

Theory of near-adiabatic collisions. I. Electron translation factor method

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(Received 24 June 1977)

The theory of near-adiabatic collisions is formulated in a fully quantum-mechanical form, correctly taking into account the role of electron translation factors (ETF's). A general form for the ETF, using switching functions, is given for systems which are electrically either asymmetric or symmetric (with or without mass asymmetry). The main result is that the close-coupled scattering equations obtained in the perturbed-stationary-states theory must be replaced by equations of identical form, but having modified nonadiabatic coupling matrices. In general, the corrections involved are substantial; their nature, and effect on coupling matrices, is discussed, and conditions when they are likely to be important are described. The remaining problem of determining the switching function is discussed briefly. The correct form for ETF's, their quantum-mechanical formulation, and the resulting correct form for the coupled equations, have not been given previously.

I. INTRODUCTION

In 1958 Bates and McCarroll¹ pointed out that a barycentric description of scattering states for atomic collisions requires inclusion of a factor representing translation of electrons bound to the collision partners. The relevance of such factors for the theory of electron transfer processes at high energies was quickly recognized, which accounts for the name "momentum-transfer factor" commonly used for them in that context. In the atomic representations best suited to fast collisions, where the interaction potential of the colliding subsystems is not diagonal and is the source of electronic transitions, the effect of these factors appears only *via* their influence on the overlap of electronic states bound to different centers. This effect becomes quite small for low collision velocities, which explains the statement often made that "momentum-transfer factors are important only for high energies."

General recognition of the more subtle but equally important role of electron translation factors in the theory of *slow* collisions has taken longer, in spite of the fact that papers by several workers¹⁻⁶ took the relevant effects into account, in at least an asymptotically correct way. For slow collisions, an *adiabatic* and *molecular* description of electronic states is appropriate; in molecular representation, the full electronic Hamiltonian is diagonal at each nuclear configuration, and transitions arise from time dependence of this Hamiltonian and its eigenfunctions produced by the motion of the nuclei. Electron translation factors (ETF's) are important to slow collision theory because they generate essential corrections to the

"nonadiabatic coupling" operators responsible for transitions. These corrections are comparable to, and have the same velocity dependence as, the uncorrected transition operators arising from the simple perturbed-stationary-states (PSS) theory. In certain cases, unless the ETF corrections are included a grossly incorrect physical result is obtained from the theory.

Although there is a growing awareness of the problem posed by these factors and their effects on nonadiabatic coupling,⁷⁻¹⁰ considerable confusion and divergence of opinion still exists in current literature. Contributions in theoretical chemistry often ignore the problem entirely and use uncorrected PSS theory. Other work¹¹ takes the point of view that the required corrections are relevant only to the asymptotic behavior of the system, an approach which leads to poor results in some important problems. Many treatments which explicitly include ETF's do so in a manner appropriate for atomic state representations^{1-3,7} but not for an adiabatic, molecular representation; this brings significant asymmetries and nonorthogonalities into the resulting theory. Still other approaches^{9,10} regard the problem as a question of the choice of reference origin for electron coordinates: if, for an electron bound to a particular atomic center, that center be taken as reference origin, then ETF's do not appear and the required corrections are automatically included—at least asymptotically. These approaches are completely equivalent to the methods (cited above) using atomic ETF's; they require the assignment of a fixed atomic reference origin to each electronic state, even though such states may have essentially molecular character during a collision. In some cases

this leads to unphysical results for the nonadiabatic couplings.

Translation factors appropriate to molecular states can be constructed using an approach first suggested by Schneiderman and Russek⁴ and developed by Thorson and co-workers^{5,6} to study the problem of direct impact ionization in proton—H (1s) collisions. The introduction of a *switching function* into the electron translation factor permits a description of electron translation which is locally adapted to the electron's position in the molecule, or, in effect, selects a locally appropriate reference origin. Formulations using switching functions avoid the difficulties of the methods described above and greatly improve the physical behavior of coupling matrix elements, especially for the case of impact ionization. However, such formulations have been lacking in rigor or generality; they have been restricted to specially symmetric systems such as H_2^+ , or to special types of transitions, and they have relied on semiclassical approximations or impact-parameter treatments to obtain their results. Finally, a systematic and unified physical interpretation of the resulting effective Hamiltonian for slow collisions has not previously been given.

In this paper and the one following it,¹² we present a rigorous formulation of the theory of slow atomic collisions, based on the use of switching functions, which remedies these defects. The effects of electron translation factors are incorporated in a fully quantum-mechanical description of slow collisions. The essential result is the set of coupled differential equations (3.13) for heavy particle motion. These are completely analogous to the usual coupled equations of molecular collision theory (e.g., those obtained by the PSS formulation), but they contain correction terms arising from electron translation. In this paper, our approach uses the electron-translation-factor concept explicitly, and at a suitable point we employ a quantum transcription formula to obtain the fully quantum-mechanical equations (3.7, 3.13). Though the results are correct, the derivation lacks rigor. In the second paper¹² we formulate the theory using an entirely different approach, originally conceived by Mittleman and his co-workers,¹³ who used it to discuss nonadiabatic effects in very low-energy elastic scattering of helium atoms. This approach is rigorous and fully quantum mechanical. The switching function is used to define a nonlinear coordinate transformation, which then generates the ETF corrections in the transformed Hamiltonian. Our derivation differs from Mittleman's in certain respects; it is more general and systematic and leads directly to the same coupled equations (3.7, 3.13) as are obtained in this paper.

Combining the two approaches allows us to obtain a unified physical interpretation of the entire problem and the resulting coupled equations.

The plan of this paper is as follows: In Sec. II, we present a brief review of the basic theory of slow collisions which shows why electron translation factors are necessary and how they have been used in the past. Although little of the material in this section is new, it is helpful to present it here because misunderstanding of this problem has been so widespread. At the end of the section, we postulate a formal definition of ETF's appropriate to a quantum-mechanical slow collision theory. In Sec. III, we derive the resulting coupled equations for scattering theory, first in three-dimensional form [Eqs. (3.7, 3.13)] and then in radial form [Eqs. (3.22), and the decoupled approximation (3.25)].

The effects of ETF's on the coupled equations are of two types. The first and most important of these is that the nonadiabatic coupling matrix \underline{P} of PSS theory is replaced by the corrected coupling ($\underline{P} + \underline{\tilde{A}}$), where the ETF correction $\underline{\tilde{A}}$ is defined in Eqs. (3.9). Secondly, there are additional and much smaller terms, which are more fully analyzed in the succeeding paper. In Sec. IV we give a brief discussion of the correction matrix $\underline{\tilde{A}}$ and its effects on the nonadiabatic couplings in Eqs. (3.12) for a variety of physical situations.

The *switching function*, which plays a central role in either formulation of the theory, and which explicitly determines the correction matrix $\underline{\tilde{A}}$, is not uniquely prescribed by the theory, though it must satisfy certain asymptotic constraints. Given a choice for the switching function, a formally rigorous set of close-coupled equations for heavy-particle motion is obtained, but no criterion for selecting the switching function is evolved by the derivation, and there is no guarantee that any particular choice is an optimal or even a good one. As a matter of fact, we can obtain corrected nonadiabatic couplings which are equivalent to those obtained by the methods cited earlier, and in certain cases are obviously much more sensible, by taking very simple or even trivial choices for the switching function. Nevertheless, the development of useful criteria for the determination of the switching function remains an important unsolved problem. In Sec. V, we briefly discuss this problem, and some perspectives on it. A related question is whether a formulation of this type really offers significant *practical* (as well as formal) improvements over earlier methods. While the state of both theory and experiment is such that no good experimental test of this equation is yet available, we believe that arguments for the practical superiority of this method can be made;

we discuss these arguments, and some possible test problems, in Sec. V as well.

In both these papers, we restrict discussion to the case of one electron, mainly to avoid confusing and unnecessary complications. The theory can be generalized to a many-electron system without essential difficulties.

II. ASYMPTOTIC STATES AND TRANSLATION FACTORS

A. System description

We consider a system of one electron (mass m_0) and two heavy particles A, B (masses M_A, M_B) to which it may be bound. With respect to an external origin these have coordinates $\vec{r}^0, \vec{R}_A^0, \vec{R}_B^0$; we also introduce the center of mass and some other coordinates (Fig. 1): Center of mass:

$$\vec{R}_{\text{CM}}^0 = M^{-1}(M_A \vec{R}_A^0 + M_B \vec{R}_B^0 + m_0 \vec{r}^0), \quad (2.1a)$$

$$M_T = M_A + M_B + m_0. \quad (2.1b)$$

Center of mass of nuclei (CMN):

$$\vec{R}_{\text{CMN}}^0 = (M_A + M_B)^{-1}(M_A \vec{R}_A^0 + M_B \vec{R}_B^0). \quad (2.1c)$$

Relative heavy particle coordinate:

$$\vec{R} = \vec{R}_B^0 - \vec{R}_A^0. \quad (2.1d)$$

Several relative electron coordinates:

$$\vec{r} = \vec{r}^0 - \vec{R}_{\text{CMN}}^0, \quad (2.2a)$$

$$\vec{r}_g = \vec{r}^0 - \frac{1}{2}(\vec{R}_A^0 + \vec{R}_B^0), \quad (2.2b)$$

$$\vec{r}_A = \vec{r}^0 - \vec{R}_A^0, \quad (2.2c)$$

$$\vec{r}_B = \vec{r}^0 - \vec{R}_B^0. \quad (2.2d)$$

\vec{r}_g is the electron coordinate from the *geometric* center of the system, while \vec{r} is measured from

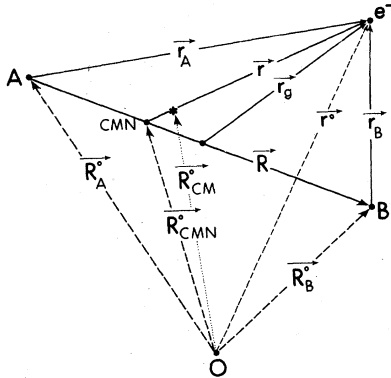


FIG. 1. Coordinates for the general molecular system A, B, e . Vectors with superscript zero are measured from an external origin O . \vec{r}_g is the vector to e from the geometric center; CMN is the center of mass of the nuclei and is the origin for \vec{R} . The points CMA, CMB, and the relative vectors \vec{R}_A, \vec{R}_B are not shown [cf. Eqs. (2.10) ff].

CMN. As is well known the kinetic energy T_{total} can be expressed in terms of the center of mass motion and momenta \vec{P}, \vec{p} , conjugate, respectively, to relative heavy particle and electron coordinates \vec{R}, \vec{r}

$$T_{\text{total}} = T_{\text{CM}} + T, \quad (2.3a)$$

$$T_{\text{CM}} = (\vec{P}_{\text{CM}}^0)^2 / 2M_T, \quad (2.3b)$$

$$T = \vec{p}^2 / 2\mu + \vec{p}^2 / 2m \quad (2.3c)$$

with reduced masses μ, m given by

$$\mu = M_A M_B / (M_A + M_B), \quad (2.4a)$$

$$m = m_0 (M_A + M_B) / M_T. \quad (2.4b)$$

We will call m the "molecular electronic reduced mass."

