

***T*-matrix study of resonant reactive scattering and comparison between direct and indirect scattering contributions to the dissociative attachment process of $e + AB \rightarrow A + B^-$**

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A rigorous derivation of the T matrix is presented to study the effects of direct and indirect reactive scattering processes of $e + AB \rightarrow A + B^-$, involving electron(e)-molecule(AB) systems. Analysis of dissociative attachment processes $e + H_2 \rightarrow H + H^-$ and $e + HCl \rightarrow H + Cl^-$ is presented, with emphasis on the individual role of the direct and indirect processes in affecting the total cross sections. Marked differences among different electron-molecule collision systems are found from this analysis, and the cause of such differences is explained.

I. INTRODUCTION

Recently, various levels of progress in the theoretical studies of resonant scattering processes¹⁻⁴⁷ have been made. The use of energy-dependent nonlocal potential was found to be necessary for the accurate evaluation of both the inelastic and reactive scattering.^{1-11,36,37} Computation of the matrix elements of Green's functions have been greatly facilitated partially due to the use of the simple recurrence relations¹⁻³ that are derived from the tri-diagonality of a Morse Hamiltonian in the Lanczos basis by construction.⁴⁸⁻⁵⁰ For the analysis of dissociative attachment processes, we compute $e + H_2 \rightarrow H + H^-$ and $e + HCl \rightarrow H + Cl^-$, by using the energy-dependent nonlocal potential mentioned above. The present work differs from previous studies^{1,2} in that we focus our attention primarily on how the indirect (resonant) process competes with the direct process in causing the dissociative attachment processes. In addition, manifest differences in the structures of the direct and resonant scattering cross sections among the different electron-molecule collision systems mentioned above are explicitly pointed out.

In short, the objectives of the present study are twofold: (1) a rigorous description of reactive scattering transition amplitude applicable to the study of dissociative attachment processes, $e + AB \rightarrow A + B^-$ and (2) an analysis on the individual role of the direct and indirect (resonant) processes in reactive scattering.

II. FORMAL EXPRESSION OF REACTIVE TRANSITION AMPLITUDE (T MATRIX) INVOLVING ELECTRON-MOLECULE COLLISIONS

In our earlier studies,⁵¹⁻⁵⁴ we presented the formal descriptions of transition amplitudes in both the distorted-wave^{51,52} and coupled-channel-wave^{53,54} representations in order to treat reactive scattering (rearrangement collisions) processes involving atom-diatom molecule collisions systems, $A + BC \rightarrow B + AC$. For such systems, the use of the target molecular states as a complete basis set for the expansion of the total wave function was

found to be convenient.^{53,54} On the other hand, in treating reactive collisions involving electron-diatom molecule ($e + AB$) systems, electronic states describing relative motion between electron e and target diatomic molecule AB yield a convenient basis set for the expansion of the total wave function.

The Schrödinger equation for the electron-molecule system of interest is written

$$H |\Psi\rangle = E |\Psi\rangle, \quad (2.1)$$

where

$$H = H_T + H_{eT}. \quad (2.2)$$

Here H_T is the Hamiltonian for the target molecule,

$$H_T = K_T + V_T(\mathbf{R}), \quad (2.3)$$

with K_T the nuclear kinetic energy and $V_T(\mathbf{R})$ the interatomic potential at internuclear separation \mathbf{R} . H_{eT} is the effective electronic single-particle Hamiltonian (H , in the symbolism of Mundel, Berman, and Domcke¹), and it is atomic units,

$$H_{eT} = -\frac{1}{2}\nabla_r^2 + V_{eT}(\mathbf{r}; \mathbf{R}), \quad (2.4)$$

where $-\frac{1}{2}\nabla_r^2$ is the relative kinetic energy and $V_{eT}(\mathbf{r}; \mathbf{R})$ [equivalent to Σ of Eq. (6) in Ref. 1(b)] can be chosen to be made of the energy-dependent, nonlocal self-energy and the static-exchange potential^{8,55,56} to represent effective interaction between the electron and the target molecule as a function of interparticle displacement \mathbf{r} between the electron and the target molecule at a given internuclear displacement \mathbf{R} of the molecule AB .

