Theory of electron-molecule scattering: Comments on the adiabatic-nuclei approximation

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(Received 8 April 1975)

The adiabatic-nuclei theory of electron-molecule scattering is extended to account for electronic excitation of the target. The approximate expressions for the wave function and the scattering amplitude are derived from a formally exact expansion in terms of the fixed-nuclei, electronic-scattering solutions. The formalism treats molecular-bound and continuum states on an equal footing. We also propose a modified expression for the adiabatic-scattering amplitude which is expected to have an increased range of validity near excitation thresholds.

I. INTRODUCTION

During the last few years, both purely theoretical and computational evidence has been accumulating which shows that the adiabatic-nuclei approximation[1] provides an accurate description of electron-molecule scattering when the collision time is short compared with the rotational and vibrational periods of the molecule. The basic formula for the adiabatic scattering amplitude was first derived by Chase[2] in the context of nuclear physics. Temkin and co-workers obtained detailed expressions which are appropriate for the rotational[3] and vibrational excitation[4] of homonuclear diatomics. Similar expressions were also derived by Hara,[5] who calculated the rotational-excitation cross section for H_2. Other applications of the adiabatic-nuclei theory include the early work of Mittleman, Peacher, and Rozsnyai on the rotational excitation of polar molecules,[6] the study of e^--N_2 collisions by Burke and co-workers,[7] the formulation of electron scattering from polyatomic molecules,[8] Henry and Chang's calculation of the simultaneous rotational-vibrational excitation of H_2,[9] and the recent study of the e^--CO system by Chandra and Gianturco.[10]

Recently, Bottcher[11] and Chang and Fano[12] have examined the fundamental justification of the adiabatic-nuclei theory of electron-molecule collisions by studying its relationship to the close-coupling formalism[1] with the aid of frame transformations. Unfortunately, in this form the derivation of the approximation bears little resemblance to the usual adiabatic (Born-Oppenheimer) treatment of bound molecular states.[13] Thus, the interesting question still remains, is it possible to obtain a unified adiabatic description of the nuclear motion in molecules which treats the bound and scattering (continuum) states on an equal basis?

Our work was originally motivated by the fact that the previous treatments of the adiabatic-

nuclei approximation did not include explicitly the molecular electrons and therefore could not describe the electronic excitation of the target. In this paper, we present the outlines of a general theory[14] which accounts for all the possible excitations of the molecule by electron impact except breakup (ionization or dissociation). Thus, our theory applies explicitly to electronic excitation which is always possible for sufficiently large impact energies.

Our derivation of the adiabatic-nuclei approximation is similar to the usual treatment of bound states,[13,14] but it emphasizes those aspects which are the most relevant for electron-molecule scattering. This approach has the advantage that it provides a unified formalism which treats all the molecular states, bound or continuum, on an equal footing. In addition, our analysis shows that the adiabatic-nuclei theory is no less justified formally than the close-coupling formalism.[1] Each method is based on the expansion of the total wave function in a complete set of basis functions; however, these functions are eigenstates of different zeroth-order Hamiltonians in the two cases. Each method is exact as long as all the terms are retained in the expansions. Since, in practice, one must deal with truncated, hence approximate, expansions, it is the rate of convergence of the alternative expansions which ultimately determine the success of the two methods. For sufficiently low impact energies, only a few target channels are open, and the close-coupling method is known to give accurate results.[1] On the other hand, when very many rotational and vibrational states (including dissociating states) are energetically accessible, the adiabatic-nuclei approximation seems to be more appropriate.

Another purpose of this paper is to propose a modification of the usual adiabatic scattering amplitude for inelastic electron scattering which may extend the range of its validity. We propose to replace the fixed-nuclei, electronic scattering

amplitude (which is on the energy shell) by a corresponding off-shell amplitude which satisfies exactly the requirement that the total energy (electronic plus nuclear) be conserved during the collision. This modification eliminates from the adiabatic theory the usual assumption that the difference between the initial and final energies of the scattered electrons is negligible.[2] Consequently, we expect that the modified formula will be more accurate near excitation thresholds, where this assumption breaks down.[1,12] From the practical point of view, only minor additional calculations are required to evaluate the cross section because the fixed-nuclei, electronic wave function, which must be calculated to extract the on-shell amplitude, contains the necessary off-shell information as well. However, a different off-shell amplitude is required for each rotational-vibrational transition as a result of energy conservation. Although the proposed formula appears in Chase's derivation[2] of the usual adiabatic formula, as far as we know, no one has ever suggested its possible usefulness or used it in numerical work.

Section II of the paper formulates the problem of electron-molecule collisions in general terms and establishes the notation. In Sec. III we derive the form of the adiabatic wave function, and then use its asymptotic behavior to extract the approximate scattering amplitude in Sec. IV. In Sec. V we obtain a modified expression for the scattering amplitude by using the adiabatic function directly in the exact T matrix. Section VI summarizes our conclusions.

