PHYSICAL REVIEW A VOLUME 37, NUMBER 8 APRIL 15, 1988

Theory of associative ionization

Dumont M. Jones* and John S. Dahler†

Departments of Chemistry and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

(Received 17 July 1987)

The theory of atomic associative ionization (AI) presented here is a many-channel treatment incorporating radial Born-Oppenheimer and Coriolis couplings among the reactant channels as well as analogous couplings among the ionized, final states. Careful attention is paid to characterizing the basis sets used to represent the pre- and post-collisional states, especially with regard to the internal and relative angular momenta of the fragments. Particularly noteworthy in this context is our use of a total angular momentum representation. This representation is excellently adapted to the derivation of selection rules needed in the analysis of AI experiments involving atoms excited into oriented hyperfine states by means of polarized lasers. Selection rules previously obtained by heuristic means are derived more rigorously here. Finally, explicit and compact formulas are constructed for the lowest-order (two-state) approximation to the AI scattering amplitude and for the first-order Born-Oppenheimer corrections as well.

I. INTRODUCTION

This paper is devoted to the theory of associative ionization (AI), a collision process in which two atoms react to produce a free electron and a bound diatomic ion. The symbol i will be used to denote the composite initial electronic state of the two atoms; the state of the product diatomic ion will be denoted by the symbol f. The AI event then can be represented schematically as follows:

$$A(i)+B(i)\rightarrow AB^{+}(f)+e^{-} . \tag{1.1}$$

We[1] recently presented heuristic arguments for a number of selection and sum rules applicable to AI. One goal of the present investigation is the development of a theory in terms of which the formal proofs of these rules will be manifest. A second goal is the construction of a theoretical apparatus that will facilitate the calculation of AI cross sections, including corrections not accounted for in previous treatments.

The theory presented here is a natural extension of the projection-operator formalism that originally was adapted to collisional ionization by O'Malley[2] and subsequently refined by Bieniek.[3] According to this earlier theory the atomic reactants approach one another along a single Born-Oppenheimer (BO) potential energy curve $E_i(R)$. Ionization occurs only after this reactant pair enters a region of the (E_i,R) plane in which the bound initial electronic state becomes imbedded in the continuum associated with the final state, $AB^{+}(f)+e^{-}$. While there is no reason to doubt that this is the dominant mechanism by which AI takes place, it is an oversimplified picture. Corrections to the scattering amplitude for AI can result from a number of other mechanisms. For example, Coriolis coupling provides a way for the reactant atoms to jump to a second BO state from which ionization then may occur. We shall modify the earlier formalism to allow for the systematic incorporation of corrections such as this, a generalization which amounts to relaxing the "two-state approximation" common to many projection-operator formalisms.

Formulas for the scattering amplitudes appropriate to AI usually[3] are expressed in terms of a basis labeled with electronic quantum numbers and the quantum numbers specific to the orbital angular momentum of the *nuclei.* (However, see Ref. 4.) This choice is very natural but it is neither the only possibility nor, for some purposes, even the most convenient. Here the basis kets will be labeled by electronic quantum numbers and by the quantum numbers associated with the *total* orbital angular momentum of the system. Although this choice makes the formal analysis of AI slightly more difficult, it leads to at least one substantial simplification. Thus, since (to the neglect of spin-orbit coupling) the total orbital angular momentum is a constant of the motion, it is to be expected that the transition operator for AI will be a scalar, diagonal in the quantum numbers associated with this dynamical variable. We shall see that this is, in fact, the case. Furthermore, by adopting the total orbital angular momentum representation we are able to derive the previously mentioned selection rules for AI with far less difficulty and with considerably greater mathematical authority than previously possible:[5] the use of this basis enables us to mimic formally the physical arguments presented in Ref. 1.