We assume that the system potential energy can be expressed in terms of (\vec{r}, \vec{R}) and at least asymptotically has the usual pairwise form

$$V(\vec{r}; \vec{R}) = V_e^A(r_A) + V_e^B(r_B) + V_N(R). \quad (2.5)$$

(If \vec{r} is expressed in coordinates rotating with the axis \vec{R} , V depends only upon $R = |\vec{R}|$, but for the moment we need not use this fact). The Hamiltonian for relative motion is

$$H = T + V, \quad (2.6a)$$

$$H = T_R + h(\vec{r}; \vec{R}), \quad (2.6b)$$

where

$$h(\vec{r}; \vec{R}) = \vec{p}^2 / 2m + V(\vec{r}; \vec{R}) \quad (2.6c)$$

is the usual molecular electronic Hamiltonian. These equations define either the classical functions or the corresponding quantum-mechanical operators.

B. Molecular and atomic electronic states

The usual adiabatic (Born-Oppenheimer) molecular electronic states $\phi_n(\vec{r}; \vec{R})$ are defined as the eigenfunctions of $h(\vec{r}; \vec{R})$, which depend parametrically upon \vec{R} ,

$$h(\vec{r}; \vec{R}) \phi_n(\vec{r}; \vec{R}) = \epsilon_n(R) \phi_n(\vec{r}; \vec{R}). \quad (2.7)$$

These molecular functions eventually form the backbone of our electronic state description for slow collisions, but we must now look at them more carefully.

Interactions of the electron with centers A, B have been represented by the potentials of structureless cores (which need not be bare nuclei). Since we assume that $V_e^J(r_J)$ ($J=A, B$) goes to zero at least as fast as r_J^{-1} when $r_J \rightarrow \infty$, bound electronic states of Eq. (2.7) must become asymptotic bound states of center A or center B . However to describe this correlation we must distinguish be-

tween *symmetric* systems, where V_e^A and V_e^B are identical functions of their respective arguments, and *asymmetric* systems, where they are different.

(i) For *asymmetric systems*, as $R \rightarrow \infty$ we may associate, in one-to-one fashion, to each bound molecular state ϕ_n , a corresponding bound "atomic" state, either of *A* or of *B*,

$$\lim_{R \rightarrow \infty} [\epsilon_n(R)] = \epsilon_{n_J}, \quad (2.8)$$

$$\lim_{R \rightarrow \infty} [\phi_n(\vec{r}; \vec{R})] = \phi_{n_J}(\vec{r}_J), \quad (2.9a)$$

($J = \text{either } A, \text{ or } B$). The limiting correlation $n \leftrightarrow (J, n_J)$ may be subsumed in the state designation n . (We ignore accidental degeneracies of *A* levels with *B* levels.)

(ii) For *symmetric systems*, the electronic Hamiltonian has parity symmetry about the geometric center; it follows that the eigenfunctions $\phi_n(\vec{r}; \vec{R})$ are parity eigenstates and always occur in exactly degenerate pairs (ϕ_n^s, ϕ_n^u) as $R \rightarrow \infty$. These are related to an equally degenerate pair of limiting bound "atomic" states $\phi_{n_J}(\vec{r}_J)$ by the equation

$$\begin{aligned} \phi_{n_J}(\vec{r}_J) &= \lim_{R \rightarrow \infty} [2^{-1/2} (\phi_n^s \pm \phi_n^u)], \\ + \leftrightarrow J = B, \quad - \leftrightarrow J = A. \end{aligned} \quad (2.9b)$$

Although bound molecular states $\phi_n(\vec{r}, \vec{R})$ are thus asymptotically related to limiting states of atomic character, $\phi_{n_J}(\vec{r}_J)$, these asymptotic states are not the exact atomic eigenstates, as we shall see below. We now discuss the description of atomic states of the system.

In an asymptotic condition $R \rightarrow \infty$, we may have bound states of "A" [$(A + e^-) + B$], or of "B" [$A + (B + e^-)$], but for truly separated subsystems the molecular coordinates used above are inappropriate. For instance, in channel *B*, the logical coordinates are: \vec{R}_A^0 ; the center-of-mass of subsystem *B*, $\vec{R}_{\text{CMB}}^0 = (M_B \vec{R}_B^0 + m_0 \vec{r}^0) / (M_B + m_0)$; and the relative electron coordinate \vec{r}_B . In terms of the corresponding conjugate momenta, the kinetic energy is

$$T_{\text{total}} = (\vec{P}_A^0)^2 / 2M_A + (\vec{P}_{\text{CMB}}^0)^2 / 2(M_B + m_0) + (\vec{p}_B)^2 / 2m_B, \quad (2.10a)$$

where

$$m_B = m_0 M_B / (M_B + m_0). \quad (2.10b)$$

Again we can extract the center-of-mass motion for the whole system, if we define the *B*-channel relative coordinate \vec{R}_B ,

$$\vec{R}_B = \vec{R}_{\text{CMB}}^0 - \vec{R}_A^0.$$

The relative kinetic energy is then given by

$$T = (\vec{P}_B)^2 / 2\mu_B + (\vec{p}_B)^2 / 2m_B, \quad (2.10c)$$

where

$$\mu_B = M_A(M_B + m_0) / M_T. \quad (2.10d)$$

Obviously the next step is to define the atomic electronic Hamiltonian,

$$h_0^B(\vec{r}_B) = \vec{p}_B^2 / 2m_B + V_e^B(\vec{r}_B) \quad (2.11a)$$

and its eigenstates $\phi_{n_B}^0(\vec{r}_B)$,

$$h_0^B(\vec{r}_B) \phi_{n_B}^0(\vec{r}_B) = \epsilon_{n_B}^0 \phi_{n_B}^0(\vec{r}_B). \quad (2.11b)$$

An analogous result holds for channel *A*, except that we define $\vec{R}_A = \vec{R}_B^0 - \vec{R}_{\text{CMA}}^0$ to preserve the sense of this vector with respect to \vec{R} .

Because $m_J \neq m$, the limiting form of the molecular electronic Hamiltonian $h(\vec{r}; \vec{R})$ in channel *J* is *not* equal to h_0^J , and the eigenfunctions $\phi_{n_J}^0$ and eigenvalues $\epsilon_{n_J}^0$ are not equal to ϕ_{n_J} and ϵ_{n_J} , the asymptotic limits of the molecular quantities, given by Eqs. (2.7)–(2.9). However, the differences are of order $\sim (m/\mu)$ in both energies and wave functions, and from this it follows, using perturbation theory, that

$$\begin{aligned} \epsilon_{n_J}^0 - \epsilon_{n_J} &= \frac{1}{2}(m_J^{-1} - m^{-1}) \langle \phi_{n_J} | (-\hbar^2 \vec{\nabla}_{n_J}^2) | \phi_{n_J} \rangle \\ &+ O(m/\mu)^2 \epsilon_{n_J}^0, \end{aligned} \quad (2.12)$$

i.e., to errors $\sim (m/\mu)^2 \epsilon_{n_J}^0$ we can calculate the correct atomic energies by computing expectation values of the difference between atomic and molecular electronic Hamiltonians upon the molecular approximations ϕ_{n_J} to the exact states $\phi_{n_J}^0$. Equation (2.12) will be useful later.

C. Asymptotic scattering states

1. Origin of electron translation factors

Scattering boundary conditions are expressed in terms of asymptotic channel wave functions which satisfy the Schrödinger equation exactly in the limit $R \rightarrow \infty$. Such wave functions are eigenfunctions of the "free" or "interactionless" Schrödinger equation with a given total momentum and energy, and are easily expressed in the atomic coordinates appropriate to that channel;

$$\begin{aligned} \Psi_{\text{total}}^J &= \phi_{n_J}^0(\vec{r}_J) \exp(i\vec{k}_J^0 \cdot \vec{R}_J^0) \\ &\times \exp(i\vec{k}_{\text{CMJ}}^0 \cdot \vec{R}_{\text{CMJ}}^0). \end{aligned} \quad (2.13a)$$

Here $\hbar\vec{k}_J^0$ and $\hbar\vec{k}_{\text{CMJ}}^0$ are the eigenvalues of momenta conjugate to \vec{R}_J^0 and \vec{R}_{CMJ}^0 respectively: J' denotes the center to which the electron is *not* bound. Extracting and suppressing the free center-of-mass motion, we write this in terms of the relative coordinates for channel *J* as

$$\Psi^J = \phi_{n_J}^0(\vec{r}_J) \exp[i\vec{k}_J \cdot \vec{R}_J], \quad (2.13b)$$

where $k_J = |\vec{k}_J|$ is defined so as to conserve the relative energy E ,

$$\hbar^2 k^2 / 2\mu_J + \epsilon_{n_J}^0 = E. \quad (2.14)$$

Now let us reexpress this wave function (2.13b) for relative motion in terms of the molecular coordinates (\vec{r}, \vec{R}) ; to do this we need the easily proven relations

$$\begin{aligned} \vec{R}_B &= [M_B M_T / (M_B + m_0)(M_A + M_B)] \\ &\quad + [m_0 / (M_B + m_0)] \vec{r}, \end{aligned} \quad (2.15a)$$

$$\begin{aligned} \vec{R}_A &= [M_A M_T / (M_A + m_0)(M_A + M_B)] \vec{R} \\ &\quad - [m_0 / (M_A + m_0)] \vec{r}. \end{aligned} \quad (2.15b)$$

The result obtained is

$$\begin{aligned} \Psi^J &= \exp[i\vec{k} \cdot \vec{R}] \phi_{n_J}^0(\vec{r}_J) \\ &\quad \times \exp[\pm i(m/M_J)\vec{k} \cdot \vec{r}], \end{aligned} \quad (2.16)$$

where

$$\begin{aligned} \vec{k} &= [M_J M_T / (M_J + m_0)(M_A + M_B)] \vec{k}_J \\ &= (\mu / \mu_J) \vec{k}_J. \end{aligned} \quad (2.17)$$

The first factor in (2.16) is the plane wave representing the motion of the nuclei with momentum $\hbar\vec{k}$; the speed of this motion is

$$|\vec{v}| = |\hbar\vec{k} / \mu| = |\hbar\vec{k}_J / \mu_J|, \quad (2.18)$$

i.e., the same as the speed of atom J relative to nucleus J' . The second and third factors in (2.16) together make up what is considered to be the electronic part of the wave function; the exact atomic eigenstate centered on nucleus J is multiplied by the *electron translation factor*, representing the momentum of the electron (with respect to CMN) as it is carried along with that nucleus.

2. An illuminating proof

In this subsection we verify directly that the wave function (2.16) expressed in molecular coordinates (\vec{r}, \vec{R}) is indeed an exact solution of the asymptotic Schrödinger equation whose Hamiltonian is expressed in these coordinates. This is performing a trivial proof of the hard way, since it is obvious that (2.16) and (2.13) are equivalent and that (2.13) satisfies the free Schrödinger equation. However, we can learn a great deal from this proof since it makes very clear the significance of the ETF and its role in the solution.