Following Feshbach^{57,58} we define the projection operators,

$$P = \int d\varepsilon_k |\xi_k^{(+)}\rangle \langle \xi_k^{(+)}|, \quad (2.5)$$

for projection onto the Hilbert subspace of electronic continuum states $|\xi_k^{(+)}\rangle$, and

$$\begin{aligned} Q &= 1 - P \\ &= \sum_i |\psi_i\rangle \langle \psi_i|, \end{aligned} \quad (2.6)$$

for projection onto the Hilbert subspace of electronic discrete states $|\psi_i\rangle$. ϵ_k in (2.5) is the energy of the continuum electronic state k . The total wave function $|\Psi\rangle$ is then written as

$$\begin{aligned} |\Psi\rangle &= (P+Q)|\Psi\rangle \\ &= \sum_k |\xi_k^{(+)}\rangle \langle \xi_k^{(+)} | \Psi \rangle + \sum_i |\psi_i\rangle \langle \psi_i | \Psi \rangle. \end{aligned} \quad (2.7)$$

For simplicity the summation symbol \sum_k in the first term above and other places below is used to represent integration over ϵ_k .

The plane wave $|\Phi\rangle$ in the initial arrangement is described by

$$\left(-\frac{1}{2}\nabla_r^2 + K_T + V_T\right)|\Phi\rangle = E|\Phi\rangle, \quad (2.8)$$

by setting $V_{eT}=0$ in (2.1). Φ is formally

$$|\Phi\rangle = |\xi_k^0\rangle \langle \xi_k^0 | \Psi \rangle \equiv |\xi_k^0\rangle |\phi_c^0\rangle, \quad (2.9)$$

where $|\xi_k^0\rangle$ for the relative motion between the electron and target molecule at $r \rightarrow \infty$ satisfies

$$\left(-\frac{1}{2}\nabla_r^2 - \epsilon_k\right)|\xi_k^0\rangle = 0, \quad (2.10)$$

and $|\phi_c^0\rangle$ represents the unperturbed molecular state of the target molecule at $r \rightarrow \infty$ defined by

$$|\phi_c^0\rangle \equiv \langle \xi_k^0 | \Psi \rangle. \quad (2.11)$$

We rewrite Schrödinger equation (2.1),

$$(H_0 + V_{eT})|\Psi\rangle = E|\Psi\rangle, \quad (2.12)$$

where

$$H_0 = -\frac{1}{2}\nabla_r^2 + K_T + V_T. \quad (2.13)$$

Using the projection operators (2.5) and (2.6), we write V_{eT} in (2.12) above,

$$\begin{aligned} V_{eT} &= \sum_k \sum_{k'} |\xi_k^{(+)}\rangle \langle \xi_k^{(+)} | V_{eT} | \xi_{k'}^{(+)}\rangle \langle \xi_{k'}^{(+)} | \\ &\quad + \sum_k \sum_i |\xi_k^{(+)}\rangle \langle \xi_k^{(+)} | V_{eT} | \psi_i\rangle \langle \psi_i | \\ &\quad + \sum_i \sum_k |\psi_i\rangle \langle \psi_i | V_{eT} | \xi_k^{(+)}\rangle \langle \xi_k^{(+)} | \\ &\quad + \sum_i \sum_{i'} |\psi_i\rangle \langle \psi_i | V_{eT} | \psi_{i'}\rangle \langle \psi_{i'} |. \end{aligned} \quad (2.14)$$

We define the row matrices

$$\xi_c^{(+)} = (|\xi_0^{(+)}\rangle, |\xi_1^{(+)}\rangle, \dots) \quad (2.15)$$

for the electronic continuum (unbound) states and

$$\psi_d = (|\psi_0\rangle, |\psi_1\rangle, \dots) \quad (2.16)$$

for the electronic discrete (bound) states, and the column matrices

$$\tilde{\phi}_c = \begin{pmatrix} \langle \xi_0^{(+)} | \Psi \rangle \\ \langle \xi_1^{(+)} | \Psi \rangle \\ \vdots \end{pmatrix} \quad (2.17)$$

for the molecular states associated with the continuum electronic states and

$$\tilde{\chi}_d^{(+)} = \begin{pmatrix} \langle \psi_0^{(+)} | \Psi \rangle \\ \langle \psi_1^{(+)} | \Psi \rangle \\ \vdots \end{pmatrix} \quad (2.18)$$