Section II deals with some preliminary considerations, including the establishment of notation. Then in Sec. III we construct the basis kets of the total orbital angular momentum representation. Section IV is devoted to a projection operator analysis of AI, the results of which are explicit formulas for the scattering amplitude. In Sec. V the formalism is used to construct cross-section expressions suitable for numerical calculation and proofs are given of the previously mentioned selection rules for AI. Throughout the paper it is assumed that the atomic nuclei are distinguishable. The adaptation of the theory to the case of indistinguishable nuclei can be made using the format given in Ref. 1.

II. PRELIMINARY CONSIDERATIONS

Since all of the items in this section have been treated elsewhere, our discussion will be brief: the reader is referred to the literature for details.[6–8] We begin by introducing laboratory-frame particle coordinates, all of which are referred to an arbitrary but common origin. The positions of the two nuclei are denoted by $\mathbf{x}_A$ and $\mathbf{x}_B$ and that of electron j by $\mathbf{x}_j$. It is convenient to define the alternative set of coordinates,

$$\mathbf{R}=\mathbf{x}_A-\mathbf{x}_B,\quad \mathbf{x}_c=\frac{1}{M_T}\left[M_A\mathbf{x}_A+M_B\mathbf{x}_B+m_e\sum_{j=1}^{N}\mathbf{x}_j\right],$$

and

$$\mathbf{r}_j=\mathbf{x}_j-\mathbf{x}_N\ ,$$

with

$$\mathbf{x}_N=\frac{1}{M_N}(M_A\mathbf{x}_A+M_B\mathbf{x}_B)\ . \tag{2.1}$$

Here M_A, M_B, and m_e are the masses of nucleus A, nucleus B, and an electron, respectively; M_T is the total mass and M_N is the total nuclear mass. It should be observed that $\mathbf{r}_j$ has its origin at the nuclear, rather than the total, center of mass.

Associated with the coordinates $\mathbf{R}$ and $\mathbf{r}=(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ are the "coordinate eigenkets"

$$|\mathbf{r},\mathbf{R}\rangle\rangle\equiv|\mathbf{R}\rangle|\mathbf{r}\rangle\equiv|\mathbf{R}\rangle\prod_{j=1}^{N}|\mathbf{r}_j\rangle\ , \tag{2.2}$$

with

$$\begin{aligned}&\mathbf{R}_{\text{op}}|\mathbf{R}\rangle=\mathbf{R}|\mathbf{R}\rangle,\quad \langle\mathbf{R}|\mathbf{R}'\rangle=\delta(\mathbf{R}-\mathbf{R}')\ ,\\ &\mathbf{r}_{j,\text{op}}|\mathbf{r}_j\rangle=\mathbf{r}_j|\mathbf{r}_j\rangle,\quad \langle\mathbf{r}_j|\mathbf{r}_i'\rangle=\delta(\mathbf{r}_j-\mathbf{r}_i')\delta_{ji}\ .\end{aligned} \tag{2.3}$$

Here, $\mathbf{R}_{\text{op}}$ and $\mathbf{r}_{j,\text{op}}$ are the coordinate operators corresponding to $\mathbf{R}$ and $\mathbf{r}_j$. The subscript op will be dropped when no confusion can arise.

The symbol H is used for the Hamiltonian specific to the center-of-mass frame. Because we neglect spin-orbit interactions, this operator is given by the expression

$$H=\frac{1}{2\mu}\mathbf{P}_R^2+\left[\frac{1}{2m_e}\sum_{j=1}^{N}\mathbf{p}_j^2+V\right]+\frac{1}{2M_N}\left[\sum_{j=1}^{N}\mathbf{p}_j\right]^2\ . \tag{2.4}$$