When the molecular form of the Hamiltonian [Eqs. (2.3c) and (2.6)] acts on the wave function (2.16), the result is

$$\begin{aligned} H\Psi^J &= \exp(i\vec{k} \cdot \vec{R}) \exp[\pm i(m/M_J)\vec{k} \cdot \vec{r}] \\ &\quad \times \{[(\hbar^2 k^2 / 2\mu) + (\hbar^2 k^2 / 2m)(m/M_J)^2] \phi_{n_J}^0 - [(i\hbar^2 \vec{k} / \mu) \cdot \vec{\nabla}_R \phi_{n_J}^0 \pm (i\hbar^2 \vec{k} / m)(m/M_J) \cdot \vec{\nabla}_r \phi_{n_J}^0] \\ &\quad + [-(\hbar^2 / 2\mu) \vec{\nabla}_R^2 \phi_{n_J}^0 - (\hbar^2 / 2m) \vec{\nabla}_r^2 \phi_{n_J}^0 + V(\vec{r}; \vec{R}) \phi_{n_J}^0]\}. \end{aligned} \quad (2.19)$$

Now, since $\phi_{n_J}^0$ is a function only of \vec{r}_J , and since we can write

$$\vec{r}_J = \vec{r} - \frac{1}{2}(\lambda \pm 1)\vec{R}, \quad (2.20)$$

where

$$\lambda = (M_A - M_B) / (M_A + M_B), \quad (2.21)$$

it then follows that the second term in (2.19), containing the gradients of $\phi_{n_J}^0$, vanishes exactly:

$$\begin{aligned} [\vec{\nabla}_R \pm (\mu/M_J)\vec{\nabla}_r] \phi_{n_J}^0(\vec{r}_J) \\ = [-\frac{1}{2}(\lambda \pm 1) \pm (\mu/M_J)] \vec{\nabla}_r \phi_{n_J}^0(\vec{r}_J) \equiv 0. \end{aligned} \quad (2.22)$$

(In all above expressions the upper sign is used if $J=B$, the lower if $J=A$.) Note that (2.22) is valid for *any* function only of \vec{r}_J .

Of the two terms in (2.22), the first arises from the nuclear kinetic energy operator acting on the nuclear wave function in Ψ , and it also appears in the PSS theory; note especially that it generally *does not vanish* as $R \rightarrow \infty$. It is well known that the PSS theory leads to infinite-range matrix elements that have no physical meaning. Equation (2.22) shows us that *these spurious infinite-range terms*

are exactly cancelled by the asymptotic terms arising from the ETF.

Again with the use of (2.20) it is easily shown that the kinetic energy terms in the last part of Eq. (2.19) combine to yield

$$\begin{aligned} \{-\frac{1}{2}\hbar^2[m^{-1} + (\lambda \pm 1)/4\mu] \vec{\nabla}_r^2 + V\} \phi_{n_J}^0 \\ = \{-\frac{1}{2}\hbar^2[m_J^{-1} \vec{\nabla}_r^2] + V\} \phi_{n_J}^0 = \epsilon_{n_J}^0 \phi_{n_J}^0. \end{aligned} \quad (2.23)$$

Now, the terms $-(\hbar^2/2\mu)\vec{\nabla}_R^2$ also arise in the PSS theory, except that there of course ϕ_{n_J} appears instead of $\phi_{n_J}^0$. Equation (2.23) shows that at large R these terms just modify the reduced mass from m to m_J , and from Eq. (2.12) we know that this gives the correct atomic electronic binding energy (to within errors $\sim (m/\mu)^2 \epsilon_{n_J}^0$).

The terms in (2.19) thus simplify to

$$\hbar^2 k^2 / 2\mu + (\hbar^2 k^2 / 2m)(m/M_J)^2 + \epsilon_{n_J}^0 = E, \quad (2.24)$$

which is equivalent [via (2.17)] to the conservation of energy condition (2.14). The first term in (2.24) is the nuclear kinetic energy and the second is the translational kinetic energy of the electron carried along with nucleus J . This

completes our proof that (2.16) satisfies the free Schrödinger equation and shows clearly the part played by the ETF in it.

D. Molecular basis sets

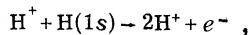
In the "close-coupled" treatment of the theory of fast atomic collisions, the full wave function is expanded in a set of electronic channel eigenstates such as those in Eq. (2.16), i.e., exact atomic states times the associated "atomic" ETF's. However, for slow, nearly adiabatic collisions, such an atomic representation is unsuitable, and we need instead to use molecular eigenfunctions and some sort of "molecular" ETF. In this section we discuss some types of molecular state descriptions used in the past, and we introduce a new form for such a description.

1. Unmodified Born-Oppenheimer states (PSS theory)

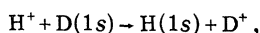
In the perturbed-stationary-states formulation of slow collision theory the electronic basis states are taken to be simply the Born-Oppenheimer states $\phi_n(\vec{r}; \vec{R})$, with no electron translation factors; the full wave function is expanded in the form

$$\Psi = \sum_n \chi_n(\vec{R}) \phi_n(\vec{r}; \vec{R}). \quad (2.25)$$

This formulation is still used in most calculations of cross sections for slow atomic collisions. However, it is evident from the analysis of the preceding section that individual terms in (2.25) do not satisfy the scattering boundary conditions because they can never be solutions of the free Schrödinger equation. Terms involving $\vec{\nabla}_R \phi_n$ arise, which do not vanish asymptotically and in this case no ETF corrections arise to cancel them; this leads to fictitious infinite-range couplings. Secondly, even those PSS nonadiabatic couplings $\langle \phi_{n'} | \vec{\nabla}_R | \phi_n \rangle$ which do vanish asymptotically can often be unrealistically large in the interaction region. For example, (a) in the calculation of the cross section for low-energy impact ionization of hydrogen atoms by protons,^{5,6}



Thorson and co-workers found that the PSS matrix elements are implausibly large and many of them are cancelled by the ETF corrections; (b) in resonant charge transfer in isotopic systems, such as



the PSS theory gives a large but completely fictitious (g, u) coupling which is exactly can-

celled by the ETF corrections¹²; (c) more generally, the PSS matrix elements for all transitions involving electron transfer are likely to be in error, even though they vanish asymptotically. Although in certain specific cases the PSS theory does give reliable results, the simple expansion (2.25) is not generally satisfactory.

In addition to these serious defects of the PSS expansion, there are also some other infinite-range PSS couplings which are *not* important physically. These arise from the off-diagonal matrix elements $\langle \phi_{n'} | \vec{\nabla}_R^2 | \phi_n \rangle$, rather than the gradient couplings; as we have seen above, they reflect the fact that the molecular asymptotic approximations $\phi_{n'}$ to atomic states differ from the exact atomic states $\phi_{n'}$ by errors of order (m/μ) . If $\phi_{n'}$ and ϕ_n are states belonging to a degenerate level (as occurs in symmetric molecules as $R \rightarrow \infty$) these matrix elements should be retained to produce the isotopic electronic energy splittings, but otherwise a negligible error $[\sim(m/\mu)^2 \epsilon_n]$ is incurred by merely ignoring them. In the paper following this one we present a formulation of slow collisions in which even this unimportant defect is also exactly removed, and we discuss the isotopic splitting problem in detail.¹²

As Eqs. (2.20) and (2.22) make clear, the infinite-range PSS couplings associated with states bound to center J will not appear if \vec{r}_J , rather than \vec{r} , be taken consistently as the electron coordinate. It has frequently been proposed that the difficulties of PSS theory may be avoided in this way, and recently a thorough close-coupling calculation has been done in this manner for the HeH^{++} system by Winter and Lane.¹⁴ Of course, infinite-range couplings associated with states bound asymptotically to the other center ($J' \neq J$) will remain, and the other serious defects of PSS theory discussed above are also present in such approaches.

2. Molecular eigenstates with atomic translation factors (Bates and McCarroll)

Bates and McCarroll^{1,2} were the first to point out the defects of the PSS theory and they developed a modification which at least removes the asymptotic defects. For nonsymmetric systems, they divide the molecular states into those that are asymptotically atomic states of A and those that are states of B . They then multiply the " J "-type states by the appropriate asymptotic electronic translation factor for the " J " channel. The electronic basis functions are then products of molecular eigenstates and atomic ETF's,

$$\phi_n(\vec{r}; \vec{R}) \exp[\pm i(m/M_J)\vec{k} \cdot \vec{r}]. \quad (2.26)$$

This modification eliminates the asymptotic, infinite-range gradient couplings. (A related definition can also be made for symmetric systems, based on linear combinations of \underline{g} and \underline{u} pairs of ϕ_n 's with atomic ETF's.^{1,2})

However, basis functions like (2.26) are still not really satisfactory. They introduce complicated nonorthogonalities into the basis set, they destroy the parity symmetry of symmetric systems such as H_2^+ , and above all they are physically inappropriate because they assign to an electron in state ϕ_n a transport velocity associated with a single center (A or B) in spite of the fact that a molecular electron may actually be near either center. We should emphasize that forms of the type (2.26) are really quite different from those described below and lead to different physical results for many problems.

Instead of using atomic ETF's explicitly as Bates and McCarroll do, various formalisms using projection operators have been used to achieve the same physical results.^{9,15,16} In effect, these schemes refer electrons asymptotically bound to center J to that center as origin, and again each *molecular* state is assigned to a particular center. A good summary of many of these methods and their difficulties has been given by Riera and Salin.⁸

3. A molecular form for the ETF

We have pointed out that the major defect of the form (2.26) is that the ETF associated with each *molecular* state has a fixed atomic form, so that no matter how the molecular state is adiabatically distorted by the interaction, the electron in the ETF retains its asymptotic translational motion. In a slow collision, where the electron moves rapidly between the two center, it would be more reasonable to assume that it quickly forgets this asymptotic motion and locally picks up the motion of the nearer nucleus.¹⁷

To construct such a "molecular" ETF, the first step needed is to express the asymptotic plane-wave states (2.13b) or (2.16) in a channel-independent manner. To do this formally we define a two-valued function f_J , $J=A, B$; $f_B = +1$, while $f_A = -1$. Noting that

$$M_J/(M_A + M_B) = \frac{1}{2}(1 + \lambda f_J) \quad (2.27a)$$

and

$$\mu/(M_A + M_B) = \frac{1}{4}(1 - \lambda^2), \quad (2.27b)$$

where λ is the mass asymmetry defined in Eq.(21), we may now write channel coordinates \vec{R}_J and reduced masses μ_J as

$$\begin{aligned} \vec{R}_J &= [M_T/(M_A + M_B)][1 + \frac{1}{2}(m_o/\mu)(1 + \lambda f_J)]^{-1} \\ &\times [\vec{R} + \frac{1}{2}(m/\mu)(f_J + \lambda)\vec{r}] \end{aligned} \quad (2.28)$$

and

$$\mu_J = [(M_A + M_B)/M_T][1 + \frac{1}{2}(m_o/\mu)(1 + \lambda f_J)]\mu. \quad (2.29)$$

Now we define a "molecular" wave vector \vec{k}' such that

$$\hbar^2(\vec{k}')^2/2\mu + \epsilon_{n_J}^0 = E. \quad (2.30)$$

This definition [unlike Eq.(2.14)] eliminates the *intrinsic* dependence of the wave vector upon the channel J , since μ appears in place of μ_J . The *extrinsic* dependence implied through $\epsilon_{n_J}^0$ remains. Then, using Eqs. (2.27)–(2.30), expanding in powers of (m/μ) and keeping all first-order terms, we obtain

$$\vec{k}_J \cdot \vec{R}_J = \vec{k}' \cdot [\vec{R} + (m/\mu)\vec{s}], \quad (2.31)$$

where \vec{s} is given by

$$\vec{s} = \frac{1}{2}(f_J + \lambda)[\vec{r} - \frac{1}{4}(f_J + \lambda)\vec{R}] \quad (2.32)$$

or (since $f_J^2 = 1$) by

$$\vec{s} = \frac{1}{2}(f_J + \lambda)\vec{r}_g - \frac{1}{8}(1 - \lambda^2)\vec{R}, \quad (2.33)$$

where we have introduced $\vec{r}_g = \vec{r} - \frac{1}{2}\lambda\vec{R}$. These equations may be taken to define the form of the ETF.