for the molecular states associated with the discrete electronic states. Using (2.15) through (2.16), we rewrite (2.14) above,

$$\begin{aligned} V_{eT} &= \xi_c^{(+)} \mathbf{v}_{cc} \xi_c^{(+)\dagger} + \xi_c^{(+)} \mathbf{v}_{cd} \psi_d^\dagger + \psi_d \mathbf{v}_{dc} \xi_c^{(+)\dagger} \\ &\quad + \psi_d \mathbf{v}_{dd} \psi_d^\dagger. \end{aligned} \quad (2.19)$$

Here the matrix elements of \mathbf{v}_{cc} between the electronic states are defined as follows:

$$[\mathbf{v}_{cc}]_{kk'} = \langle \xi_k^{(+)} | V_{eT} | \xi_{k'}^{(+)} \rangle, \quad (2.20)$$

$$[\mathbf{v}_{cd}]_{ki} = \langle \xi_k^{(+)} | V_{eT} | \psi_i \rangle, \quad (2.21)$$

$$[\mathbf{v}_{dc}]_{ik} = \langle \psi_i | V_{eT} | \xi_k^{(+)} \rangle, \quad (2.22)$$

and

$$[\mathbf{v}_{dd}]_{ii'} = \langle \psi_i | V_{eT} | \psi_{i'} \rangle. \quad (2.23)$$

The use of (2.15) through (2.18) for Ψ in (2.7) leads to

$$\Psi = \xi_c^{(+)} \tilde{\phi}_c + \psi_d \tilde{\chi}_d^{(+)}. \quad (2.24)$$

The insertion of (2.24) into the Schrödinger equation (2.1) and the introduction of proper inner products using $|\xi_k^{(+)}\rangle$ and $|\psi_i\rangle$ lead to the matrix representation of the resulting coupled Schrödinger equations,

$$\begin{bmatrix} \mathbf{H}_{cc} & \mathbf{V}_{cd} \\ \mathbf{V}_{dc}^\dagger & \mathbf{H}_{dd} \end{bmatrix} \begin{bmatrix} \tilde{\phi}_c \\ \tilde{\chi}_d^{(+)} \end{bmatrix} = E \begin{bmatrix} \tilde{\phi}_c \\ \tilde{\chi}_d^{(+)} \end{bmatrix}, \quad (2.25)$$

where

$$\mathbf{H}_{cc} = (K_T + V_T) \mathbf{1}_c + \epsilon_c, \quad (2.26)$$

with $\mathbf{1}_c$, the unit matrix and the matrix elements of ϵ_c ,

$$[\epsilon_c]_{kk'} = \langle \xi_k^{(+)} | H_{eT} | \xi_{k'}^{(+)} \rangle, \quad (2.27)$$

$$\mathbf{H}_{dd} = (K_T + V_T) \mathbf{1}_d + \epsilon_d, \quad (2.28)$$

with $\mathbf{1}_d$, the unit matrix and the matrix elements of ϵ_d ,

$$[\epsilon_d]_{ii'} = \langle \psi_i | H_{eT} | \psi_{i'} \rangle. \quad (2.29)$$

Finally, \mathbf{V}_{cd} and \mathbf{V}_{dc}^\dagger are the potential matrices. They represent coupling between the continuum and discrete states, and thus allow resonant scattering. Their matrix elements are defined as follows:¹

$$[\mathbf{V}_{cd}]_{ki} = \langle \xi_k^{(+)} | H_{eT} | \psi_i \rangle \quad (2.30)$$

and

$$[\mathbf{V}_{dc}^\dagger]_{ik} = \langle \psi_i | H_{eT} | \xi_k^{(+)} \rangle. \quad (2.31)$$

It is of note that the potential matrices in (2.30), and (2.31) above are denoted by \mathbf{V} and the expression (2.20) through (2.23), by \mathbf{v} .

