} P_{\nu} (V_R \chi_0(R)) \]  \hspace{1cm} (4.23)

Again we observe the mass-dependent, nonadiabatic coupling terms appearing in the transition matrix. Now if we assume that the electronic matrices are primarily determined at \( R = R_e \), the equilibrium nuclear configuration of the ground target state, we obtain for dissociative attachment amplitude the familiar expression

\[ g_v (k_0, R) = B(R_e) \langle G^{(o)} \chi_0(R) \rangle + A(R_e) \cdot \langle G^{(o)} \chi_0(R) | V_R \chi_0(R) \rangle. \]  \hspace{1cm} (4.24)

V. 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. 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 \( ^2\Sigma^+ \) state of \( H_2^- \), which is assumed to be responsible for the lowest resonance dissociative...
attachment peak of the cross section in the \((e, H_2^-)\) system, it was suggested that the third electron in the \(^2\Sigma_u^+\) state of \(H_2^-\) is not stationary at small nuclear configurations. This then violates the applicability of the expansion method, since the intermediate state in this case does not rigorously belong to the complete set used in the expansion.

In order to account for the observation that the intermediate \(^2\Sigma_u^+\) state of \(H_2^-\) for the dissociation attachment is a resonance state, Bardsley, Herzenberg, and Mandl have later treated the problem in the adiabatic approximation using the Kapur-Peierls resonance formalism. No calculation was reported in this treatment. It can be shown however that their expression is equivalent to the "static" approximation equation (4.24) with the nonadiabatic terms and the recoil in the rearranged channel neglected. We will show later that these nonadiabatic terms are of great importance in dissociative attachment processes.

Unfortunately, a complete calculation using formulae derived in Section IV for resonance dissociative attachment is not yet practical at the present stage. The difficulty still lies in the calculation of the resonance state \(\phi_r\) appearing in the expression for \(P_{\gamma_1}\) [Eqs. (4.9) and (4.11)]. Nevertheless, we will show here how the striking feature on isotope effects recently observed for dissociative attachment in \((e, H_2^-)\) system can be understood in terms of the present theory.

We start our discussion with the amplitude for dissociative attachment \(g_0(\hat{R}_1, \hat{R})\) [Eq. (4.18)] in the "static" approximation \(\mathcal{H} = \mathcal{H}_{\text{II}}\). Substituting \(P_{\gamma_1}\) from Eq. (4.9) for a fixed nuclear configuration into \(\mathcal{J}_e\), we may separate the electronic transition matrix into two terms:
\[ \mathcal{J}_e^{(R)} = \mathcal{J}_e^{(d)}(R) + \mathcal{J}_e^{(r)}(R) \] (5.1)

The first term is simply the contribution due to direct transition of the Born type

\[ \mathcal{J}_e^{(d)}(R) = \langle f, \nu | \psi_\nu^{(+)} \rangle - \frac{1}{2\mu} \langle f, \nu | (\nabla_R^2 \psi_\nu^{(+)} \rangle - \frac{1}{\mu} \langle f, \nu | (\nabla_R \psi_\nu^{(+)} \rangle \] (5.2)

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

\[ \mathcal{J}_e^{(r)}(R) = \Lambda_r(R) \langle f, \nu | \psi_\nu \frac{1}{\alpha} | \alpha \phi_r \rangle - \frac{1}{\mu} \Lambda_r(R) \langle f, \nu | (\nabla_R \frac{1}{\alpha} \psi_\nu) \rangle \cdot \nabla_R \]

\[ - \frac{1}{\mu} (\nabla_R \Lambda_r(R)) \langle f, \nu | \frac{1}{\alpha} \psi_\nu \rangle \cdot \nabla_R \] (5.3)

with

\[ \alpha^{-1} = (\mathcal{E}(R) - \mathcal{H}_e^r + i\eta)^{-1} \] (5.4)

where we have dropped the term involving \((\nabla_R^2 \psi_\nu)\) in Eq. (5.3) due to its smallness in comparison with \(\Lambda(R) \cdot \nabla_R\).

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

\[
\sigma = \frac{1}{k_i} \int \frac{1}{4\pi} |G_v^{(0)}(R)|^2 \left| \mathcal{J}_e^{(r)}(R) \right| \left| \chi_o(R) \right|^2 \, d(k'_i, R) \quad (5.5)
\]

where we have chosen to normalize \( G_v^{(o)} \) in the \( \kappa_{fv} \) scale, so that the wave number \( \kappa_{fv} \) for the relative motion of the two nuclei in the final state is included in \( G_v^{(o)} \). The three terms appearing in the expression for \( \mathcal{J}_e^{(r)} \) [Eq. (5.3)] have simple physical interpretations. The first term gives, in the adiabatic sense, the product of probability of capturing the incident electron into the \( \Phi_r \) state of \( H_2^- \) (i.e. \( \Lambda_r(R) \)) and the matrix element for propagating from the \( \Phi_r \) state into the desired final state via a propagator \( \alpha^{-1} \). 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 \( \Phi_r \), dissociation of \( AB^- \) may take place with an acceleration depending on the steepness of the repulsive potential generated by \( \Phi_r \) 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 \( \Gamma_d \) (see also Figs. 1 and 3). The dissociative process is, however, damped because \( \Phi_r \) is coupled with continuum states having a resonance width for autoionization. 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 \( (e, H_2) \) system is much smaller than for other systems.
Now, we would like to show how the observed large isotope effects can be interpreted with the aid of the present theory. In Section II, we observe that if the intermediate state of $AB^-$ is a stationary state, the interactions responsible for the rearrangement process are primarily the nonadiabatic terms. The reason for this is that the collision duration $\tau_e$ between the incident electron and the target molecule is very long in comparison with the time period $\tau_n$ associated with the internal nuclear motion leading to dissociation. For resonance dissociative attachment, the intermediate state is a resonance state; the collision duration $\tau_e$ is shortened considerably due to the width for autoionization. An estimation of the collision duration $\tau_e$ is given by