Here $\mathbf{P}_R$ and $\mathbf{p}_j$ are the momenta conjugate to $\mathbf{R}$ and $\mathbf{r}_j$, respectively, and $\mu\equiv M_AM_B/(M_A+M_B)$ is the reduced nuclear mass. The potential energy V is defined by

$$\langle\langle\mathbf{r},\mathbf{R}|V|\mathbf{r},\mathbf{R}'\rangle\rangle=\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{R}-\mathbf{R}')e^2\left[\frac{z_Az_B}{R}-\sum_{j=1}^{N}\left[\frac{z_A}{|(M_B/M_N)\mathbf{R}-\mathbf{r}_j|}+\frac{z_B}{|(M_A/M_N)\mathbf{R}+\mathbf{r}_j|}\right]+\sum_{\substack{i,j=1\\ i>j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right], \tag{2.5}$$

with Z_α denoting the charge number of nucleus α. Because it is of little importance to the processes treated here, the very small "mass-polarization" energy

$$(1/2M_N)\left[\sum_{j=1}^{N}\mathbf{p}_j\right]^2$$

in (2.4) will be neglected. Then, using the identity

$$\frac{1}{2\mu}\mathbf{P}_R^2=T_R+\frac{1}{2\mu R^2}\mathbf{N}^2\ ,$$

with

$$\langle\mathbf{R}|T_R|\mathbf{R}'\rangle=\delta(\mathbf{R}-\mathbf{R}')\left[-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\partial_R(R^2\partial_R)\right]$$

and

$$\mathbf{N}=\mathbf{R}\times\mathbf{P}_R\ , \tag{2.6}$$

we rewrite the Hamiltonian in the form

$$H=T_R+\frac{1}{2\mu R^2}\mathbf{N}^2+H_{\text{el}}\ . \tag{2.7}$$

Here H_{el} is the electronic Hamiltonian, equal to the sum of the second and third terms of (2.4). Although all of the electrons are taken into account here, the theory would not be significantly different if H_{el} were replaced with an effective Hamiltonian limited to the valence electrons.

Much of our analysis will be concerned with how wave functions are transformed by rotations about the nuclear center of mass. All rotations are defined in the "passive" sense,[9] that is, as rotations of coordinate frames rather than rotations of particles. The rotation operator is denoted by the symbol $D(\alpha\beta\gamma)$, with α, β, and γ the Euler angles defined by Edmonds;[6] α and β are identical with the polar spherical angles ϕ and θ, respectively. These Euler angles are to be regarded as parameters without dynamical significance.

It is well known that $D(\alpha\beta\gamma)$ has the explicit representation

$$D(\alpha\beta\gamma)=\exp\left[\frac{i\gamma K_z}{h}\right]\exp\left[\frac{i\beta K_y}{h}\right]\exp\left[\frac{i\alpha K_z}{h}\right] \tag{2.8}$$

in terms of the laboratory-frame components of the total orbital angular momentum operator

$$\mathbf{K}=\mathbf{R}\times\mathbf{P}_R+\sum_j \mathbf{r}_j\times\mathbf{p}_j \ . \tag{2.9}$$

The single most important property of $D(\alpha\beta\gamma)$ is that it commutes with all scalar operators S, that is,

$$[D(\alpha\beta\gamma),S]=0 \ . \tag{2.10}$$

Associated with $D(\alpha\beta\gamma)$ are the "rotation coefficients" $D^K_{MM'}(\alpha\beta\gamma)$ defined according to the prescription

$$D^K_{MM'}(\alpha\beta\gamma)\delta_{KK'}=\langle KM \mid D(\alpha\beta\gamma) \mid K'M'\rangle \ . \tag{2.11}$$

These objects satisfy the eigenvalue equations[6]

$$-i\hbar\frac{\partial}{\partial\alpha}D^K_{MM'}(\alpha\beta\gamma)=\hbar M' D^K_{MM'}(\alpha\beta\gamma) \ , \tag{2.12}$$

$$-i\hbar\frac{\partial}{\partial\gamma}D^K_{MM'}(\alpha\beta\gamma)=\hbar M D^K_{MM'}(\alpha\beta\gamma) \ , \tag{2.13}$$