We readily find the Hermitian adjoint to \mathbf{V}_{cd} , from (2.30) and (2.31) above,

$$[\mathbf{V}_{dc}^\dagger]_{ik} = [\mathbf{V}_{cd}]_{ki}^* . \quad (2.32)$$

The formal solutions to the coupled Schrödinger equations (2.25) above are then

$$\tilde{\phi}_c = \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} \tilde{\chi}_d^{(+)} \quad (2.33)$$

and

$$\tilde{\chi}_d^{(+)} = \frac{1}{E\mathbf{1}_d - \mathbf{H}_{dd}} \mathbf{V}_{dc}^\dagger \tilde{\phi}_c . \quad (2.34)$$

The use of (2.33) and (2.34) for (2.25) leads to the form of a block diagonalized matrix,

$$\begin{bmatrix} \mathcal{H}_{cc} & 0 \\ 0 & \mathcal{H}_{dd} \end{bmatrix} \begin{bmatrix} \tilde{\phi}_c \\ \tilde{\chi}_d^{(+)} \end{bmatrix} = E \begin{bmatrix} \tilde{\phi}_c \\ \tilde{\chi}_d^{(+)} \end{bmatrix} , \quad (2.35)$$

where the effective Hamiltonians are

$$\mathcal{H}_{cc} = \mathbf{H}_{cc} + \mathbf{V}_{cd} \frac{1}{E\mathbf{1}_d - \mathbf{H}_{dd}} \mathbf{V}_{dc}^\dagger \quad (2.36)$$

for the continuum states, and

$$\mathcal{H}_{dd} = \mathbf{H}_{dd} + \mathbf{V}_{dc}^\dagger \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} \quad (2.37)$$

for the discrete states.

Applying (2.26) through (2.34) we now obtain the following uncoupled Schrödinger equations equivalent to (2.35):

$$(E\mathbf{1} - \mathbf{H}_{cc})\tilde{\phi}_c = \mathbf{V}_{cd} \frac{1}{E\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d(\mathbf{R})} \mathbf{V}_{dc}^\dagger \tilde{\phi}_c , \quad (2.38)$$

with

$$\mathbf{V}_d(\mathbf{R}) = V_T(\mathbf{R})\mathbf{1}_d + \varepsilon_d(\mathbf{R}) \quad (2.39)$$

and

$$\begin{aligned} [E\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d(\mathbf{R})]\tilde{\chi}_d^{(+)} \\ = \mathbf{V}_{dc}^\dagger \frac{1}{E\mathbf{1}_c - (K_T + V_T)\mathbf{1}_c - \varepsilon_c} \mathbf{V}_{cd} \tilde{\chi}_d^{(+)} . \end{aligned} \quad (2.40)$$

The complete solution to (2.40) is, in closed form,

$$\begin{aligned} \tilde{\chi}_d^{(+)} = \tilde{\chi}_d^{0(+)} + \frac{1}{E\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d - \mathbf{V}_{dc}^\dagger (E\mathbf{1}_c - \mathbf{H}_{cc})^{-1} \mathbf{V}_{cd}} \\ \times \mathbf{V}_{dc}^\dagger \frac{1}{E\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} \tilde{\chi}_d^{0(+)} , \end{aligned} \quad (2.41)$$

where $\tilde{\chi}_d^{0(+)}$ is the solution of

$$[E\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d(\mathbf{R})]\tilde{\chi}_d^{0(+)} = 0 . \quad (2.42)$$

The insertion of (2.41) into (2.33) yields

$$\tilde{\phi}_c = \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} (\mathbf{1}_d + \Omega) \tilde{\chi}_d^{0(+)} , \quad (2.43)$$

where

$$\begin{aligned} \Omega = \frac{1}{E\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d - \mathbf{V}_{dc}^\dagger (E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc})^{-1} \mathbf{V}_{cd}} \\ \times \mathbf{V}_{dc}^\dagger \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} . \end{aligned} \quad (2.44)$$

By defining¹

$$\mathbf{F} = \mathbf{V}_{dc}^\dagger \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} \quad (2.45)$$

and

$$\mathbf{G}_1^{(+)} = \frac{1}{E^{(+)}\mathbf{1}_d - K_T\mathbf{1}_d - \mathbf{V}_d} , \quad (2.46)$$

we rewrite (2.44)

$$\Omega = \mathbf{G}_1^{(+)} \mathbf{F} (\mathbf{F} - \mathbf{F} \mathbf{G}_1^{(+)} \mathbf{F})^{-1} \mathbf{F} . \quad (2.47)$$