Using an idea first proposed by Schneiderman and Russek,⁴ we introduce now a continuous "switching function", $f(\vec{r}; \vec{R})$, which has the following properties but is otherwise not yet fully defined:

$$\lim_{R \rightarrow \infty} [f(\vec{r}; \vec{R})] = f_J, \quad \text{if } (r_J/R) \rightarrow 0, \quad (2.34a)$$

$$\lim_{r \rightarrow \infty} [f(\vec{r}; \vec{R})] = 0, \quad \text{if } (R/r) \rightarrow 0. \quad (2.34b)$$

Equation (2.34a) states that if the electron is asymptotically in a bound state of center J , f assumes the appropriate value f_J . (2.34b), which appears to be of less practical importance, asserts that an escaped electron does not follow either center. Note that the essential feature of the switching function is its dependence upon the locality of the electron.

We can now define ETF-modified molecular basis functions

$$\Phi_n(\vec{r}; \vec{R}) = \phi_n(\vec{r}; \vec{R}) \exp[i\vec{k}' \cdot (m/\mu)\vec{s}] \quad (2.35)$$

for nuclei translating with momentum $\hbar\vec{k}'$, where \vec{s} is defined by either (2.32) or (2.33) with the switching function f in place of f_J . Using the methods of Sec. II C 2, it is easily proved that the plane-wave state

$$\Psi = \exp[i\vec{k}' \cdot \vec{R}] \Phi_n(\vec{r}; \vec{R}) \quad (2.36)$$

is a solution to the free Schrödinger equation as $R \rightarrow \infty$, to within errors of order $(m/\mu)^2$. The errors in question are (i) those residual errors of order $(m/\mu)^2$ in the gradient couplings (2.22), resulting from errors of this order in the approximation (2.31); (ii) the errors of order $(m/\mu)^2 \epsilon_{n_J}^0$ which are the result (just as in PSS theory) of using the molecular-state approximations ϕ_{n_J} to represent the exact atomic states $\phi_{n_J}^0$. These errors are of no practical importance for the theory of slow collisions, and we ignore them.

A simple meaning can be given the electron translation factor in a classical description of nuclear motion. Let $\vec{v} = \hbar \vec{k}' / \mu$ be the velocity of relative nuclear motion, and define

$$\vec{w} = \frac{1}{2} [f(\vec{r}; \vec{R}) + \lambda] \vec{v}, \quad (2.37)$$

where \vec{w} is a local velocity of the electron at point \vec{r} , with respect to the center of mass of the nuclei (CMN). $\frac{1}{2} \lambda \vec{v}$ is just the velocity of the geometric center with respect to CMN, while $\frac{1}{2} f(\vec{r}; \vec{R}) \vec{v}$ is the velocity of an electron at \vec{r} , with respect to the geometric center. Near B , where $f \approx +1$, the electron moves with center B ; near A , $f \approx -1$ and it moves with A ; between the two, its velocity is suitably interpolated. Using (2.37) and (2.32) we can write the exponent of the ETF as

$$i \vec{k}' \cdot (m/\mu) \vec{S} = (im/\hbar) [\vec{w} \cdot \vec{r} - \frac{1}{2} \vec{w}^2 t] \quad (2.38)$$

where we have used the rectilinear trajectory approximation $\vec{R} = \vec{b} + \vec{v}t$ (\vec{b} being the impact parameter). This "molecular" ETF therefore represents (exactly, as $R \rightarrow \infty$) the *local* momentum and transport kinetic energy of the electron as it moves with the nuclei relative to the CMN.

Since $f^2(\vec{r}; \vec{R})$ may differ from unity at some points in the molecule, the forms (2.32) and (2.33) are exactly equivalent only as $R \rightarrow \infty$; at finite R they give rise to slightly different expressions for the nonadiabatic couplings and other terms in the coupled equations (cf. Sec. III). Since either gives rise to a formally acceptable theory, we shall consider both, for the time being at least.

If we can assume that a classical or semiclassical description of nuclear motion is valid, so that a velocity $\vec{v}(\vec{R})$ is defined at each point \vec{R} , the fully molecular electronic basis functions defined by Eq. (2.35) (with $\mu \vec{v} = \hbar \vec{k}'$) may be used (with suitable care) to treat slow collision theory. However, we wish to treat the heavy-particle motion quantum mechanically—at least in principle—and this means that the explicit appearance of the classical velocity \vec{v} in the ETF is unacceptable.

In unpublished work leading to these papers, we devised a scheme which gives very nearly the correct result and begins straightforwardly from (2.38). It is based on the following ideas: (a) The

purpose of the basis states given in (2.38) is to provide an expansion of the full wave function,

$$\Psi(\vec{r}, \vec{R}) = \sum_n \Phi_n(\vec{r}; \vec{R}) \chi_n(\vec{R}). \quad (2.39)$$

Using (2.39) one obtains a set of coupled equations for the scattering wave functions $\chi_n(\vec{R})$ and it is these equations which are really the goal of the theory. (b) As is shown very clearly in the proof presented in Sec. II C 2, the main function of the ETF in slow collision theory is to provide corrections to the coupled equations. At low velocities the ETF's themselves have a negligible effect on the overlap of electronic wave functions, and very little error results if, when computing matrix elements with the Φ_n 's, we simply replace them by the Born-Oppenheimer states ϕ_n (i.e., replace ETF's by unity). (c) In the resulting coupled equations for the $\chi_n(\vec{R})$ we can obtain fully quantum-mechanical equations, if we formally replace the velocity \vec{v} by the corresponding quantum-mechanical operator. We do not give this heuristic derivation here because it is inelegant, and also not quite correct, but it is clearly linked conceptually to existing ideas about electron translation factors, to which we have been referring so far.

The approach we shall actually present here has the virtue of giving exactly the correct result, though the idea it involves is a strange one. We postulate that we may replace the formal quantity \vec{k}' in (2.35) by the operator $-i \vec{\nabla}_R$, so that formally the basis functions are now expressed as

$$\Phi_n(\vec{r}; \vec{R}) = \exp[(m/\mu) \vec{S} \cdot \vec{\nabla}_R] \phi_n(\vec{r}; \vec{R}), \quad (2.40)$$

and in using this expression in an expansion, (2.39), it is implicitly assumed that $\vec{\nabla}_R$ acts on both the electronic *and* nuclear wave functions. At first this seems like a wild idea, since in effect (2.40) thus defines an operator-valued basis set. However, it could be regarded as just another form of the operator transcription postulate, used here at an earlier state in the derivation; and it gives the correct coupled equations (3.7), which we will derive by an independent and completely rigorous method in the paper following this one. The unusual postulate (2.40) provides a simple way to get these correct equations by the ETF approach, and thus is justified by its success.

III. COUPLED EQUATIONS FOR SLOW COLLISIONS

With (2.40) as the ETF-modified expansion basis, the full wave function is

$$\Psi(\vec{r}, \vec{R}) = \sum_n \exp[(m/\mu) \vec{S} \cdot \vec{\nabla}_R] \phi_n(\vec{r}; \vec{R}) \chi_n(\vec{R}). \quad (3.1)$$

To obtain coupled equations for the heavy-particle

wave functions $\chi_n(\vec{R})$, we put (3.1) in the Schrödinger equation and multiply by $\langle \phi_m | \exp[-(m/\mu) \vec{s} \cdot \vec{\nabla}_R]$:

$$\sum_n \langle \phi_m | \exp[-(m/\mu) \vec{s} \cdot \vec{\nabla}_R] (H - E) \times \exp[+(m/\mu) \vec{s} \cdot \vec{\nabla}_R] | \phi_n \rangle \chi_n(\vec{R}) = 0. \quad (3.2)$$

Here the integration implied by the angular brackets is only over the electronic coordinates, and the operators $\exp[\pm(m/\mu) \vec{s} \cdot \vec{\nabla}_R]$ act implicitly on both ϕ_n and χ_n .

However, the final effect of the ETF's can also be computed by looking at the operator in (3.2) as a modified Hamiltonian. To compute it, we note first that (to first order in m/μ)

$$\exp[-(m/\mu) \vec{s} \cdot \vec{\nabla}_R] (-i\hbar \vec{\nabla}_R) \exp[+(m/\mu) \vec{s} \cdot \vec{\nabla}_R] = -i\hbar \vec{\nabla}_R + (m/\mu) (\vec{\nabla}_R \vec{s}) \cdot (-i\hbar \vec{\nabla}_R), \quad (3.3a)$$

$$\exp[-(m/\mu) \vec{s} \cdot \vec{\nabla}_R] (-i\hbar \vec{\nabla}_r) \exp[+(m/\mu) \vec{s} \cdot \vec{\nabla}_R] = -i\hbar \vec{\nabla}_r + (m/\mu) (\vec{\nabla}_r \vec{s}) \cdot (-i\hbar \vec{\nabla}_r), \quad (3.3b)$$

$$\exp[-(m/\mu) \vec{s} \cdot \vec{\nabla}_R] V(\vec{r}; \vec{R}) \exp[+(m/\mu) \vec{s} \cdot \vec{\nabla}_R] = V(\vec{r}; \vec{R} - (m/\mu) \vec{s}). \quad (3.3c)$$

In Eqs. (3.3a), (3.3b) the scalar product connects \vec{s} with the gradient $-i\hbar \vec{\nabla}_R$ following it, while the gradient immediately preceding \vec{s} acts only upon that function. We can express this in terms of Cartesian components if we define

$$\gamma_{kj}(\vec{r}; \vec{R}) = (\partial s_j / \partial r_k)_{\vec{r}}, \quad (3.4)$$

$$\Gamma_{kj}(\vec{r}; \vec{R}) = (\partial s_j / \partial R_k)_{\vec{r}},$$

and

$$\hat{p}_k = -i\hbar (\partial / \partial r_k)_{\vec{r}}, \quad (3.5)$$

$$\hat{P}_k = -i\hbar (\partial / \partial R_k)_{\vec{r}},$$

Eqs. (3.3a), (3.3b) then become

$$\hat{P}'_k = \hat{P}_k + (m/\mu) \Gamma_{kj} \hat{P}_j, \quad (3.3a')$$

$$\hat{p}'_k = \hat{p}_k + (m/\mu) \gamma_{kj} \hat{p}_j, \quad (3.3b')$$

where summation over repeated indices is assumed.