II. GENERAL CONSIDERATIONS

For simplicity, we consider the scattering of an electron from a diatomic molecule with N elec-

trons. In terms of the relative coordinates, the total Hamiltonian describing the collision (and the bound states of the $N+1$ electron system, if any exist) is written in the form[15]

$$H^{(N+1)} = P_R^2/2\mu + H_{el}^{(N+1)}(\vec{r}, \vec{r}', \vec{R}) , \quad (1)$$

where the first term represents the relative kinetic energy of the nuclei, with μ denoting their reduced mass. The electronic Hamiltonian $H_{el}^{(N+1)}$ contains all the potential energy terms (including the nuclear-nuclear repulsion), and depends parametrically on the internuclear position vector $\vec{R}$. The superscript denotes the number of electrons involved, while $\vec{r}$ and $\vec{r}'$ label the scattered and target electrons, respectively. $H_{el}^{(N+1)}$ can be decomposed according to

$$H_{el}^{(N+1)}(\vec{r}, \vec{r}', \vec{R}) = H_{el}^{(N)}(\vec{r}', \vec{R}) + \tfrac{1}{2}P_e^2 + V(\vec{r}, \vec{r}', \vec{R}) , \quad (2)$$

where $\tfrac{1}{2}P_e^2$ is the kinetic energy of the projectile[16] and V represents the electron-molecule interaction. The total scattering wave function satisfies the equation

$$H^{(N+1)}\Psi_{E\Omega\alpha}^+ = E\Psi_{E\Omega\alpha}^+ . \quad (3)$$

Here α denotes the initial state of the target (electronic vibrational-rotational state) and Ω specifies the direction of the incident momentum vector $\vec{k}_\alpha$. The target states Φ_α are eigenstates of $H^{(N)}$ with energies w_α,

$$H^{(N)}\Phi_\alpha = [P_R^2/2\mu + H_{el}^{(N)}(\vec{r}', \vec{R})]\Phi_\alpha = w_\alpha\Phi_\alpha . \quad (4)$$

If $V(\vec{r}, \vec{r}', \vec{R})$ vanishes sufficiently rapidly as the coordinate of the scattered electron, $\vec{r}$, approaches infinity, $\Psi_{E\Omega\alpha}^+$ has the asymptotic form[17]

$$\Psi_{E\Omega\alpha}^+ \underset{r\to\infty}{\sim} k_\alpha^{1/2}(2\pi)^{-3/2} \sum_\beta^{\text{open}} [\delta_{\alpha\beta}e^{i\vec{k}_\alpha \cdot \vec{r}} - (2\pi)^2(k_\alpha k_\beta)^{-1/2}T_{\beta\alpha}(\Omega', \Omega)e^{ik_\beta r}/r]\Phi_\beta(\vec{r}', \vec{R}) , \quad (5)$$

where Ω and Ω' specify the directions of incident and final momentum vectors $\vec{k}_\alpha$ and $\vec{k}_\beta$, respectively. The conservation of energy requires that

$$E = \tfrac{1}{2}k_\beta^2 + w_\beta \quad (6)$$

for all open channels. The differential cross section for excitation of the molecule from state α to state β is given by

$$d\sigma_{\beta\alpha}/d\Omega' = (2\pi)^4 k_\alpha^{-2}|T_{\beta\alpha}(\Omega', \Omega)|^2 . \quad (7)$$

In the close-coupling formalism[1] of electron-molecule scattering, one chooses the internal states of the target molecule, $\{\Phi_\beta\}$, as basis states and expands $\Psi_{E\Omega\alpha}^+$ in the form[17]

$$\Psi_{E\Omega\alpha}^+ = \sum_\beta g_{\beta\alpha}(\vec{r})\Phi_\beta(\vec{r}', \vec{R}) , \quad (8)$$

where $\sum$ implies summation over the discrete states and integration over the continuum states. This choice of basis functions corresponds to a zeroth-order Hamiltonian which is correct asymptotically for $r\to\infty$, i.e., one which is obtained from $H^{(N+1)}$ by neglecting the electron-molecule interaction V [Eqs. (1) and (2)]. The functions $g_{\beta\alpha}(\vec{r})$ are the solutions of an infinite set of coupled equations in which the matrix elements of V in the basis $\{\Phi_\beta\}$ act as the couplings. Comparison of Eqs. (5) and (8) shows that the expression inside

the brackets in Eq. (5) gives the asymptotic form of $g_{\alpha\beta}(\vec{r})$. For practical calculations, the expansion in Eq. (8) and the corresponding coupled equations must be truncated at a manageable number of terms.