The introduction of (2.44) and (2.47) into (2.41) leads to

$$\tilde{\chi}_d^{(+)} = \tilde{\chi}_d^{0(+)} + \mathbf{G}_1^{(+)} \mathbf{F} (\mathbf{F} - \mathbf{F} \mathbf{G}_1^{(+)} \mathbf{F})^{-1} \mathbf{F} \tilde{\chi}_d^{0(+)} . \quad (2.48)$$

Using (2.47) we rewrite (2.43)

$$\tilde{\phi}_c = \frac{1}{E\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} [\mathbf{1}_d + \mathbf{G}_1^{(+)} \mathbf{F} (\mathbf{F} - \mathbf{F} \mathbf{G}_1^{(+)} \mathbf{F})^{-1} \mathbf{F}] \tilde{\chi}_d^{0(+)} . \quad (2.49)$$

The matrix element or transition amplitude for reactive scattering from an initial arrangement channel α to a final arrangement channel β is formally

$$\mathbf{T}_{\beta\alpha} = \langle \Psi_\beta^{(-)} | V_{eT} | \Phi_\alpha \rangle . \quad (2.50)$$

By consideration of

$$\langle \xi_k^{(+)} | \xi_{k'}^0 \rangle \simeq \delta_{kk'} \quad (2.51)$$

and

$$\langle \psi_i | \xi_k^0 \rangle = 0 , \quad (2.52)$$

the use of (2.9) and (2.19) and the substitution of (2.48) and (2.49) into (2.24) for the expression of the T matrix yields

$$\begin{aligned} \mathbf{T}_{\beta\alpha} = \langle \chi_d^{0(-)} | (1 + \tau \mathbf{G}_1^{(+)}) \mathbf{V}_{dc}^\dagger | \tilde{\phi}_c^0 \rangle \\ + \langle \chi_d^{0(-)} | (1 + \tau \mathbf{G}_1^{(+)}) \mathbf{V}_{dc}^\dagger \frac{1}{E^{(+)}\mathbf{1}_c - \mathbf{H}_{cc}} \mathbf{V}_{cd} | \tilde{\phi}_c^0 \rangle , \end{aligned} \quad (2.53)$$

where τ is defined as^{1,59}

$$\tau = \mathbf{F} (\mathbf{F} - \mathbf{F} \mathbf{G}_1^{(+)} \mathbf{F})^{-1} \mathbf{F} . \quad (2.54)$$

$\chi_d^{0(-)}$ in (2.53) above is the row matrix for the scattering state of the final arrangement particles A and B^- obtainable from (2.42) and $\tilde{\phi}_c^0$ is the column matrix for a free (unperturbed) state of the target molecule AB corresponding to (2.7) at $r = \infty$. For a direct comparison with the transition amplitude of Mundel, Berman, and Domcke, by realizing

$$\begin{aligned} [\mathbf{V}_{dc}]_{ik} &= \langle \psi_i | -\frac{1}{2}\nabla_r^2 + V_{eT} | \xi_k^0 \rangle \\ &= \langle \psi_i | V_{eT} | \xi_k^0 \rangle = [\mathbf{v}_{dc}]_{ik}, \end{aligned} \quad (2.55)$$

we rewrite (2.53)

$$\begin{aligned} \mathbf{T}_{\beta\alpha} &= \langle \chi_d^{0(-)} | (1 + \tau\mathbf{G}_1^{(+)})\mathbf{V}_{dc}^\dagger | \tilde{\phi}_c^0 \rangle \\ &+ \left\langle \chi_d^{0(-)} \left| (1 + \tau\mathbf{G}_1^{(+)})\mathbf{V}_{dc}^\dagger \frac{1}{E^{(+)}\mathbf{1} - \mathbf{H}_{cc}} \mathbf{v}_{cc} \right| \tilde{\phi}_c^0 \right\rangle, \end{aligned} \quad (2.56a)$$

or

$$\mathbf{T}_{\beta\alpha} = \langle \chi_d^{0(-)} | (1 + \tau\mathbf{G}_1^{(+)})\tilde{\mathbf{V}}_{dc}^\dagger | \tilde{\phi}_c^0 \rangle, \quad (2.56b)$$

where

$$\tilde{\mathbf{V}}_{dc}^\dagger = \mathbf{V}_{dc}^\dagger \left[\mathbf{1} + \frac{1}{E^{(+)}\mathbf{1} - \mathbf{H}_{cc}} \mathbf{v}_{cc} \right]. \quad (2.57)$$