$$\left[\frac{\partial^2}{\partial\beta^2}+\cot\beta\frac{\partial}{\partial\beta}+\frac{1}{\sin^2\beta}\left[\frac{\partial^2}{\partial\alpha^2}+\frac{\partial^2}{\partial\gamma^2}-2\cos\beta\frac{\partial^2}{\partial\alpha\,\partial\gamma}\right]+K(K+1)\right]D^K_{MM'}(\alpha\beta\gamma)=0 \ , \tag{2.14}$$

and the normalization condition

$$\int_{-1}^{1} d(\cos\beta)\int_0^{2\pi}d\alpha\int_0^{2\pi}d\gamma\, D^{K*}_{MQ}(\alpha\beta\gamma)D^{K'}_{M'Q'}(\alpha\beta\gamma)=8\pi^2(2K+1)^{-1}\delta_{K,K'}\delta_{M,M'}\delta_{Q,Q'} \ . \tag{2.15}$$

III. ROTATIONAL-ELECTRONIC STATES

In this section we construct kets that later serve as the bases for the scattering formalism of Sec. IV. These objects characterize both the electronic motion and the heavy-particle rotational motion.

A. Bound states

First to be considered are the bound electronic kets $|\Lambda n\mathbf{R}\rangle$ characterizing the initial channels. These are chosen to be eigenkets of H_{el} and of the internuclear vector $\mathbf{R}_{\mathrm{op}}$ with which H_{el} commutes. The quantum numbers n are eigenvalues of a *set* of operators $\hat{\mathfrak{n}}$ that includes the nuclear spin and the *total* electron spin. This set also may incorporate other electronic operators such as parity. Associated with the electronic kets $|\Lambda n\mathbf{R}\rangle$ are the product kets, $|\Lambda n\mathbf{R}\rangle|\mathbf{R}\rangle\equiv|\Lambda n\mathbf{R}\rangle\rangle$, defined by

$$\begin{aligned}
&\langle\langle\Lambda'n'\mathbf{R}'\mid QH_{\mathrm{el}}Q\mid\Lambda n\mathbf{R}\rangle\rangle=E_{\Lambda n}(\mathbf{R})\delta_{\Lambda'\Lambda}\delta_{n'n}\delta(\mathbf{R}'-\mathbf{R}) \ ,\\
&\hat{\mathbf{R}}\cdot\mathbf{K}\mid\Lambda n\mathbf{R}\rangle\rangle=\hbar\Lambda\mid\Lambda n\mathbf{R}\rangle\rangle \ ,\\
&\mathbf{R}_{\mathrm{op}}\mid\Lambda n\mathbf{R}\rangle\rangle=\mathbf{R}\mid\Lambda n\mathbf{R}\rangle\rangle \ ,\\
&\hat{\mathfrak{n}}\mid\Lambda n\mathbf{R}\rangle\rangle=n\mid\Lambda n\mathbf{R}\rangle\rangle \ ,
\end{aligned}\tag{3.1}$$

and the orthonormality conditions

$$\langle\langle\Lambda n\mathbf{R}\mid\Lambda'n'\mathbf{R}'\rangle\rangle=\delta_{\Lambda\Lambda'}\delta_{nn'}\delta(\mathbf{R}-\mathbf{R}') \ . \tag{3.2}$$

The operator $\hat{\mathbf{R}}\cdot\mathbf{K}$ appearing here is the component of total orbital angular momentum (or equivalently the component of total electronic orbital angular momentum) in the direction of $\hat{\mathbf{R}}=\mathbf{R}/R$. Q is the projection operator on a selected set of bound electronic states to be specified in the next paragraph. The operators $QH_{\mathrm{el}}Q$, $\hat{\mathbf{R}}\cdot\mathbf{K}$, $\mathbf{R}_{\mathrm{op}}$, and (all the members of) $\hat{\mathfrak{n}}$ form a mutually commutative set. Furthermore, with a suitable choice of Q (see below), the operators $QH_{\mathrm{el}}Q$, $\hat{\mathbf{R}}\cdot\mathbf{K}$, and $\hat{\mathfrak{n}}$ all commute with $D(\alpha\beta\gamma)$.