III. SCATTERING FUNCTION IN THE ADIABATIC-NUCLEI APPROXIMATION

Simple physical arguments show[2,12] that, for nonresonant scattering of electrons from neutral molecules, the collision time is short compared to the rotational and vibrational periods, provided the incident energy is greater than 0.1 eV. This fact suggests that one can neglect the kinetic energy of the nuclei in Eq. (1) to obtain another physically reasonable, zeroth-order Hamiltonian, $H_{\text{el}}^{(N+1)}$. The electronic wave functions ψ are solutions of the equation

$$H_{\text{el}}^{(N+1)}\psi(\vec{r},\vec{r}',\vec{R}) = \mathcal{S}(R)\psi(\vec{r},\vec{r}',\vec{R}) , \qquad (9)$$

where we indicate explicitly that both ψ and $\mathcal{S}$ depend parametrically on the internuclear distance. The discrete solutions of Eq. (9), denoted by ψ_ν, $\nu = 1, 2, \ldots, \nu_0$, represent the bound electronic

states of the electron-target system (negative ion) if any exist. The continuum solutions of Eq. (9) represent the scattering of an electron from the molecule in which the nuclei are fixed at a relative position $\vec{R}$; hence, these are called the fixed-nuclei scattering functions. Similarly, the bound electronic states of the target are represented by the usual Born-Oppenheimer functions $\phi_n(\vec{r}',\vec{R})$ which satisfy

$$H_{\text{el}}^{(N)}\phi_n(\vec{r}',\vec{R}) = \epsilon_n(R)\phi_n(\vec{r}',\vec{R}) . \qquad (10)$$

For sufficiently large $\mathcal{S}$, electronic excitation of the target is possible, and there are several linearly independent solutions of Eq. (9) with the same energy. For each $\vec{R}$, the scattering solution ψ^+ are normalized according to

$$\langle \psi_{\mathcal{S}\omega n}^+ \psi_{\mathcal{S}'\omega'n'}^+ \rangle = \delta(\mathcal{S}-\mathcal{S}')\delta(\omega-\omega')\delta_{nn'} . \qquad (11)$$

The subscript n labels the initial electronic state and ω specifies the orientation of the incident momentum vector $\vec{k}_n$. In the asymptotic region, $\psi_{\mathcal{S}\omega n}^+$ has the form

$$\psi_{\mathcal{S}\omega n}^+ \underset{r\to\infty}{\sim} k_n^{1/2}(2\pi)^{-3/2}\sum_{n'}^{\text{open}} [\delta_{nn'}e^{i\vec{k}_n\cdot\vec{r}} - (2\pi)^2(k_n k_{n'})^{-1/2}t_{n'n}(\omega',\omega;\vec{R})e^{ik_{n'}r}/r]\phi_{n'}(\vec{r}',\vec{R}) , \qquad (12$$

where ω' denotes direction of the final momentum vector $\vec{k}_{n'}$. The fixed-nuclei scattering amplitude $t_{n'n}(\omega'\omega;\vec{R})$ is a simple generalization of the elastic amplitude[3-5,9] ($n'=n$) to include electronic excitation

$$t_{n'n}(\omega',\omega;\vec{R}) = k_n^{1/2}(2\pi)^{-3/2}\int\int d\vec{r}\,d\vec{r}'\,e^{[-i\vec{k}_{n'}\cdot\vec{r}]}\phi_{n'}^*(\vec{r}',\vec{R})V(\vec{r},\vec{r}',\vec{R})\psi_{\mathcal{S}\omega n}^+(\vec{r},\vec{r}',\vec{R}) . \qquad (13)$$

We choose to label the scattering states in such a way that

$$\mathcal{S} = \epsilon_n(R) + \tfrac{1}{2}k_n^2 , \qquad (14)$$

where k_n is taken to be independent of R for the initial state. Consequently, one has the conservation relation

$$\tfrac{1}{2}k_{n'}^2 = \tfrac{1}{2}k_n^2 + \epsilon_n(R) - \epsilon_n'(R) , \qquad (15)$$

and, in general, both ϵ and $k_{n'}$ ($n'\neq n$) depend parametrically on R (see Fig. 1).

For each value of $\vec{R}$, the solutions of Eq. (9) form a complete set in the space of electronic coordinates. Hence, the exact scattering function can be expanded in the form

$$\Psi_{E\Omega\alpha}^+(\vec{r},\vec{r}',\vec{R}) = \sum_{\nu=1}^{\nu_0}\chi_\nu^{E\Omega\alpha}(\vec{R})\psi_\nu(\vec{r},\vec{r}',\vec{R}) + \sum_n\int_0^\infty k_n\,dk_n\int d\omega\,\chi_{\mathcal{S}\omega n}^{E\Omega\alpha}(\vec{R})\psi_{\mathcal{S}\omega n}^+(\vec{r},\vec{r}',\vec{R}) . \qquad (16)$$

This equation is simply the generalization of the usual Born-Oppenheimer expansion of the total wave function to the case of electron scattering or continuum states. The first sum contains the bound states of the electron-target system, if any exist, while the second term involves the fixed-nuclei scattering functions. It should be noted that the integration over k_n implies an integration over $\mathcal{S}$, the total *electronic* energy. In contrast, the total energy (electronic and nuclear) of the system, E, is constant [see Eqs. (6) and (14) and Fig. 1(a) for a comparison of E and $\mathcal{S}$].