Equation (2.56b) is now seen to be equivalent to Eq. (40) of Mundel *et al.*^{1(a)} except the fact that (2.56b) above is formally more general in that (2.57) the nuclear kinetic energy operator is included in \mathbf{H}_{cc} . The first term in (2.56a) above is expected to yield major contribution to the total cross section. The second term represents the contribution of intermediate states owing to coupling potential \mathbf{v}_{cc} between the electronic continuum states. We rewrite (2.56b)

$$\mathbf{T}_{\beta\alpha} = \langle \chi_d^{0(-)} | \tilde{\mathbf{V}}_{dc}^\dagger | \tilde{\phi}_c^0 \rangle + \langle \chi_d^{0(-)} | \tau\mathbf{G}_1^{(+)}\tilde{\mathbf{V}}_{dc}^\dagger | \tilde{\phi}_c^0 \rangle. \quad (2.58)$$

Obviously the first term in the expression (2.58) above represents the direct reactive scattering process and the second term, the indirect process (decay processes due to the effect of short lifetime of resonance) in reactive scattering.

III. DIRECT AND RESONANT REACTION SCATTERING FOR $e + \text{H}_2$ AND $e + \text{HCl}$

Using computational procedures similar to those Mundel, Berman, and Domcke,¹ and of Domcke and Mundel,² we were able to reproduce their reported cross sections for $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ and $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$. In the following, we examine the individual contribution of the direct and indirect (resonant) processes to the total cross sections, including interference effects between the two processes. In this regard the present work supplements the earlier studies of Domcke and co-workers,^{1,2} who examined only the sum contribution of both processes.

Figures 1(a), 1(b), and 1(c) show the predicted results of the dissociative attachment process $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ associated with the low vibrational states $v=0, 1,$ and 2 of H_2 . The total (denoted by TOTAL) cross section in the figures represents the sum of the direct and indirect (resonant) processes and the interference effects between the two. Note from the figures the marked differences in magnitude scale among different total cross sections. It is quite interesting to see that both the direct and indirect

(resonant) processes yielded the maximum cross sections at almost the same electron collision energies and with nearly indistinguishable structures (shape) in the cross sections. Thus in $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$, the two processes are equally important in their contribution to the total cross sections. Interference between the two processes is seen to be destructive at all collision energies. This implies that the transition amplitudes tend to be in opposite phase between the two.

In all the reactive transitions examined above, the peak positions of the combined (total) cross sections were found to occur at lower electron collision energies compared to the peak positions which are contributed by the direct and resonant reactive scattering. Further, the frequency of oscillation in both the direct and indirect processes increases as the initial vibrational excitation energy of H_2 increases. Indeed, this trend is seen to persist in the cross sections of much higher vibrational states, as shown in Fig. 1(d), for $e + \text{H}_2(v=10) \rightarrow \text{H} + \text{H}^-$. Both the direct and resonant processes yielded identical oscillatory structures for all the vibrational states of H_2 investigated. In addition, the peak cross-section position of both processes tends to converge as the vibrational quantum number v of the reactant molecule increases.

To make a comparison with $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ above, similar cross sections for the reactive transition of $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$ are plotted in Figs. 2(a), 2(b), and 2(c). The first peak positions of the indirect (resonant) scattering cross sections are plotted to agree with those of the total cross sections in all the reactive transitions in-