The projection Q can be chosen in a variety of ways. For our purposes, it is convenient to demand that (1) Q project onto a subspace that includes all bound electronic states which are significantly populated in the associative ionization process of interest, and (2) that Q commute with $D(\alpha\beta\gamma)$. The first of these conditions implies that the minimal subspace associated with Q depends on the relative kinetic energy and initial electronic state of the colliding atoms. The second condition is not difficult to satisfy, for once a particular state $|x\mathbf{R}\rangle\rangle$ has been chosen for inclusion in the "Q subspace," the scalar character of Q is assured by adding to this space all others $|x\mathbf{R}'\rangle\rangle$, obtained from it by rotations.

With $\hat{\mathbf{z}}$ the direction of the laboratory-frame polar axis and $\hat{\mathbf{R}}=(\phi,\theta)$, it then follows that $D^{-1}(\phi,\theta,0)\mid\Lambda n,R\hat{\mathbf{z}}\rangle\rangle$ is an eigenket obeying (3.1). We therefore can make the identification

$$D^{-1}(\phi,\theta,0)\mid\Lambda n,R\hat{\mathbf{z}}\rangle\rangle\equiv\mid\Lambda n\mathbf{R}\rangle\rangle \ , \tag{3.3}$$

and, in addition, conclude that the energy $E_{\Lambda n}(\mathbf{R})=E_{\Lambda n}(R)$ of the bound electronic state does not depend on the orientation of the internuclear axis. (3.3) also leads directly to the condition

$$\begin{aligned}
\langle\langle\mathbf{r},\mathbf{R}_0\mid\Lambda n\mathbf{R}\rangle\rangle&=\phi_{\Lambda n}(\mathbf{r}\mid\mathbf{R})\delta(\mathbf{R}-\mathbf{R}_0)\\
&=\phi_{\Lambda n}(\xi\mid R\hat{\mathbf{z}})\delta(\mathbf{R}-\mathbf{R}_0)
\end{aligned}\tag{3.4}$$

on the electronic wave functions

$$\phi_{\Lambda n}(\mathbf{r}\mid\mathbf{R})=\phi_{\Lambda n}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\mid\mathbf{R}) \ ,$$

associated with the antisymmetric ket $|\Lambda n\mathbf{R}\rangle\rangle$. In this formula ξ denotes the set of electronic coordinates obtained when $D(\phi,\theta,0)$ is applied to $|\mathbf{r},\mathbf{R}\rangle\rangle$. (3.4) is an expression of the well-known invariance of the electronic wave function under an overall rotation. We shall call the set of numbers ξ the "molecular frame" (MF) coordinates, for they specify the positions of the electrons in a reference frame that has $\hat{\mathbf{R}}$ as its polar axis. Indeed, $\mathbf{R}$ and ξ may be used in place of $\mathbf{R}$ and $\mathbf{r}$ as coordinates specifying the particle positions. Two points must be made about this coordinate transformation. First, the electronic coordinates ξ are, by definition, invariant under rotations. Second, the coordinate $\hat{\mathbf{R}}$ coupled with ξ is the same pair of numbers (ϕ,θ) as that associated with $\mathbf{r}$, but its dynamical significance is different. In the pair $(\mathbf{r},\mathbf{R})$, $\hat{\mathbf{R}}$ represents the orientation of the internuclear axis, and corresponds to an operator that is "conjugate"[10] to the nuclear angular momentum $\mathbf{N}$. However, in the pair $(\xi,\mathbf{R})$, $\hat{\mathbf{R}}$ indicates the orientation of the polar axis of the diatomic quasimolecule, and corresponds to an operator that is conjugate to the *total* orbital angular momentum $\mathbf{K}$. Subject to this understanding, we can regard the two coordinate kets $|\xi,\mathbf{R}\rangle\rangle$ and $|\mathbf{r},\mathbf{R}\rangle\rangle$ as interchangeable, provided that $\mathbf{r}$ and ξ are related to one another by the connection mentioned above.