The standard procedure of substituting the expansion for Ψ^+ into Eq. (3) and then eliminating the electronic coordinates results in an infinite set of coupled equations for the nuclear wave functions $\chi(\vec{R})$. In the special case where no bound state of the negative ion exists ($\nu_0 = 0$), the coupled equations have the form[18]

$$[(1/2\mu)\nabla_R^2 + \mathcal{E}'(R) - E]\chi_{\mathcal{E}'\omega'n'}^{E\Omega\alpha}(\vec{R}) = \sum_n \int_0^\infty k_n \, dk_n \int d\omega \, U_{\mathcal{E}'\omega'n',\,\mathcal{E}\omega n}(\vec{R})\chi_{\mathcal{E}\omega n}^{E\Omega\alpha}(\vec{R}) , \qquad (17)$$

where

$$U_{\mathcal{E}'\omega'n',\,\mathcal{E}\omega n}(\vec{R}) = (2\mu)^{-1}\Big[\int \psi_{\mathcal{E}'\omega'n'}^{+*}(\vec{r},\vec{r}',\vec{R})\nabla_R^2 \psi_{\mathcal{E}\omega n}^+(\vec{r},\vec{r}',\vec{R})\,d\vec{r}\,d\vec{r}'$$

$$+ 2\int \psi_{\mathcal{E}'\omega'n'}^{+*}(\vec{r},\vec{r}',\vec{R})\vec{\nabla}_R \psi_{\mathcal{E}\omega n}^+(\vec{r},\vec{r}',\vec{R})\,d\vec{r}\,d\vec{r}'\cdot\vec{\nabla}_R\Big]. \qquad (18)$$

The matrix operator U represents the dynamic coupling of the electrons to the vibration and rotation of the nuclei. The adiabatic-nuclei approximation is based on the assumption that such coupling is negligible. This assumption is valid when the fixed-nuclei electronic functions are sufficiently slowly varying functions of $\vec{R}$ so that U ~0. Thus, the adiabatic nuclear wave functions $\chi(R)$ are solutions of the uncoupled equations

$$[-(1/2\mu)\nabla_R^2 + \epsilon_n(R) + \tfrac{1}{2}k_n^2 - E]\,\chi_{\mathcal{E}\omega n}^{E\Omega\alpha}(\vec{R}) = 0 , \qquad (19)$$
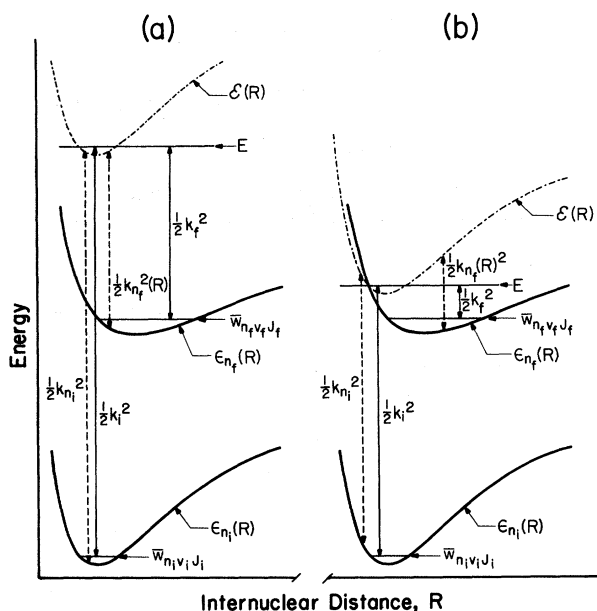

FIG. 1. Relationships between the various energies and electron momenta as a function of the internuclear distance R. The potential-energy curves of typical initial and final electronic states are labeled by ϵ_n. E is the total energy; $\mathcal{E}(R)$ is the total electronic energy (target electrons plus projectile) for fixed nuclei. The full vertical arrows indicate the energies of the incident and outgoing electrons; the dashed vertical arrows show the corresponding fixed-nuclei quantities. The energies of the target states are denoted by $\bar{w}$. The subscripts i and f distinguish quantities which refer to the initial and final states. Purely electronic energies, $\mathcal{E}(R)$, $\epsilon_n(R)$, and $\tfrac{1}{2}k_n^2(R)$ depend parametrically on R.