Before proceeding further, we note that the new momentum operators \hat{P}'_k , \hat{p}'_k are not Hermitian, a result which springs from the fact that the generator of the transformation, $(m/\mu) s_k \hat{P}_k$, is also not Hermitian and should be replaced by the symmetrized Hermitian form $(m/2\mu) (s_k \hat{P}_k + \hat{P}_k s_k)$. The only effect on the transformed Hamiltonian is to remove some small non-Hermitian terms from the $\sim m/\mu$ corrections to electronic binding energies; the nonadiabatic couplings are unaffected. With this modification we have

$$\hat{P}'_k = \hat{P}_k + \frac{1}{2}(m/\mu) (\Gamma_{kj} \hat{P}_j + \hat{P}_j \Gamma_{kj}) \quad (3.3a'')$$

and

$$\hat{p}'_k = \hat{p}_k + \frac{1}{2}(m/\mu) (\gamma_{kj} \hat{p}_j + \hat{p}_j \gamma_{kj}). \quad (3.3b'')$$

If we neglect all terms $O(m/\mu)^2$ and smaller, and also neglect terms proportional to $(m/\mu)^2 \text{grad}f$, the transformed Hamiltonian is given by

$$\begin{aligned} H' = (2\mu)^{-1} & [\hat{P}'_k \hat{P}'_k + \frac{1}{2} (\hat{P}'_k \gamma_{kj} + \gamma_{kj} \hat{P}'_k) \hat{P}'_j \\ & + \frac{1}{2} \hat{P}'_j (\hat{P}'_k \gamma_{kj} + \gamma_{kj} \hat{P}'_k)] \\ & + (2m)^{-1} \hat{p}'_k \hat{p}'_k + V(\vec{r}; \vec{R} - (m/\mu) \vec{s}) \\ & + (m/\mu) (2\mu)^{-1} [(\gamma_{kj} \gamma_{kl} + 2\Gamma_{kj} \delta_{kl}) \hat{P}'_j \hat{P}'_l]. \end{aligned} \quad (3.6)$$

If we define the vector \vec{s} using Eq. (2.32), the last term in Eq. (3.6) vanishes, while if \vec{s} is given by (2.33) it becomes

$$(m/4\mu) (f^2 - 1) (2\mu)^{-1} \hat{P}'_k \hat{P}'_k.$$

Coupled equations for the $\chi_n(\vec{R})$ are obtained (after some manipulation) by taking the matrix elements of (3.6) between the Born-Oppenheimer states:

$$\{(2\mu)^{-1} [-i\hbar \vec{\nabla}_R + \vec{P} + \vec{A}]^2 + \epsilon + [\underline{\Delta} - (2\mu)^{-1} \vec{A} \cdot \vec{A}] + (m/\mu) \underline{D} (2\mu)^{-1} (-i\hbar \vec{\nabla}_R)^2\} \chi(\vec{R}) = E \chi(\vec{R}) \quad (3.7)$$

Here ϵ is the diagonal matrix of Born-Oppenheimer eigenvalues and the matrices \vec{P} , \vec{A} , and $\underline{\Delta}$ are given by

$$\vec{P}_{mn}(\vec{R}) = \langle \phi_m | -i\hbar \vec{\nabla}_R | \phi_n \rangle, \quad (3.8)$$

$$\vec{A}_{mn}(\vec{R}) = -i\hbar \langle \phi_m | (\vec{\nabla}_r \vec{s}) \cdot \vec{\nabla}_r + \frac{1}{2} (\nabla_r^2 \vec{s}) | \phi_n \rangle \quad (3.9a)$$

$$= (im/\hbar) \langle \phi_m | [h, \vec{s}] | \phi_n \rangle \quad (3.9b)$$

$$= (im/\hbar) (\epsilon_m - \epsilon_n) \langle \phi_m | \vec{s} | \phi_n \rangle, \quad (3.9c)$$

$$\Delta_{mn}(\vec{R}) = \langle \phi_m | V(\vec{r}; \vec{R} - (m/\mu) \vec{s}) - V(\vec{r}; \vec{R}) | \phi_n \rangle. \quad (3.10)$$

The remaining matrix D arises from the last term in (3.6); it vanishes when \vec{s} is defined by Eq. (3.32), but when (2.33) is used it is given by

$$D_{mn}(\vec{R}) = \frac{1}{4} \langle \phi_m | (f^2 - 1) | \phi_n \rangle. \quad (3.11)$$

Equations (3.7) replace the coupled equations of PSS theory,¹³

$$\{(2\mu)^{-1} [-i\hbar \vec{\nabla}_R + \vec{P}]^2 + \epsilon\} \chi(\vec{R}) = E \chi(\vec{R}) \quad (3.12)$$

which lack the corrections due to \vec{A} , $\underline{\Delta}$, or D .

The most important modification produced by the ETF's in these equations is the replacement of the nonadiabatic couplings \vec{P} by the corrected couplings $\vec{P} + \vec{A}$ in the kinetic-energy term. The terms $\underline{\Delta} - (2\mu)^{-1} \vec{A} \cdot \vec{A}$ and the term involving D are much smaller. They describe, respectively, re-

duced-mass effects on electron binding energies $\sim(m/\mu)\epsilon_n$, and a small correction to the transport kinetic energy of the electron $\sim(m/\mu)E$. We will discuss them in more detail in the following paper. For nearly all scattering problems we may neglect these terms and use the simple equations

$$\{(2\mu)^{-1}[-i\hbar\vec{\nabla}_R + \vec{P} + \vec{A}]^2 + \epsilon\}\chi(\vec{R}) = E\chi(\vec{R}), \quad (3.13)$$

which have the same form as (3.12).

Since the "derivation" given here rests upon the postulate (2.40), it is no stronger than that somewhat unusual assumption; its ultimate justification is that the same final result is obtained by the independent and fully rigorous derivation described in the next paper. There, by employing a non-linear transformation of the coordinates, we obtain just Eqs. (3.7) as the scattering equations in the new "scattering coordinate". In the terms of that approach, the ETF form (2.40) acquires a new significance, since an operator of the type $\exp(\pm(m/\mu)\vec{s} \cdot \vec{\nabla}_R)$ is a formal representation of a coordinate transformation's effects upon the wave function.

A. Transformation to rotating molecular coordinates

Though we have not discussed it explicitly, up to now we have expressed electronic wave functions ϕ_n in terms of the "laboratory" coordinates (\vec{r}, \vec{R}) . Thus, for example, the matrices \vec{P} involve derivatives with respect to \vec{R} holding electron coordinates fixed in a nonrotating "lab" system. This is inconvenient since the wave functions ϕ_n and the electronic Hamiltonian h which defines them are defined in terms of coordinates \vec{r}' rotating with the internuclear axis vector \vec{R} . We must therefore express $(\vec{\nabla}_R)_{\vec{r}}$ in terms of $(\vec{\nabla}_R)_{\vec{r}'}$.^{18,19,20}

Let $\vec{r} = (x, y, z)$ then be coordinates of the electron expressed in the space-fixed frame, while $\vec{r}' = (x', y', z')$ denotes the same vector in the rotating molecular reference frame. Figure 2 depicts the relation of the two sets of reference axes; the relation between them is

$$\begin{aligned} x' &= x \cos\Theta \cos\Phi + y \cos\Theta \sin\Phi - z \sin\Theta, \\ y' &= -x \sin\Phi + y \cos\Phi, \\ z' &= x \sin\Theta \cos\Phi + y \sin\Theta \sin\Phi + z \cos\Theta. \end{aligned} \quad (3.14)$$

Here (Θ, Φ) are the usual spherical polar angles of the vector \vec{R} in the lab frame (note that this definition of the rotating frame axes does not correspond to the usual one in terms of Eulerian angles since the y' axis, not the x' axis, lies on the line of nodes). In spherical polar coordinates, the gradient $(-i\hbar\vec{\nabla}_R)$ (keeping \vec{r} fixed) can be written

$$\begin{aligned} -i\hbar\vec{\nabla}_R &= \vec{e}_R(-i\hbar\partial/\partial R)_{xyz} + \vec{e}_\Theta[R^{-1}(-i\hbar)(\partial/\partial\Theta)_{xyz}] \\ &+ \vec{e}_\Phi[(R \sin\Theta)^{-1}(-i\hbar)\partial/\partial\Phi]_{xyz}, \end{aligned} \quad (3.15)$$

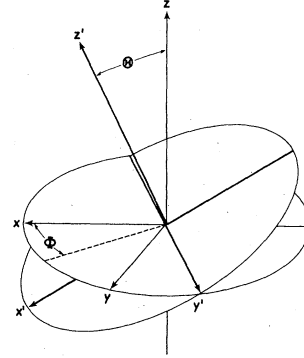


FIG. 2. Space-fixed and molecule-fixed reference frames for the molecular electron. (x, y, z) denote space-fixed axes, (x', y', z') , molecule-fixed axes, and they are related via rotations by angles (Θ, Φ) as shown. Note that this differs from the usual relations and definitions using Euler angles.

where \vec{e}_R , \vec{e}_Θ , and \vec{e}_Φ are the unit vectors of the spherical polar system at \vec{R} (they coincide with the z' , x' , and y' axes, respectively). Using Eq. (3.14) the components of this operator can be rewritten

$$-i\hbar(\partial/\partial R)_{xyz} = -i\hbar(\partial/\partial R)_{x'y'z'}, \quad (3.16a)$$

$$-i\hbar(\partial/\partial\Theta)_{xyz} = -i\hbar(\partial/\partial\Theta)_{x'y'z'} - \hat{L}_{y'}, \quad (3.16b)$$

$$\begin{aligned} -i\hbar(\partial/\partial\Phi)_{xyz} &= -i\hbar(\partial/\partial\Phi)_{x'y'z'} \\ &+ [\sin\Theta \hat{L}_{x'} - \cos\Theta L_{z'}], \end{aligned} \quad (3.16c)$$

where $\hat{L}_{x', y', z'}$ are the components of the electronic orbital angular momentum operator (with respect to CMN).

The \vec{P} matrix is therefore expressed as¹³

$$\vec{P}_{mn} = P_{mn}^R \vec{e}_R + P_{mn}^\Theta \vec{e}_\Theta + P_{mn}^\Phi \vec{e}_\Phi, \quad (3.17a)$$

where

$$P_{mn}^R = \langle \phi_m | (-i\hbar\partial/\partial R) | \phi_n \rangle, \quad (3.17b)$$

$$P_{mn}^\Theta = -R^{-1} \langle \phi_m | \hat{L}_{y'} | \phi_n \rangle, \quad (3.17c)$$

$$P_{mn}^\Phi = +R^{-1} [\langle \phi_m | \hat{L}_{x'} | \phi_n \rangle - \Lambda_n \hbar \cot\Theta \delta_{mn}], \quad (3.17d)$$

(and we have assumed that ϕ_n is an eigenstate of $\hat{L}_{z'}$, with eigenvalue $\Lambda_n \hbar$).

The corresponding form for \vec{A} is obtained simply by expressing the vector \vec{s} in terms of its components on the x', y', z' axes:

$$A_{mn}^R \equiv A_{mn}^{z'} = (im/\hbar)(\epsilon_m - \epsilon_n) \langle \phi_m | s_{z'} | \phi_n \rangle, \quad (3.18a)$$

$$A_{mn}^\Theta \equiv A_{mn}^{x'} = (im/\hbar)(\epsilon_m - \epsilon_n) \langle \phi_m | s_{x'} | \phi_n \rangle, \quad (3.18b)$$

$$A_{mn}^\Phi \equiv A_{mn}^{y'} = (im/\hbar)(\epsilon_m - \epsilon_n) \langle \phi_m | s_{y'} | \phi_n \rangle. \quad (3.18c)$$

B. Coupled radial equations

Given the components of \vec{P} and \vec{A} by Eqs. (3.17) and (3.18) we can construct explicit solutions to

the close-coupled equations (3.13) for inelastic scattering in a finite manifold of molecular electronic states. Equations (3.13) can be reduced to coupled one-dimensional (radial) equations using a partial wave expansion. Since Eqs. (3.13) and the PSS equations (3.12) have *identical form*, the detailed description of this reduction and the form of the radial equations is precisely the same as it is in PSS theory except for the replacement of the components of \vec{P} by those of $(\vec{P} + \vec{A})$. Our main concern in these papers is the development of the theory of these corrections, so for the sake of brevity we simply summarize the results.