We now can use the $|\Lambda n\mathbf{R}\rangle\rangle$ as building blocks for a basis set that includes the heavy-particle rotational motion. For this purpose it is convenient to have at our disposal kets which are eigenstates of $\mathbf{K}^2$ and K_z as well as of $\hat{\mathbf{R}}\cdot\mathbf{K}$ and $\hat{\mathbf{n}}$. The two operators K_z and $\mathbf{K}^2$ are given in terms of $\hat{\mathbf{R}}=(\phi,\theta)$ and ξ by the expressions

$$K_z=-i\hbar\partial_\phi \tag{3.5}$$

and

$$\mathbf{K}^2=-\hbar^2\int d\xi\int d\mathbf{R}\,|\xi,\mathbf{R}\rangle\rangle\left[\frac{1}{\sin^2\theta}\partial_\phi^2+\cot\theta\partial_\theta-2\frac{\cot\theta}{\sin\theta}\partial_\phi\left[\frac{i}{\hbar}\hat{\mathbf{R}}\cdot\mathbf{L}\right]+\partial_\theta^2+\frac{1}{\sin^2\theta}\left[\frac{i}{\hbar}\hat{\mathbf{R}}\cdot\mathbf{L}\right]^2\right]\langle\langle\xi,\mathbf{R}|\ . \tag{3.6}$$

Here $\mathbf{L}=\mathbf{K}-\mathbf{N}$ is the total electronic orbital angular momentum, $\partial_\phi\equiv(\partial/\partial\phi)_{R,\theta,\xi}$ and $\partial_\theta\equiv(\partial/\partial_\theta)_{R,\phi,\xi}$.

From (2.12)–(2.14), (3.1), (3.5), and (3.6) it follows that the required eigenkets of $\mathbf{K}^2$, K_z, $\hat{\mathbf{R}}\cdot\mathbf{K}$ and $\hat{\mathbf{n}}$ may be written in the form

$$|KM\Lambda nR\rangle\rangle=N_K\int d\xi\int d\hat{\mathbf{R}}\,|\xi,\mathbf{R}\rangle\rangle \times D^K_{\Lambda M}(\hat{\mathbf{R}})\phi_{\Lambda n}(\xi\,|\,R\hat{\mathbf{z}})\ , \tag{3.7}$$

with $D^K_{\Lambda M}(\hat{\mathbf{R}})\equiv D^K_{\Lambda M}(\phi,\theta,0)$. The factor $N_K=[(2K+1)/\ 4\pi]^{1/2}$ has been chosen so that these basis kets satisfy the normalization condition

$$\langle\langle K'M'\Lambda'n'R'\,|\,KM\Lambda nR\rangle\rangle =R^{-2}\delta(R-R')\delta_{KK'}\delta_{MM'}\delta_{\Lambda\Lambda'}\delta_{nn'}\ . \tag{3.8}$$

B. Continuum states

Our next task is to construct analogues of $|\Lambda n\mathbf{R}\rangle\rangle$ and $|KM\Lambda nR\rangle\rangle$ appropriate to *continuum* electronic states. These kets will be used to describe the scattering channels (cf. Sec. IV) specific to the products of AI. As in the case of $|\Lambda n\mathbf{R}\rangle\rangle$, we begin with an electronic state $|\Lambda cq\mathbf{R}\rangle$ and the associated product ket $|\Lambda cq\mathbf{R}\rangle\rangle=|\Lambda cq\mathbf{R}\rangle\,|\mathbf{R}\rangle$. Here c includes quantum numbers n like those of $|\Lambda n\mathbf{R}\rangle\rangle$, along with others soon to be specified. q is the "asymptotic wave number" characteristic of the translational motion of the ionized electron when it is far from the AB^+ ion. As implied by the notation, the ket $|\Lambda cq\mathbf{R}\rangle\rangle$ satisfies the last three of Eqs. (3.1).