where we dropped the primes on $\mathcal{E}$, ω, and n, and substituted Eq. (14) for $\mathcal{E}(R)$. In neglecting the dynamic coupling between the electrons and nuclei for the electron-target system, one implicitly assumes that it is negligible for the target molecule itself. Therefore, in order to have an internally consistent approximation, one must represent the target states by the usual Born-Oppenheimer product, $\phi_n(\vec{r}',\vec{R})F_{nvJ}(\vec{R})$, where $\phi_n(\vec{r}',\vec{R})$ is just the electronic function of the target [see Eq. (10)]. The nuclear functions $F(\vec{R})$ are the solutions of the equation,

$$[-(1/2\mu)\nabla_R^2 + \epsilon_n(R) - \bar{w}_{nvJ}]F_{nvJ}(R) = 0 , \qquad (20)$$

where the bar on $\bar{w}_{nvJ}$ indicates that it is the adiabatic approximation to the exact molecular energy w_α. The vibrational and rotational states are labeled by v and J, respectively. A comparison of Eqs. (19) and (20) shows that

$$\chi_{\mathcal{E}\omega n}^{E\Omega\alpha}(\vec{R}) = \sum_{vJ} C_{\omega nvJ}^{E\Omega\alpha}\,\delta(\tfrac{1}{2}k_n^2 - E + \bar{w}_{nvJ})F_{nvJ}(\vec{R}) , \qquad (21)$$

where the constant C is yet to be determined by the boundary condition imposed on Ψ^+. After substituting Eq. (21) into (16), one can perform the integral over k_n to obtain (for the special case $\nu_0 = 0$),

$$\Psi_{E\Omega\alpha}(\vec{r},\vec{r}',\vec{R})$$

$$= \sum_n \int d\omega \sum_v^{v_{max}} \sum_J^{J_{max}} C_{\omega nvJ}^{E\Omega\alpha} F_{nvJ}(\vec{R})\psi_{\mathcal{E}\omega n}^+(\vec{r},\vec{r}',\vec{R}) , \qquad (22)$$

where $\mathcal{E}(R)$ is *fixed* to be

$$\mathcal{E}(R) = \epsilon_n(R) + \tfrac{1}{2}k_n^2 = \epsilon_n(\vec{R}) + E - \bar{w}_{nvJ} . \qquad (23)$$

The upper limits on the sums over v and J ensure that $(E - \bar{w}_{nvJ}) \geq 0$, since k_n^2 must be positive.

To evaluate the constants C, we compare the incoming parts of Ψ^+ and ψ^+ using Eqs. (5) and (12). If one labels the initial molecular state α (in the Born-Oppenheimer approximation) by the quantum numbers $n_i v_i J_i$, then Eq. (5) requires that

$$\Psi^{+}_{E\Omega\alpha} \xrightarrow[r\to\infty]{} k_{i}^{-1/2}(2\pi)^{-3/2} e^{i\vec{k}_{i}\cdot\vec{r}} \phi_{n_i}(\vec{r}',\vec{R})F_{n_i v_i J_i}(\vec{R})$$

$$\qquad + \text{(outgoing terms)}, \qquad (24)$$

where

$$\tfrac{1}{2}k_i^2 = E - \overline{w}_{n_i v_i J_i} \ . \qquad (25)$$

On the other hand, substitution of Eq. (12) into (22) yields,

$$\Psi^{+}_{E\Omega\alpha} \xrightarrow[r\to\infty]{} (2\pi)^{-3/2} \sum_{n} \int d\omega \sum_{v}^{v_{max}} \sum_{J}^{J_{max}} k_n^{-1/2} e^{i\vec{k}_n\cdot\vec{r}} \phi_n(\vec{r}',R)F_{nvJ}(\vec{R}) C^{E\Omega\alpha}_{\omega nvJ} + \text{(outgoing terms)} \ .$$

Recalling that Ω and ω are the solid angles of $\vec{k}_i$ and $\vec{k}_n$, respectively, one can use the orthogonality of the plane waves, ϕ_n and F_{nvJ}, to obtain

$$C^{E\Omega\alpha}_{\omega nvJ} = \delta_{nn_i}\delta_{vv_i}\delta_{JJ_i}\delta(\Omega-\omega) \ . \qquad (26)$$

Thus, in the adiabatic-nuclei approximation the total wave function has the simple form

$$\Psi^{+}_{En_i v_i J_i}(\vec{r},\vec{r}',\vec{R}) = \psi^{+}_{\mathcal{E}\Omega n_i}(\vec{r},\vec{r}',\vec{R})F_{n_i v_i J_i}(\vec{R}) \ ,$$
$$\qquad (27)$$

and energy conservation requires that

$$\mathcal{E}(R) = \epsilon_{n_i}(R) + E - \overline{w}_{n_i v_i J_i} = \epsilon_{n_i}(R) + \tfrac{1}{2}k_i^2 \ . \qquad (28)$$

The physical content of the result in Eq. (27) is completely consistent with the assumption that the collision time is short compared with the rotational and vibrational periods. The electronic part of $\Psi^{+}_{E\Omega\alpha}$ is just the fixed-nuclei scattering function ψ^{+} that describes the collision between the electron and target in which the *nuclei are fixed in space*. Furthermore, since the incident electron spends relatively little time near the nuclei, it does not contribute to the potential which governs the motion of the nuclei. Hence, it is the vibrational-rotational wave function of the initial state of the *target* which appears in Eq. (27) for $\Psi^{+}_{E\Omega\alpha}$.