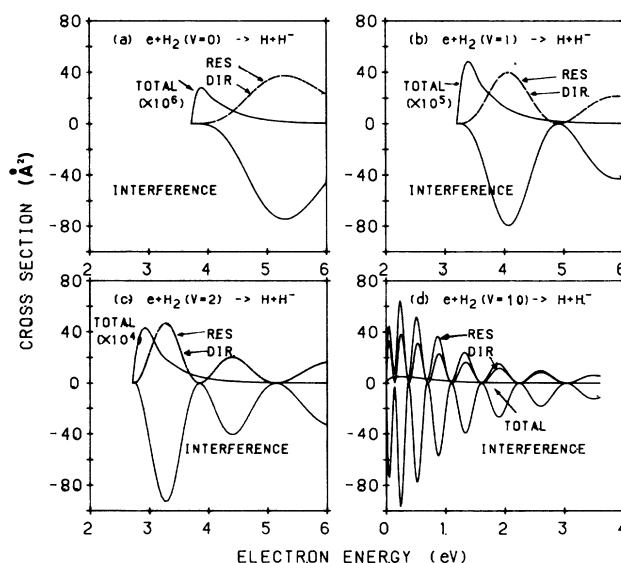


FIG. 1. Total (TOTAL), indirect (resonant) (RES) and direct (DIR) cross sections, including interference effect for dissociative attachment $e + \text{H}_2(v) \rightarrow \text{H} + \text{H}^-$ as a function of electron collision energy. (a) $v=0$, (b) $v=1$, (c) $v=2$, and (d) $v=10$. The total cross sections in $v=0, 1,$ and 2 have been magnified by factors of $10^6, 10^5,$ and 10^4 , respectively. The indirect (resonant) cross sections are seen to coincide with the direct cross sections in (a), (b), and (d).

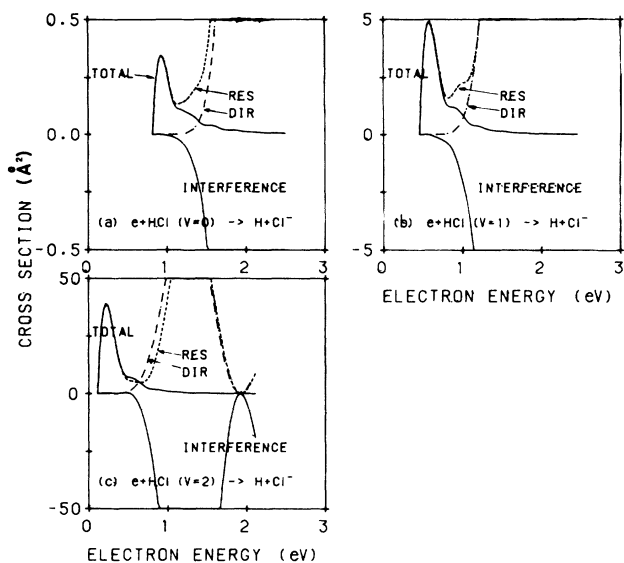


FIG. 2. Total (TOTAL), indirect (resonant) (RES) and direct (DIR) cross sections, including interference effect for dissociative attachment $e + \text{HCl}(v) \rightarrow \text{H} + \text{Cl}^-$ as a function of electron collision energy. (a) $v=0$, (b) $v=1$, and (c) $v=2$. The total cross sections are seen to coincide with the indirect (resonant) cross sections in the peak position area.

volving the initial low vibrational states $v=0, 1$, and 2 of HCl. This is quite different from the reactive system of $e + \text{H}_2$. The resonant scattering process is found to dominate over the direct scattering process (in the region of the first peak collision energy $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$). However, common to both $e + \text{HCl}$ and $e + \text{H}_2$ is the universality of the destructive interference observed at all the collision energies. In both systems the destructive interference tends to reach the maximum at the collision energy where both the direct and resonant scattering contributions are the largest. This implies that the phase of transition amplitudes for the two processes are opposite (180° apart), particularly at this collision energy.

In $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$, the peak position of the resonant scattering cross section tends to coincide with that of the combined (total) cross section only for the high vibrational states (e.g., $v=10$) of H_2 . This implies that the closer the vibrational state of the target molecule to the dissociative limit of the compound state molecule AB^- , the greater the contribution of the resonant. From Figs. 3 and 4 we observe marked differences in both the structure and depth of potentials^{1,2,60-62} between the two electron-molecule collision systems, $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ and $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$. In $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$, the potential well^{2,61,62} of the target molecule HCl in the initial arrangement is much closer to the dissociation limit of the compound state molecule HCl^- for the final arrangement, compared to the interatomic potential^{1,60} of H_2 . This promotes coupling to resonant states. This is the cause of why the resonant reactive process dominates over the direct reactive scattering process in the case of $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$ despite the low vibrational states $v=0, 1$, and 2 of HCl.