1. Exact equations.

The reduction to radial equations may be done exactly by expanding $\chi_n(\vec{R})$ in appropriate eigenstates of total angular momentum. When the electronic orbital angular momentum is coupled to the figure axis with component $\Lambda_n \hbar$, as it is in the molecular states ϕ_n (for simplicity, we have not considered spin), the appropriate expansion may be written

$$\chi_n(\vec{R}) = R^{-1} \sum_{K, M_K} C_{KM_K}^n F_n^K(R) \mathcal{Y}_{M_K \Lambda_n}^K(\Theta, \Phi). \quad (3.19)$$

The functions $\mathcal{Y}_{M_K \Lambda}^K$, which are closely related to symmetric top eigenfunctions, obey the differential equation

$$\begin{aligned} & [(\sin\Theta)^{-1} \partial/\partial\Theta (\sin\Theta \partial/\partial\Theta) \\ & + (1/\sin^2\Theta) (\partial/\partial\Phi - i\Lambda \cos\Theta)^2] \mathcal{Y}_{M_K \Lambda}^K \\ & = -[K(K+1) - \Lambda^2] \mathcal{Y}_{M_K \Lambda}^K, \end{aligned} \quad (3.20)$$

and are given by

$$\mathcal{Y}_{M_K \Lambda}^K(\Theta, \Phi) = (-1)^{\Lambda+M_K} d_{M_K \Lambda}^{(K)}(\Theta) e^{iM_K \Phi}, \quad (3.21)$$

where $d_{M_K \Lambda}^{(K)}$ are the representations of finite rotation defined by Edmonds.²¹ K is the total angular momentum, M_K its (lab frame) z -axis component, and Λ the figure-axis component. In this representation, the angular components of $\vec{P} + \vec{A}$ couple states n with different Λ_n but are diagonal in K , M_K , and a system of coupled radial equations arises for each K [as Eq. (3.19) implies, these equations do not depend on M_K ; the expansion in M_K must be included to meet initial- and final-state boundary conditions expressed in the lab frame, since initial and final electronic states may possess electronic orbital angular momentum characterized by L, M_L]. The coupled radial equations [for the components of the abstract vector $\underline{F}^K(R)$] may be written as

$$\begin{aligned} & \{(2\mu)^{-1} [-i\hbar d/dR + \underline{P}^R(R) + \underline{A}^R(R)]^2 \\ & + \underline{\epsilon}(R) + [K(K+1)\hbar^2/2\mu R^2] \underline{1} \\ & + (2\mu)^{-1} [\underline{\pi}^2(R) - \underline{Q}^{K\pm}(R)] \underline{F}^K(R) = E \underline{F}^K(R), \end{aligned} \quad (3.22)$$

where

$$(\underline{\pi}^2)_{mn} = (\underline{P}^\Theta + \underline{A}^\Theta)_{mn}^2 + (\underline{P}^\Phi + \underline{A}^\Phi)_{mn}^2 - \delta_{mn} \Lambda_n^2 \hbar^2 / R^2 \quad (3.23a)$$

and

$$\begin{aligned} & (\underline{Q}^{K\pm})_{mn} = \delta(\Lambda_m, \Lambda_n \pm 1) (\hbar R^{-1}) [(K \mp \Lambda_n)(K \pm \Lambda_n + 1)]^{1/2} \\ & \times [(\underline{P}^\Theta + \underline{A}^\Theta) \pm i(\underline{P}^\Phi + \underline{A}^\Phi)]_{mn}, \end{aligned} \quad (3.23b)$$

with

$$(\underline{P}^\Theta)_{mn} = R^{-1} \langle \phi_m | \hat{L}_{z'} | \phi_n \rangle. \quad (3.23c)$$

The remainder of \underline{P}^Φ has been absorbed in the rotational kinetic energy [cf. Eq. (3.20)]. $\underline{Q}^{K\pm}$, which couples states whose Λ values differ by ± 1 , is the angular or "Coriolis" coupling; $\underline{\pi}^2$ is diagonal in Λ ($\Lambda_m = \Lambda_n$) and represents a small correction to the rotational kinetic energy.

Solution of Eqs. (3.22) would not only describe the effect of angular coupling on the electron system but would also give a detailed quantum-mechanical account of the corresponding reaction of the heavy-particle system in conserving angular momentum. However, care must be taken to establish the correct asymptotic relations between amplitudes appearing in the expansion (3.19) and the required amplitudes for decoupled angular momentum states expressed in the lab reference frame. (cf. Sec. IV B). For a discussion of this problem, see the paper by Thorson²² and a more complete account by Mies.²³ The complications introduced by the angular-momentum coupling problem make solution of the exact equations (3.22) unnecessarily tedious for most purposes.

2. Approximate radial equations

Happily it is almost never of interest to solve the exact equations (3.22), because electronic transitions seldom involve the transfer of more than one or two units of angular momentum while typically the collisional angular momentum of the heavy particles is very large. Classically this means that angular momentum transfer to the electron system has a nearly negligible deflection effect on the heavy particles, i.e., the collision occurs in a plane ($\Phi = \text{const}$) and the heavy-particle angular momentum N is approximately conserved. To express this idea, the solution to the scattering problem can be written in a more conventional partial wave expansion,

$$\Psi = R^{-1} \sum_N C_N P_N^0(\cos\Theta) \left[\sum_n F_n^N(R) \phi_n \right], \quad (3.24)$$

and the components F_n^N of the abstract vector \underline{F}^N obey the much simpler equations

$$\begin{aligned} & \{(2\mu)^{-1}[-i\hbar d/dR + \underline{P}^R + \underline{A}^R]^2 + \underline{\epsilon}(R) \\ & + [N(N+1)\hbar^2/2\mu R^2] \underline{1} \} ([N(N+1)]^{1/2}\hbar/\mu R) \\ & \times [\underline{P}^0 + \underline{A}^0] \} \underline{F}^N(R) = E \underline{F}^N(R). \quad (3.25) \end{aligned}$$

The relation of (3.25) to (3.22) is evident if we put $k \approx N \gg |\Lambda_n|$ in the latter equation. We have neglected the π^2 term for consistency in the decoupling approximation. The effects of the Coriolis coupling ($\underline{P}^0 + \underline{A}^0$) on the electron system remain, but no account is given of the heavy-particle *reaction*, since (3.24) is azimuthally symmetric and N is conserved.

Equations (3.25) reduce exactly to the correct form in the semiclassical and impact parameter limits.

IV. EFFECTS OF ETF CORRECTIONS \vec{A}

Here we examine the consequences of replacing the PSS nonadiabatic coupling matrix \vec{P} by the ETF-corrected coupling $\vec{P} + \vec{A}$.

A. General features

1. Asymptotic cancellation

One general property of \vec{A} is evident immediately; asymptotically it exactly cancels the fictitious infinite-range couplings contained in \vec{P} ,

$$\lim_{R \rightarrow \infty} [\vec{P}(R) + \vec{A}(R)] = 0. \quad (4.1)$$

This is easily proved; from Eqs. (2.20) and (2.9a) we have (for the asymmetric case)

$$\begin{aligned} \vec{P}_{mn}(R) & \underset{R \rightarrow \infty}{\sim} \langle \phi_{m_j}(\vec{r}_j) | (-i\hbar \vec{\nabla}_R) | \phi_n(\vec{r}_j) \rangle \\ & = -\frac{1}{2} (f_j + \lambda) \langle \phi_{m_j} | (-i\hbar \vec{\nabla}_{r_j}) | \phi_n \rangle, \end{aligned} \quad (4.2a)$$

while from (3.9a) and (2.32) or (2.33),

$$\vec{A}_{mn}(R) = \frac{1}{2} (f_j + \lambda) \langle \phi_{m_j} | (-i\hbar \vec{\nabla}_{r_j}) | \phi_n \rangle. \quad (4.2b)$$

Of course, the ETF's were designed from the outset to achieve this.

2. "Constant \vec{A} " approximation

In view of this asymptotic cancellation it has sometimes been proposed¹¹ that an adequate description of slow collisions may be obtained simply by subtracting from $\vec{P}(R)$ its asymptotic value. This is equivalent here to approximating $\vec{A}(R)$ by a constant equal to its asymptotic value. While this might be adequate in a few cases, in general it will give incorrect results. Many of the PSS

matrix elements tend to *zero* asymptotically, yet are spuriously large at finite R values; the corresponding elements of \vec{A} also vanish asymptotically but at finite R values cancel off such spurious couplings.

3. "Asymptotic f " approximation

Fundamentally, the "constant \vec{A} " approximation is inadequate because the cancellation of \vec{P} and \vec{A} is a cancellation of the *operators* whose asymptotic forms appear in Eqs. (4.2); individual matrix elements of these operators also depend upon the overlap of the molecular states involved. A much better approximation is provided, therefore, if a formalism is constructed in which the \vec{A} matrix is approximated by the matrix elements of the asymptotic operator $\frac{1}{2} (f_j + \lambda) (-i\hbar \vec{\nabla}_{r_j})$ appearing in Eq. (4.2b). Within the present framework, this is not possible *except* asymptotically, since it requires the specification of a state-dependent constant, $f = f_j$, in the molecular region, but in effect this is the approximation resulting from the approach used by Bates and McCarroll,^{1,2} Matveeyenko,⁹ and others,^{15,16} if we neglect the nonorthogonalities and other complications ensuing in such a representation. [If one of the atoms (J) be taken as a fixed reference origin for the electron (cf. for example the work of Winter and Lane¹⁴), the same effect is achieved for matrix elements associated with the states asymptotically bound to center J .] Riera and Salin⁸ have discussed these approximations and commented on some of the difficulties they present. Nevertheless, this approximation is a substantial improvement over both PSS theory and the "constant \vec{A} " approximation, since the long-range behavior of most coupling matrix elements is rendered correct by this method.

Questions about this approach arise in connection with nonadiabatic couplings at moderate R values, where electronic states have molecular character; in many instances it is just these regions for which the nonadiabatic couplings are of physical interest. Matrix elements linking states associated asymptotically with different centers are not Hermitian, in the case of asymmetric systems. For symmetric systems, couplings can arise which link states of different parity, although it can be proved using our formulation that no such couplings are possible. Lastly, approximations at this level have little effect on matrix elements such as those for ionization, which are extremely sensitive to the detailed form of f .^{5,6} Though few detailed studies yet exist to provide general conclusions, we can expect that this type of simple asymptotic approximation will be less satisfactory for transitions involving significant transfer of

charge from one center to the other or to the molecule as a whole (Rydberg transitions, ionization).

4. Physical interpretation of ETF corrections

In an adiabatic representation such as the Born-Oppenheimer states are presumed to provide, the electronic states change with R , undergoing polarization, deformation, and rotation as the strong molecular potential alters. "Nonadiabatic couplings" are produced by these changes. In the unmodified PSS theory, it is implicitly assumed that this change of character is represented by the $\bar{\mathbf{P}}$ matrix. However, $\bar{\mathbf{P}}$ actually contains not only the effects of this change of character but also the effects of simple translation of the atomic basis functions; the asymptotic behavior of $\bar{\mathbf{P}}$ represents precisely the effects of simple translation of atomic states, without any deformation, and it is these effects that are removed by the asymptotic $\bar{\mathbf{A}}$ matrix. At finite R , the role of $\bar{\mathbf{A}}$ is really the same, though the situation is more complicated. At each configuration R , the Born-Oppenheimer basis functions are undergoing distortion and rotation which can cause transitions, but they also may be said to exhibit at each point $\bar{\mathbf{r}}$ a local "simple displacement with R " that does not lead to real transitions. The role of the matrix $\bar{\mathbf{A}}$ is to identify and remove that part of $\bar{\mathbf{P}}$ which represents this "simple displacement" of the basis functions.

A little thought will reveal that there is no simple and obvious scheme for separating "deformation" and "simple displacement" effects by a direct examination of the adiabatic states themselves, and this state of affairs is reflected in the fact that no specification of the switching function $f(\bar{\mathbf{r}}; \bar{\mathbf{R}})$ appears to be provided by the theory [apart from the asymptotic constraints (2.34)]. To the extent that a method exists to determine f , or alternatively to determine $\bar{\mathbf{A}}$, the "best possible" separation of displacement and deformation effects is also specified. We give a brief discussion of this problem in the next section.