The above analysis shows that, mathematically, the adiabatic-nuclei approximation involves the truncation of the expansion for $\Psi^{+}_{E\Omega\alpha}$ in Eq. (16), which is formally exact, to a single term. This truncation uncouples the equations which determine the nuclear functions $\chi(\vec{R})$. In principle, systematic improvements of the approximation are possible, just as in the close-coupling formalism. However, in practice, the solution of the problem is complicated by the continuous nature of the coupling. Perhaps a higher-order approximation could be obtained by converting a truncated set of equations [Eq. (17) for $n \leq n_{max}$ and $k_n \leq k_{max}$] into coupled integral equations. After the singularities are treated by a subtraction procedure,[19] the continuum can be "discretized" without the loss of accuracy. Such a procedure would lead to a finite number of coupled equations which may be handled by standard numerical techniques.

IV. SCATTERING AMPLITUDE IN THE ADIABATIC-NUCLEI APPROXIMATION

Once the form of the total scattering function is known, one can obtain an expression for the scattering amplitude which describes the simultaneous electronic-vibrational-rotational excitation of the target molecule. In the conventional approach,[3] one compares the outgoing parts of the exact and approximate wave functions, $\Psi^{+}_{E\Omega\alpha}$, in the asymptotic region. Using the Born-Oppenheimer approximation for the molecular states, Eq. (5) can be written in the form,

$$\Psi^{+}_{E\Omega\alpha} \xrightarrow[r\to\infty]{} (2\pi)^2 r^{-1} \sum_{n_f v_f J_f} (k_f k_i)^{-1} T_{n_f v_f J_f, n_i v_i J_i}(\Omega'\Omega)$$
$$\times e^{ik_f r}\phi_{n_f}(\vec{r}',\vec{R})F_{n_f v_f J_f}(\vec{R})$$

$$+ \text{(incoming terms)} \ , \qquad (29)$$

where the quantum numbers $(n_f v_f J_f)$ label the possible final states. Of course,

$$E = \tfrac{1}{2}k_f^2 + \overline{w}_{n_f v_f J_f} \ , \qquad (30)$$

and the incident momentum k_i is related to E as in Eq. (25). Substitution of the asymptotic form of the fixed-nuclei electronic function [Eq. (12)] into Eq. (27) gives

$$\Psi^{+}_{E\Omega\alpha} \xrightarrow[r\to\infty]{} (2\pi)^2 r^{-1} \sum_{n_f} (k_{n_f} k_{n_i})^{-1} t_{n_f n_i}(\Omega'\Omega;\vec{R})$$
$$\times e^{ik_{n_f}r}\phi_{n_f}(\vec{r}',\vec{R})F_{n_i v_i J_i}(\vec{R})$$

$$+ \text{(incoming terms)} \ . \qquad (31)$$

The initial and final "fixed-nuclei" momenta, k_{n_i} and k_{n_f}, are related through Eq. (15) and, as shown in Fig. 1(a), $k_{n_i} \equiv k_i$. Since the Born-Oppenheimer product functions $\phi_n(\vec{r}',\vec{R})F_{nvJ}(\vec{R})$ form an orthonormal set, a comparison of Eqs. (29) and (31) gives, for the T matrix,

$$T_{n_f v_f J_f, n_i v_i J_i}(\Omega'\Omega) = \int d\vec{R}\, F^{*}_{n_f v_f J_f}(\vec{R}) t_{n_f n_i}(\Omega'\Omega;\vec{R})$$
$$\times F_{n_i v_i J_i}(\vec{R})(k_f/k_{n_f})e^{i(k_{n_f}-k_f)r} \ .$$

$$\qquad (32)$$

The result in Eq. (32) suffers from two difficulties. For electronically inelastic collisions $(n_f \neq n_i)$, the "fixed-nuclei" momentum, k_{n_f} is a function of the internuclear distance R, unless the potential curves of the two electronic states are parallel [see Eq. (15) and Fig. 1(a)]. Even in the case of pure vibrational-rotational excitation $(n_f = n_i)$, k_{n_f} differs from k_f because the former, being a "fixed-nuclei" quantity, does not take into account the vibrational and rotational energy of the target.[3,12] Consequently, the above expression for the scattering amplitude is not independent of r, as it should be. In order to obtain a physically meaningful result, one must assume that, in the Franck-Condon region, i.e., for values of R at which the integrand in Eq. (32) is nonzero, the potential curves of the initial and final electronic states are reasonably parallel, and that $k_{n_f} \approx k_f$. The latter assumption is valid if the kinetic energy of the outgoing electron is large compared to the energy spacing between the rotational-vibrational levels, i.e., when the electron leaves the interaction region in a time short compared to the rotational and vibrational periods.[3,12] This situation is illustrated in Fig. 1(a), which shows the magnitudes of the relevant momenta for typical potential-energy curves. On the other hand, Fig. 1(b) illustrates the case when E is near the excitation threshold, k_f is small, and the assumption that $k_{n_f} \approx k_f$ is not valid.