One could identify the kets $|\Lambda cq\mathbf{R}\rangle$ with continuum states of the N-electron Hamiltonian operator H_{el}, that is, with solutions of the Schrödinger equation $(H_{\text{el}}-E)\psi=0$ specific to one or more unbound electrons. However, this approach is fraught with difficulties, not the least of which is the horrendous task of constructing these N-electron wave functions. The alternative scheme which we adopt replaces the true continuum with an approximate continuum, each state of which is represented by the (antisymmetrized) product of an $(N-1)$-electron state of the "free" AB^+ ion and a continuum orbital characteristic of an electron interacting with an AB^+ ion in an unperturbed, "electronically frozen" state. (Since multiply ionized states play no significant role in the AI processes of concern to us here, they are ignored.) The remainder of this Sec. III B is devoted to a detailed characterization of this "frozen-core" basis of continuum electronic states.

We begin by introducing the AB^+, ionic analog of $|\Lambda n\mathbf{R}\rangle\rangle$. This ket, $|\Lambda_I n_I\mathbf{R}m\rangle\rangle$, is antisymmetric on the product space of the $N-1$ *numbered* and *sequentially ordered* electrons $1,2,\ldots,m-1,m+1,\ldots,N$. The quantum numbers Λ_I and n_I are ionic analogs of Λ and n, respectively. The kets $|\Lambda_I n_I\mathbf{R}m\rangle\rangle$ are required to satisfy the characteristic equations

$$\begin{aligned}\langle\langle\Lambda_I'n_I'\mathbf{R}'m\,|\,H_{\text{el}}(m)\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle &=E^I_{\Lambda_I n_I}(R)\delta_{\Lambda_I'\Lambda_I}\delta_{n_I'n_I}\delta(\mathbf{R}-\mathbf{R}')\ ,\\ \hat{\mathbf{R}}\cdot\mathbf{L}(m)\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle&=\hbar\Lambda_I\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle\ ,\\ \hat{\mathbf{n}}(m)\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle&=n_I\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle\ ,\\ \mathbf{R}_{\text{op}}\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle&=\mathbf{R}\,|\,\Lambda_I n_I\mathbf{R}m\rangle\rangle\ ,\end{aligned} \tag{3.9}$$

and conform to the orthogonality conditions

$$\langle\langle\Lambda_I n_I\mathbf{R}m\,|\,\Lambda_I'n_I'\mathbf{R}'m\rangle\rangle=\delta_{\Lambda_I\Lambda_I'}\delta_{n_In_I'}\delta(\mathbf{R}-\mathbf{R}')\ . \tag{3.10}$$

The operator $\mathbf{L}(m)$ appearing in (3.9) is the total electronic orbital angular momentum less that of electron m. The operators $H_{\text{el}}(m)$ and $\hat{\mathbf{n}}(m)$ are defined similarly.

It is evident that the rotational transformation properties of the $|\Lambda_I n_I\mathbf{R}m\rangle\rangle$ are the same as those of the $|\Lambda n\mathbf{R}\rangle\rangle$. Consequently, these kets can be written as

$$|\Lambda_I n_I\mathbf{R}m\rangle\rangle=\int d\xi(m)\,|\,\xi(m)\mathbf{R}\rangle\rangle\phi^I_{\Lambda_I n_I}(\xi(m)\,|\,R\hat{\mathbf{z}})\ , \tag{3.11}$$

where $\xi(m)=(\xi_1,\ldots,\xi_{m-1},\xi_{m+1},\ldots,\xi_N)$. The ionic wave function $\phi^I_{\Lambda_I n_I}$ has the same form regardless of the choice of m. Finally, the coordinate $\mathbf{R}$ appearing in

$|\,\xi(m)\mathbf{R}\rangle\!\rangle$ is conjugate[10] to the angular momentum $\mathbf{K}(m)\equiv\mathbf{K}-\mathbf{r}_m\times\mathbf{p}_m$.