5. Removal of mass asymmetry couplings

For a system with mass asymmetry ($\lambda \neq 0$), there is a part of the PSS coupling matrix $\bar{\mathbf{P}}$ which is proportional to λ [cf. Eq. (4.2a)] and arises because the PSS formulation takes the center of mass of the nuclei (CMN) as the origin of electron coordinates. This coupling is fictitious and is removed identically (at all internuclear separations) by a corresponding term in $\bar{\mathbf{A}}$. To prove this, simply note that

$$[-i\hbar\bar{\nabla}_R]_{\bar{\mathbf{r}}} = [-i\hbar\bar{\nabla}_R]_{\bar{\mathbf{r}}_g} - \frac{1}{2}\lambda[-i\hbar\bar{\nabla}_r]_{\bar{\mathbf{r}}}, \quad (4.3a)$$

while the vector $\bar{\mathbf{s}}$ whose form is defined by Eq. (2.32) or (2.33) can be written

$$\bar{\mathbf{s}} = \bar{\mathbf{s}}_g + \frac{1}{2}\lambda\bar{\mathbf{r}}_g, \quad (4.4a)$$

where

$$\bar{\mathbf{s}}_g = \frac{1}{2}f\bar{\mathbf{r}}_g - \frac{1}{4}(1 - \lambda^2)\bar{\mathbf{R}}, \quad (4.4b)$$

or

$$\bar{\mathbf{s}}_g = \frac{1}{2}f\bar{\mathbf{r}}_g = -\frac{1}{4}(f^2 - \lambda^2)\bar{\mathbf{R}}. \quad (4.4c)$$

Using Eq. (3.9a) to define $\bar{\mathbf{A}}$, we see immediately that the second term of Eq. (4.4a) gives rise to a term in $\bar{\mathbf{A}}$ which identically cancels the effect in $\bar{\mathbf{P}}$ of the second term in Eq. (4.3a), so we can write

$$\bar{\mathbf{P}}(R) + \bar{\mathbf{A}}(R) \equiv \bar{\mathbf{P}}_g(R) + \bar{\mathbf{A}}_g(R), \quad (4.5a)$$

where

$$[\bar{\mathbf{P}}_g(R)]_{mn} = \langle \phi_m | [-i\hbar\bar{\nabla}_R]_{\bar{\mathbf{r}}_g} | \phi_n \rangle \quad (4.5b)$$

and the elements of $\bar{\mathbf{A}}_g$ are given by Eqs. (3.9) using $\bar{\mathbf{s}}_g$ in place of $\bar{\mathbf{s}}$. (Note that the term in λ^2 in $\bar{\mathbf{s}}_g$ also contributes nothing to $\bar{\mathbf{A}}_g$.) Equation (4.5a) shows that mass asymmetry does not contribute directly to nonadiabatic couplings, which should reflect properties of the electronic states alone. This is of special importance for symmetric but not homonuclear systems (e.g., HD⁺), as is shown in the paper following this one. Equation (4.5a) also provides important simplification in computing nonadiabatic couplings for any system.

B. Angular components $\bar{\mathbf{A}}^\circ$, $\bar{\mathbf{A}}^\phi$

The angular components of $\bar{\mathbf{A}}$ cancel certain fictitious asymptotic terms in the angular components of $\bar{\mathbf{P}}$ [cf. Eqs. (3.17)]. Let us show this for $\bar{\mathbf{P}}^\circ + \bar{\mathbf{A}}^\circ$: Since $\hat{L}_{y'} = -i\hbar(z'\partial/\partial x' - x'\partial/\partial z')$, and z' is measured from CMN, matrix elements of $\hat{L}_{y'}$ have a term asymptotically proportional to R and P_{mn}° tends to a constant as $R \rightarrow \infty$. This leads in PSS theory to a spuriously large asymptotic angular coupling, proportional to R^{-1} , which can be nonzero even within asymptotically degenerate manifolds. However, since $z' = z'_J + \frac{1}{2}(f_J + \lambda)R$, where z'_J is measured from center J , we have that

$$\hat{L}_{y'}^{\text{CMN}} = \hat{L}_{y'}^J - i\hbar(f_J + \lambda)\frac{1}{2}R\partial/\partial x', \quad (4.6)$$

where $\hat{L}_{y'}^J$ is the y' component of electronic angular momentum at atom J . Since $s_{x'}$ is asymptotically just equal to $\frac{1}{2}(f_J + \lambda)x'$ (plus constants), it follows from Eqs. (3.18b) and (3.9a) that the asymptotic angular coupling is

$$(\bar{\mathbf{P}}^\circ + \bar{\mathbf{A}}^\circ)_{mn} \sim -R^{-1} \langle \phi_{mJ} | \hat{L}_{y'}^J | \phi_{nJ} \rangle,$$

that is, near atom J this coupling acts as the local

atomic angular momentum \hat{L}_y^J . The analogous result is obtained for the x' component. Thus the angular corrections reduce all asymptotic Coriolis couplings within orbitally degenerate manifolds to terms which are proportional to R^{-2} [see Eq. (3.23b)].

Even this corrected asymptotic Coriolis coupling becomes dominant within a degenerate manifold as $R \rightarrow \infty$; this is not surprising, since it is the mechanism which leads to axis decoupling of the electronic angular momentum. Formally, a strong-coupling problem then arises within each degenerate manifold, as was pointed out by Laue²⁴ and by Kouri and Curtiss.²⁵ However, it has been shown by Thorson²² that for nearly all collision problems of practical interest, asymptotic Coriolis couplings have an essentially trivial effect: if initial and final electronic states are quantized in a space-fixed (axis-decoupled) reference frame, whose z axis coincides with the asymptotic molecular axis vector \bar{R} , then amplitudes for the axis-decoupled electronic states (L, M_L) are just equal to the amplitudes for the corresponding *axis-coupled* (Born-Oppenheimer) states ($L, \Lambda = M_L$) at distances R interior to the region of asymptotically dominant Coriolis coupling. In other words, no "transitions" are produced by the Coriolis coupling; the sudden approximation is valid. This approximation may be applied either to the exact equations (3.22) or to the approximate equations (3.25). More recently, work by Mies²³ considers the cases where this approximation does not hold and the coupling problem must be solved in detail.

C. Estimates of the radial component \underline{A}^R

A rough qualitative comparison of the relative magnitudes of \underline{P}^R and \underline{A}^R can be given for various situations.

\underline{P}^R can most easily be estimated as

$$|\underline{P}_{mn}^R| \sim \hbar a_1^{-1}, \quad (4.7a)$$

where a_1 is the distance over which ϕ_n changes appreciably. If we use the Hellmann-Feynman theorem,

$$|\underline{P}_{mn}^R| = (|\epsilon_m - \epsilon_n|)^{-1} |\langle \phi_m | (\partial h / \partial R) | \phi_n \rangle| \hbar,$$

and estimate the matrix element of $(\partial h / \partial R)$ as $\sim \bar{\epsilon} a_0^{-1}$ where $\bar{\epsilon}$ is a mean orbital energy, another estimate for $|\underline{P}_{mn}^R|$ is

$$|\underline{P}_{mn}^R| \sim \hbar a_0^{-1} \bar{\epsilon} / |\epsilon_m - \epsilon_n|. \quad (4.7b)$$

Correspondingly, we have from Eq. (3.9a) the simplest estimate

$$|\underline{A}_{mn}^R| \sim \hbar a_0^{-1}. \quad (4.8a)$$

The alternative formula (3.9c) gives the estimate

$$|\underline{A}_{mn}^R| \sim (m/\hbar) a_2 |\epsilon_m - \epsilon_n|, \quad (4.8b)$$

where a_2 is the size of the molecular orbital.

The simplest estimates (4.7a), (4.8a) show that $|\underline{P}_{mn}^R|$ and $|\underline{A}_{mn}^R|$ are generally comparable. For transitions *not* mediated by a degeneracy, that is, principal quantum excitations or ionizing transitions, where $|\epsilon_m - \epsilon_n| \approx \bar{\epsilon}$, we may therefore expect that \underline{A}_{mn}^R will normally provide an important partial cancellation or even a very substantial reduction in the net result, relative to \underline{P}_{mn}^R . Actual calculations for such transitions in H_2^+ and HeH^{2+} ²⁶ show that for typical cases the estimates (4.7a), (4.8a) are too large by about a factor of 5 to 10, but the two quantities are indeed comparable and the corrected matrix element may be smaller in magnitude than the uncorrected PSS value by factors ranging anywhere from 2 to 10, or more, depending on the detailed situation. Even more spectacular reductions are obtained in the case of ionization, in H_2^+ ^{5,6} and also in HeH^{2+} ²⁶.

On the other hand, for transitions mediated by a degeneracy, where $|\epsilon_m - \epsilon_n|$ is locally much smaller than $\bar{\epsilon}$, Eqs. (4.7a) and (4.8a) predict that $|\underline{P}_{mn}^R|$ becomes locally larger than normal, while $|\underline{A}_{mn}^R|$ becomes smaller. This suggests that in relation to large peaks in \underline{P}_{mn}^R associated with *avoided crossings*, or with other situations involving mixing of nearly degenerate states, the \underline{A}_{mn}^R corrections are relatively unimportant. If we construct an actual model of a curve crossing, for example, based on "mixing" of two "adiabatic" states, we actually find that $|\underline{P}_{mn}^R| \sim \hbar a_0^{-1} \bar{\epsilon}^2 / |\epsilon_m - \epsilon_n|^2$, while $|\underline{A}_{mn}^R| \sim \hbar a_0^{-1}$. Although in this case Eqs. (4.7b) and (4.8b) give an incorrect estimate of $|\underline{P}_{mn}^R|$ and $|\underline{A}_{mn}^R|$ separately, their estimate that the *relative magnitudes* should vary as $(\bar{\epsilon} / |\epsilon_m - \epsilon_n|)^2$ is correct. We conclude that in relation to "degeneracy-mediated transitions," where strong state-mixing results from effects of weak couplings between locally near-degenerate states, the corrections \underline{A}_{mn}^R are unimportant and merely provide a smoothly varying "background." This conclusion, of course, is fairly obvious on physical grounds, in view of the interpretation of the ETF corrections (cf. Sec. IV A 4 above).

Equation (4.8b) suggests another case where \underline{A}_{mn}^R is likely to be important. In near-resonant charge exchange at large internuclear distances R , or other processes involving very diffuse orbitals, \underline{A}_{mn}^R may become appreciable due to the size of orbitals. Though we should note that as yet there are no adequate calculations of \underline{A} -matrix elements for discrete-discrete transitions, the PSS calculations of Melius and Goddard on charge exchange in the system $Li^+ + Na$,²⁸ and the anomalies they found there, suggest that ETF corrections

may be quite important in long-range charge transfer problems. We are currently computing some of these corrections for some simple one-electron model problems.

V. DISCUSSION

The theory of slow collisions which is formulated here (and which is derived rigorously and more completely and systematically, by a different method, in the paper immediately following) established a framework in which all the formal and physical defects of PSS theory are removed. We can guarantee that the boundary conditions for scattering are satisfied to any required accuracy, and that no spurious infinite-range nonadiabatic couplings appear. Furthermore, given the proper defining context, this can be achieved while maintaining rigorous orthogonality of the electronic basis functions and these functions may be taken to be just the Born-Oppenheimer adiabatic molecular states which appear in PSS theory. The resulting close-coupled equations (3.7) are fully quantum mechanical, and require no semiclassical or impact parameter descriptions as a starting point. As far as we are aware, no other formulation of slow collision theory exists which meets all these criteria. In addition, the fact that exactly the same coupled equations (3.7) are obtained from two different approaches to the problem not only permits a unified and simple physical interpretation of these equations, but creates confidence that their formal structure is correct and complete.