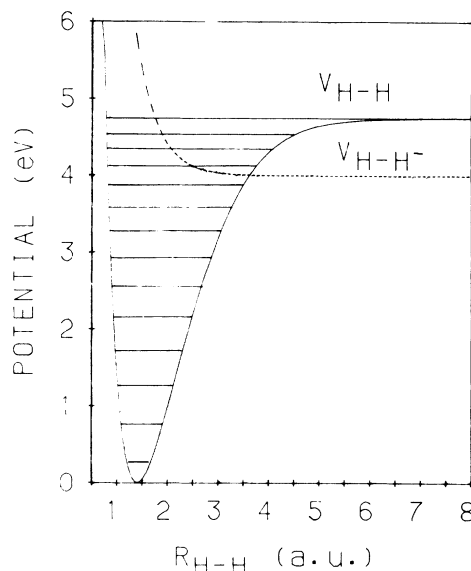


FIG. 3. H_2 (solid curve) and H_2^- (dashed curve) potential energies (taken from Refs. 60 and 61) as a function of interatomic distance $R_{\text{H-H}}$. The horizontal lines are the vibrational energy levels of H_2 .

IV. SUMMARY

In the present paper, a rigorous derivation for the reactive transition amplitude of $e + AB \rightarrow A + B^-$ is presented. We studied the two different reactive scattering systems of dissociative attachment, $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ and $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$. For analysis emphasis was placed upon the examination of competition between the direct and indirect processes to explore the importance of underlying "subprocesses" associated with the dissociative

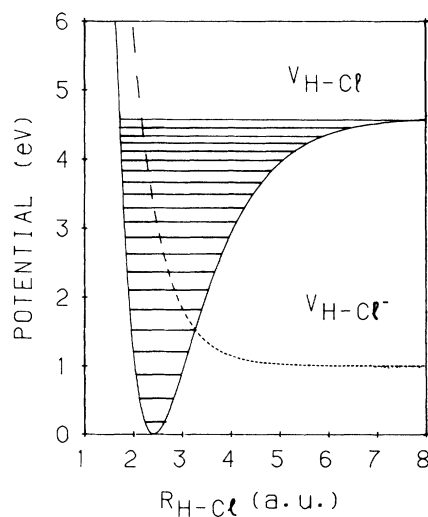


FIG. 4. HCl (solid curve) and HCl^- (dashed curve) potential energies (taken from Refs. 62 and 63) as a function of interatomic distance $R_{\text{H-Cl}}$. The horizontal lines are the vibrational energy levels of HCl.

attachement processes. From this study, we found marked differences in the contribution of the direct and indirect (resonant) processes among electron-molecule collision systems. In summary, we find the following.

(1) In $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$, the maximum contribution of both the direct and indirect processes occurs at electron collision energies other than the peak position of the total (combined) cross sections in the case of the low vibrational states of the target molecule H_2 .

(2) In $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$, the maximum contribution of the resonant scattering (corresponding to the first peak) coincides with the peak value of the total cross sections, while the contribution of the direct process is negligibly small in the region of the peak value.

(3) In both systems, interference between the direct and indirect processes is destructive at all the collision energies investigated and this manifests a tendency to have opposite phases in the transition amplitudes between the direct and indirect reactive scattering, particularly in the region of collision energy where both the direct and reso-

nant scattering parts of contributions are equally dominant.

(4) In $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$, peak positions for both the direct and indirect (resonant) scattering cross sections tend to converge to the peak position of the total cross section as the vibrational excitation energy of the reactant molecule H_2 increases.

(5) Finally, in $e + \text{HCl} \rightarrow \text{H} + \text{Cl}^-$, the contribution of resonant scattering process is dominant over the direct scattering process (in the region of the first peak position), contrary to the case of $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$, and this is caused by the relative closeness of initial vibrational excitation energy to the dissociation limit of HCl^- (see the interaction potential of HCl^- shown in Fig. 4), compared to the case of $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$.

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