For impact energies which are sufficiently larger than the excitation threshold, the expression for the scattering amplitude becomes

$$T_{n_f v_f J_f, n_i v_i J_i}(\Omega'\Omega) = \int d\vec{R}\, F^*_{n_f v_f J_f}(\vec{R})\, t_{n_f n_i}(\Omega'\Omega; \vec{R})$$
$$F_{n_i v_i J_i}(\vec{R})\ . \tag{33}$$

Thus, in the adiabatic-nuclei approximation, the T-matrix element for the transition $n_i v_i J_i \to n_f v_f J_f$ is just the fixed-nuclei amplitude "averaged over" the initial and final vibrational-rotational wave functions. The amplitude $t_{n_f n_i}$ describes the (possibly inelastic) collision of the electron with the molecule in which the nuclei are fixed in space at relative position $\vec{R}$, while the functions F_{nvJ} are the probability amplitudes for the internuclear vector having the value $\vec{R}$ in the initial and final states. In the case of electronic excitation of the target, the final nuclear wave function which appears in Eq. (33) is correctly associated with the potential-energy

curve of the final electronic state. In the case of electronically elastic collisions, Eq. (33) reduces to the results obtained previously.[2-5,12] In addition, if one chooses to evaluate $t_{n_f n_i}$ in the first Born approximation, i.e., one uses

$$t^{\text{Born}}_{n_f n_i}(\Omega', \Omega; \vec{R}) = \int\int d\vec{r}\, d\vec{r}'\, e^{i(\vec{k}_{n_i} - \vec{k}_{n_f})\cdot\vec{r}}$$
$$\times \phi^*_{n_f}(\vec{r}', \vec{R}) V(\vec{r}, \vec{r}', \vec{R})\phi_{n_i}(\vec{r}', \vec{R})\ , \tag{34}$$

then Eq. (33) reduces to the result which is expected in the Born approximation.

V. IMPROVED EXPRESSION FOR THE SCATTERING AMPLITUDE

The major shortcoming of the adiabatic-nuclei approximation for the scattering amplitude is its failure to describe correctly the energy region near excitation thresholds. It would be useful if this shortcoming could be remedied without unduly complicating the basic formalism.

Our approach to obtaining an improved expression for the amplitude consists of an alternative derivation which does not require any assumptions about the final momentum vector k_{n_f} [in addition to those assumptions which are necessary to uncouple Eq. (17)]. Instead of comparing the asymptotic behaviors of the exact and adiabatic scattering functions, one can start with the exact expression for the T matrix,

$$T_{\beta\alpha}(\Omega', \Omega)$$
$$= k_\beta^{1/2}(2\pi)^{-3/2}\int\int\int d\vec{r}\, d\vec{r}'\, d\vec{R}\, e^{-i\vec{k}_\beta\cdot\vec{r}}\, \Phi^*_\beta(\vec{r}', \vec{R})$$
$$\times V(\vec{r}, \vec{r}', \vec{R})\Psi^+_{E\alpha\Omega}(\vec{r}, \vec{r}', \vec{R})\ . \tag{35}$$

Again, Ω' specifies the direction of the final momentum vector $\vec{k}_\beta$ and Ψ^+ is the exact scattering function with the asymptotic form given in Eq. (5). The approximate T matrix can be obtained simply by substituting for Ψ^+, the adiabatic function in Eq. (27). In order to be internally consistent, one must use the Born-Oppenheimer function $\phi_{n_f} F_{n_f v_f J_f}$ to represent the final molecular state Φ_β $(\beta = n_f v_f J_f)$. Using $\vec{k}_f$ for $\vec{k}_\beta$ [see Eq. (30) and Fig. 1(a)], Eq. (35) becomes

$$T_{n_f v_f J_f, n_i v_i J_i}(\Omega'\Omega) = k_f^{1/2}(2\pi)^{-3/2}\int\int\int d\vec{r}\, d\vec{r}'\, d\vec{R}\, e^{-i\vec{k}_f\cdot\vec{r}}$$
$$\times \phi^*_{n_f}(\vec{r}', \vec{R}) F^*_{n_f v_f J_f}(\vec{R}) V(\vec{r}, \vec{r}', \vec{R})\psi^+_{\mathcal{E}\Omega n_i}(\vec{r}, \vec{r}', \vec{R}) F_{n_i v_i J_i}(\vec{R})\ , \tag{36}$$