With all these promising tokens of validity, there remains an important unsolved problem for this theory. The *switching function* $f(\vec{r}; \vec{R})$, which plays a major role in the theory, and which explicitly determines the important corrections $\underline{\hat{A}}$ to non-adiabatic couplings, is not uniquely specified, apart from the asymptotic conditions (2.34), and nowhere in either of the derivations we give in these papers does any scheme or criterion emerge for its determination.

This lack of uniqueness presents no difficulty from the viewpoint of the formal theory of scattering. Since all the formal requirements on boundary conditions, etc., are satisfied with any arbitrary choice for the switching function, the formal theory guarantees that the exact solution to a problem cannot depend on that choice. Indeed, the freedom in the definition of $f(\vec{r}; \vec{R})$ can be employed to make choices of f which are optimally *convenient* for a particular problem.

However, from a practical standpoint an important problem remains. It is not usually possible to demonstrate convergence of a calculation to a basis-invariant result. Sometimes only first ap-

proximations to physical quantities are computationally feasible, and of course these can depend very much upon the starting point for the calculation; there is a problem of optimal *accuracy* and not merely of convenience.

Two important practical questions therefore arise: (a) Can we find any useful method for determining either an unique choice for f (or for the nonadiabatic coupling matrices), or, failing that, an "optimum" choice? (b) Is there evidence that this formulation really has practical advantages over older methods for treating slow-collision problems (such as PSS theory, for example, or minor modifications of it)?

A. Determination of switching function $f(\vec{r}; \vec{R})$

Ideally it might be possible to determine the switching function by using variation principles derived from mechanics. Riley and Green²⁹ have applied the Euler-Lagrange method, within a time-dependent classical-trajectory description of atomic collisions, to a determination of the form of electron translation factors, and they obtain general equations which should determine f in principle. However, these equations are exceedingly complicated and have been solved explicitly by these authors only for cases where f is independent of \vec{R} , i.e., it is not a *switching function*. Using a coordinate transformation method, Mittleman and Tai¹³ employed the switching function to discuss nonadiabatic effects in low-energy He-He scattering, in the course of which they established, using variational methods, that in the low-velocity limit the switching function does not depend on the collision velocity; this has been assumed *a priori* in the present work. But on the whole it seems that variational methods have not yet offered a practical procedure for choosing f , and attention should be paid to this problem.

Our interest in the problem of ETF's and the corrections they produce began with the studies of ionization made by Thorson and co-workers^{5,6} for the $H^+ - H(1s)$ system. They found that PSS matrix elements $P_{mn}^R(R)$ for transitions from $1s\sigma_g$, $2p\sigma_u$, and $2p\pi_u$ bound levels to the continuum states are very large, very numerous, and physically implausible; though each individual matrix element tends asymptotically to zero, they have significant magnitudes for 30 to 40 partial waves, and matrix elements for successive partial waves reach their maxima at steadily increasing R values, so that the envelope of significant coupling extends at least to 30 a.u. Since this seems physically unrealistic, Levy and Thorson⁵ argued that, using a suitable choice for the switching function, it should be possible to find corrected matrix elements ($\underline{\hat{P}}$

$+\bar{A})_{mn}$ in which these spurious couplings disappear. After preliminary studies showing that the couplings are indeed extremely sensitive to the form of f , Lebeda, Thorson, and Levy⁶ showed that a kind of "optimum" choice is indeed possible: Using the form

$$f(\vec{r}; R) = \tanh[\beta(R)R\eta], \quad (5.1a)$$

where $R\eta = r_A - r_B$, and $\beta(R)$ is a variable parameter, they found that for each R value a definite choice for $\beta(R)$ exists, such that the corrected radial matrix elements have significant size only for the lowest two or three partial waves, and these only for the smaller internuclear distances where strong molecular interaction occurs. The value of $\beta(R)$ is independent of the continuum state properties (energy, partial wave), but is different for each of the bound states involved. SethuRaman, Thorson and Lebeda⁶ showed that the same results—and the same values of $\beta(R)$ —are found for the angular couplings. Cancellation of \bar{P}_{mn} by \bar{A}_{mn} is very spectacular, as much as four to six orders of magnitude reduction for higher partial waves. Recently completed studies by Rankin and Thorson²⁷ on asymmetric one-electron models, with nuclear charges $Z_B = 1.0$ and $1.0 \leq Z_A \leq 2.0$, show that the same effect occurs in all these systems. They used the form

$$f(\vec{r}; R) = \tanh(R[\beta(\frac{1}{2}Z_A)\{[1 + (Z_B/Z_A)]\eta + [1 - (Z_B/Z_A)]\} + \alpha \ln(Z_B/Z_A)]), \quad (5.1b)$$

where β and α are variable parameters. Again definite values of β and α are determined; they are the same for both radial and angular couplings, and do not depend on continuum state energy or quantum numbers. Just as in the H_2^+ case, spectacular cancellations of \bar{P}_{mn} by \bar{A}_{mn} occur. The parameters β and α do depend on the bound states considered ($1s\sigma$, $2p\sigma$, $2s\sigma$, and $2p\pi$ have been studied), and depend only slightly on charge asymmetry (Z_B/Z_A).

It is clear that these calculations are "variational" only in a heuristic sense, and have no clear formal justification. They are also not strictly compatible with the formalism of the present work, which assumes a *single* switching function for the whole problem. Furthermore, it appears from preliminary studies²⁶ of discrete-discrete state transitions in H_2^+ and HeH^{2+} that, while the corrected matrix elements are also much reduced in number and size by suitable choices of f , the situation is much more complicated than for ionizing transitions, and this approach may not lead to a useful method for choosing the switching function. However, we think these studies offer remarkably

convincing evidence that the switching function approach and the corrected nonadiabatic couplings it generates are physically significant. Such systematic reductions and cancellations of matrix elements are not fortuitous.

B. Critical tests of theory

Is there evidence that this formulation has practical advantages over other, older methods of treating slow collision problems?

At present there is no clear experimental test of this question. However, there are several problems where we believe it can safely be stated that our theory will predict very different results from the others.

1. Impact ionization cross sections

At present the theory of impact ionization has been formulated only in a first-order approximation to the transition amplitudes (cf. Refs. 5 and 6). Our method differs spectacularly from PSS theory and all other formulations in its predictions regarding the electronic matrix elements for ionization, and it is safe also to state that ionization cross sections computed using these matrix elements in the first-order calculation are several orders of magnitude smaller than those predicted by the other theories.

2. Isotopic systems

In our formulation there cannot be any nonadiabatic couplings ($\bar{P} + \bar{A}$) linking g and u molecular states in a symmetric but not homonuclear system such as HD^+ ; the only $g-u$ couplings are independent of collision velocity and arise from terms $\sim (m/\mu)\epsilon$ in Eqs. (3.7), associated with asymptotic isotope term splittings. Other quantum-mechanical formulations predict a $g-u$ nonadiabatic coupling.

There are also some comparative arguments in favor of our formulation for close-coupling problems:

(i) The fact that the switching function is not uniquely specified in this theory is not as serious a drawback as at first appears; at present there is no unambiguous definition of the nonadiabatic couplings in other treatments, either. It therefore comes down to a question of comparative convenience and convergence properties, in a close-coupling study. The fact is that by simple or even very trivial choices for f we can obtain matrix elements as good as those defined in most of these other formulations.

(ii) *With reasonably sophisticated forms for f* ²⁶ (as were used for the ionization studies cited earl-

ier^{5,6,27}) very great reductions in the *size, number, and range* of nonadiabatic couplings between discrete states are achieved for many problems. Thus even if we cannot specify the switching function uniquely, we can choose it in a *convenient* way to ensure more rapid convergence and less computational difficulty.

(iii) In particular, this means that if a given basis set is sufficient for convergence in a close-coupling calculation using the older methods, then with this approach we can nearly always reduce the computational effort required, by reducing the range of interactions, or the number of coupled channels, or both. A very good case where this claim can be tested is provided by the recent study of charge exchange in HeH²⁺ by Winter and Lane,¹⁴ who did a thorough close-coupling calculation using a modification of PSS theory (reference origin for electron on the He nucleus). We hope eventually to carry out a comparison calculation for this system using our formulation.

VI. SUMMARY

We have reviewed and generalized the theory of electron translation factors, showing why they are important in the theory of near-adiabatic atomic collisions, and we have proposed a quantum-mechanical form for the ETF [Eqs. (2.40), (2.39)]; inclusion of the ETF's modifies the close-coupled equations describing the multichannel scattering of the heavy particles. *Our fundamental result is that the close-coupled equations (3.12) of PSS theory should be replaced by Eqs. (3.7) for the description of slow collisions.*

The new equations (3.7) can usually be simplified by neglecting reduced-mass effects on electronic binding energies, and small corrections to the collision kinetic energy, so that Eqs. (3.13) result; Eqs. (3.13) differ from the PSS equations (3.12) only in that \bar{P} is replaced by the corrected coupling ($\bar{P} + \bar{A}$).

Using conservation of angular momentum, the three-dimensional equations (3.13) can be reduced to radial equations, either exactly [Eqs. (3.22)] or in a decoupling approximation [Eqs. (3.25)].

The \bar{A} matrix representing the ETF corrections

has the following characteristics: (i) Asymptotically, \bar{A} cancels the fictitious infinite-range couplings in \bar{P} . (ii) For isotopic systems (electrically symmetric but with nonzero mass asymmetry; e.g., HD⁺), \bar{A} exactly cancels (at all R) a spurious ($\underline{g}, \underline{u}$) coupling which appears in $\bar{P}(R)$. This problem is discussed fully in the following paper.¹⁰ (iii) The angular correction \bar{A}° cancels a fictitious long-range term (the "long moment-arm" term), proportional to R^{-1} , which appears in \bar{P}° . (iv) For "direct impact" processes, i.e., excitations not mediated by any local degeneracy, \bar{A}^R partially cancels \bar{P}^R , in some cases much reducing the transition matrix elements and resulting cross sections. (v) For processes mediated by a local degeneracy (e.g., a curve-crossing) \bar{P}^R becomes locally much larger than \bar{A}^R , which provides a small "background." However, there may be situations involving near-resonant charge exchange at large internuclear distances where exceptions to this rule occur. (vi) The small terms neglected in going from (3.7) to (3.13) reproduce reduced-mass effects on electronic binding energies and they will be important in very low-energy charge exchange or excitation exchange in isotopic systems.

More detailed calculations of \bar{A} -matrix elements will be presented in future papers.

In the paper following this one we present an alternative approach to the theory of slow collisions, which is fully rigorous and leads again to the corrected close-coupled equations. In it no reference to ETF's appears, and a coordinate transformation technique is used instead. By bringing the two formulations together we achieve a unified analysis and physical interpretation of the problem of electron translation in slow collision theory.

ACKNOWLEDGMENTS

This work has been supported in part by the National Research Council of Canada, the Research Corporation (U.S.A.), the NSF, and NASA. We thank John Rankin for some useful comments on switching functions. We thank T. G. Winter and N. F. Lane for giving us a copy of their paper of Ref. 14 in advance of publication.

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