$$\tau_e = 1/\Gamma_r \quad . \quad (5.6)$$

The time period $\tau_n$ associated with nuclear dissociation can be estimated from the Franck-Condon width $\Gamma_d$:

$$\tau_n = 1/\Gamma_d \quad . \quad (5.7)$$

This implies that in order to approximate the interaction responsible for nuclear transitions by the adiabatic term only we must have

$$\Gamma_r \gg \Gamma_d \quad ; \quad (5.8)$$

that is, the resonance width for electronic structure should be larger than the Franck-Condon width. This condition [Eq. (5.8)] is, however, not
satisfied for most cases of interest.

Examining the observed dissociative attachment cross section in the electron-hydrogen case (Fig. 4), one finds two peaks at 10.5 and 14 eV with Franck-Condon widths of the order of 3 and 1 eV respectively. These two peaks were interpreted by Schulz as belonging to two different resonance states of $H_2^-$. We assume that there is no overlapping between these two resonance states, so that they can be treated separately as isolated resonances. A typical resonance width $\Gamma_r$ for the electronic structure is of the order of $10^{-1}$ to $10^{-2}$ eV which is certainly much smaller than the Franck-Condon width 3 eV for the first resonance peak at 10.5 eV. We then expect, for the first resonance peak, that the interactions responsible for the dissociative attachment process are primarily the nonadiabatic terms. This then yields a $\mu^{-2}$ mass dependence for the dissociative attachment cross section.

$$\sigma = \mu^{-2} \sigma_n$$ (5.9)

with

$$\sigma_n = \frac{(4\pi)^{-2}}{k_i} \left| \sum \left[ K_{\nu}^{(+)} | \Lambda_r \langle f, \nu | (\nu, \frac{1}{2} \alpha \Phi \Omega \Gamma_r) \right] + (\nu, \frac{1}{2} \alpha \Phi \Omega \Gamma_r) \langle f, \nu | (\nu, \frac{1}{2} \alpha \Phi \Omega \Gamma_r) \right|^{2} \right| d(k_i, \hat{R})$$ (5.10)

where $\sigma_n$ is the part of nonadiabatic cross section which is not sensitively mass dependent.\(^{12}\)
According to Eq. (5.9), we expect the ratio in magnitudes of the cross section to be 4:2.2:1 for $\text{H}_2$, HD and $\text{D}_2$ respectively. This is the observed isotope effect for the first resonance peaks in the cross sections for dissociative attachment in the electron-hydrogen system (Fig. 4). This good agreement is obtained because the Franck-Condon width is reasonably broad for the first resonance peaks. For the second resonance peaks, the Franck-Condon width is much narrower, becoming comparable with the lower limit of $\Gamma_r$; and deviations from the 4:2.2:1 ratio are observed, indicating in this case that the adiabatic terms may become significant.
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REFERENCES AND FOOTNOTES


9. J. C. Y. Chen and M. H. Mittleman, University of California Radiation Laboratory Report, UCRL-14377. Generalization of the method to account for recoil limitation has since been developed. J.C.Y. Chen and M. H. Mittleman (to be published).


11. A single configuration calculation for the resonance state of $H_2^-$ were recently presented by Bardsley,Herzenberg and Mandl at the IVth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada August 1964. At the same conference the treatment of Bardsley et al. was discussed by T. F. O'Malley in terms of Feshbach's resonance formalism.

12. The mass dependence of the nonadiabatic cross section $\sigma_n$ can be estimated from the matrix element $\langle G^{(o)}(R) | V_R | x_0(R) \rangle$, remembering that $G^{(o)}(R)$ is normalized in the $\hbar f_\nu$ scale.
FIGURE CAPTIONS

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

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

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

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].
Interaction Potential For Nuclear Motion $E(R)$

$\Psi_i \{AB^-\}$

Franck-Condon Width $\Gamma_d$

$\Psi_i \{AB^+e\}$

Internuclear Separation $R$

Figure 1
Figure 3

Interaction Potential for Nuclear Motion $E(R)$

- $AB^r(\Phi_r) \rightarrow AB(\Psi_0) \cdot e(k')$
- $AB^r(\Phi_r) \rightarrow A(\Phi_0) \cdot B^r(\Phi'_0)$

Competing Region

Franck-Condon Width $\Gamma_d$

$AB\{\Psi_0\} \cdot e\{k_i\}$

$A\{\Phi_0\} \cdot B\{\Phi_0\} \cdot e\{k\}$

$A\{\Phi_0\} + B^r\{\Phi'_0\}$

$R_c$

Internuclear Separation $R$