where $\mathcal{S}$ is defined in Eq. (28). Performing the integrals over the electronic coordinates, one obtains

$$T_{n_f v_f J_f, \, n_i v_i J_i}(\Omega', \Omega)$$

$$= \int d\vec{R}\, F^*_{n_f v_f J_f}(\vec{R})\, t_{n_f n_i}(\mathcal{S}'\Omega', \mathcal{S}\Omega; \vec{R})\, F_{n_i v_i J_i}(\vec{R}) \, ,$$

$$(37)$$

where

$$\mathcal{S}' = \epsilon_{n_f}(\vec{R}) + \tfrac{1}{2} k_f^2 \, . \qquad (38)$$

The quantity $t_{n_f n_i}(\mathcal{S}'\Omega'; \mathcal{S}\Omega; \vec{R})$ is just the generalization of the fixed-nuclei amplitude for the electronic transition $n_i \rightarrow n_f$ [Eq. (13)] off the energy shell. It is given explicitly by

$$t_{n_f n_i}(\mathcal{S}'\Omega', \mathcal{S}\Omega; \vec{R})$$

$$= k_f^{1/2}(2\pi)^{-3/2} \int \int d\vec{r}\, d\vec{r}'\, e^{-i\vec{k}_f \cdot \vec{r}}$$

$$\times \phi_{n_f}(\vec{r}', \vec{R})\, V\psi_{\mathcal{S}\Omega n_i}(\vec{r}, \vec{r}', \vec{R}) \, .$$

$$(39)$$

It is an off-shell quantity because $k_f \neq k_{n_f}$ and hence $\mathcal{S}' \neq \mathcal{S}$ [compare Eqs. (15), (28), and (38) and see Fig. 1]. Of course, for impact energies large compared to excitation thresholds, k_f approaches k_{n_f}, and Eq. (37) reduces to our previous expression in Eq. (33) containing the on-shell $t_{n_f n_i}$.

Since the derivation of the adiabatic expression in Eq. (37) required no assumptions about k_f, we expect it to have a wider range of validity near excitation thresholds. It still has the desirable feature that the electronic part of the problem can be solved for fixed nuclei, and then the electronic amplitude is averaged over the initial and final vibrational-rotational functions. On the other hand, the magnitude of k_f depends on the final quantum numbers $n_f v_f J_f$ (in contrast to k_{n_f} which depends only on n_f) and, consequently, the off-shell amplitude $t_{n_f n_i}$ must be recalculated for each final vibrational-rotational state of interest. This should not be too cumbersome unless a great number of final states is treated. The fact that the electronic T matrix is required off the energy shell should cause no major difficulties for any computational scheme which obtains the scattering information via an approximate wave function. Once the fixed-nuclei function $\psi^+_{\mathcal{S}\Omega n}$ has been calculated, the required off-shell information can be extracted by directly integrating Eq. (39).

VI. CONCLUSIONS

In this paper we have examined the adiabatic-nuclei theory of nonresonant electron-molecule collisions. Our main results can be summarized as follows.

(i) It is possible to derive the adiabatic approximation from a *formally exact* expansion of the total scattering function in terms of the basis functions which are solutions of the electronic Hamiltonian, with the nuclei fixed in space. The approximation involves the truncation of the expansion to a single term. The resulting adiabatic scattering solution is a product of the fixed-nuclei electronic function and the vibrational-rotational wave function of the initial state. Here we have not discussed in detail the physical arguments justifying the adiabatic approximation nor the criterion for its validity, because these questions have already been examined extensively elsewhere.[2,12]

(ii) Since our approach follows closely the usual adiabatic (Born-Oppenheimer) treatment of bound molecular states,[13] we obtain a unified formalism which handles all molecular states, bound *or* scattering, on equal footing.

(iii) We have derived an expression for the adiabatic scattering amplitude which applies to the general case of (nonresonant) electronic, vibrational, and rotational excitation of molecules by electron impact. In the case of "electronically elastic" collisions, our formula reduces to previous results.[3] In the case of electronic excitations, the adiabatic theory is complicated by the fact that the potential-energy curves of the initial and final electronic states are not parallel. However, for impact energies sufficiently large compared to the excitation threshold, the adiabatic approximation should be valid. Details of the inelastic formalism[18] will be presented in another paper.

(iv) In an attempt to increase the range of validity of the adiabatic-nuclei approximation near thresholds, we have proposed an alternative expression for the scattering amplitude. It contains the fixed-nuclei amplitude for the electronic transition off the energy shell. The utility of the modified expression must still be tested by calculations. This will be possible in the near future because the numerical treatment of electronically inelastic, molecular collisions, at a level beyond the first Born approximation, is now feasible.[20]

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