The next step is to combine the $(N-1)$-electron kets $|\,\Lambda_I n_I \mathbf{R}m\,\rangle\!\rangle$ and the spin kets $|\,\tfrac{1}{2}M_e m\,\rangle$ of electron m into composites,

$$|\,\Lambda_I q_I \mathbf{R}m\,\rangle\!\rangle\equiv\sum_{M_{SI},M_e}\langle S_I M_{SI}\tfrac{1}{2}M_e\,|\,SM_S\rangle \times|\,\Lambda_I n_I\mathbf{R}m\,\rangle\!\rangle\,|\,\tfrac{1}{2}M_e m\,\rangle\ , \qquad (3.12)$$

that are eigenstates of the N-electron spin operators $\mathbf{S}^2$ and S_z. Here S_I and M_{SI} are the quantum numbers corresponding to the electron spin of the AB^+ ion and to its projection along the laboratory-frame z axis. M_e is the projection quantum number associated with the spin of the unbound electron m and S and M_S are the spin quantum numbers of the entire, N-electron system. $\langle S_I M_{SI}\tfrac{1}{2}M_e\,|\,SM_S\rangle$ is a Clebsch-Gordan coefficient. Finally, q_I is the set of quantum numbers consisting of S, M_S, and all members of n_I *except* M_{SI}. Therefore, $|\,\Lambda_I q_I\mathbf{R}m\,\rangle\!\rangle$ incorporates the spin of electron m and is an eigenket of the electronic operators $\mathbf{S}^2$, S_z, and $\hat{\mathbf{R}}\cdot\mathbf{L}(m)$ as well as of all the operators belonging to the set $\hat{\mathbf{n}}(m)$, *save* $S_z(m)$.

The basis kets of the frozen-core approximation to the continuum now may be written in the form

$$\begin{aligned}|\,\Lambda cq\mathbf{R}\rangle\!\rangle&=A[\,|\,\Lambda_I q_I\mathbf{R}m\,\rangle\!\rangle\,|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle\,]\\&=N^{-1/2}\sum_{m=1}^{N}(-1)^{m+1}\,|\,\Lambda_I q_I\mathbf{R}m\,\rangle\!\rangle\\&\qquad\times|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle\ ,\end{aligned}\qquad (3.13)$$

with $|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle$ a one-electron ket on the space associated with the translational degrees of freedom of electron m. The set of labels c consists of the eigenvalues q_I and the two indices λ and μ associated with the unbound electron; $\Lambda\equiv\Lambda_I+\mu$, cf. (3.16) below. We require the one-electron kets to be orthogonal to the bound and ionic states, that is,

$$\langle\Lambda' n'\mathbf{R}\,|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle=0$$

and

$$\langle\Lambda_I' q_I' Rm'\,|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle=0$$

for $m\neq m'$. In other words, the wave functions

$$\phi_{q\lambda\mu}^{(\Lambda_I q_I)}(\xi_m\,|\,R\hat{\mathbf{z}})=\langle\xi_m\,|\,q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,\rangle \qquad (3.14)$$

are constrained to be orthogonal to all of the molecular orbitals used in constructing the electronic bound states of AB and AB^+. The physical interpretations of the indices λ and μ are apparent from the asymptotic condition

$$\begin{aligned}\phi_{q\lambda\mu}^{(\Lambda_I q_I)}(\mathbf{r}_m\,|\,\mathbf{R})\underset{r_m\to\infty}{\sim}\pi^{-1/2}r_m^{-1}\\ \times\{\exp[iqr_m+i(a_0q)^{-1}\ln(2qr_m)\\ +i\eta_{\lambda\mu}]i^{-\lambda}Y_{\lambda\mu}(\hat{\mathbf{r}}_m)_{\hat{\mathbf{R}}}\\ +\phi_{\text{in}}(\mathbf{r}_m\,|\,\mathbf{R})\}\ ,\end{aligned}\qquad (3.15)$$

to which the one-electron wave function is required to conform. Here a_0 denotes the Bohr radius, ϕ_{in} an incoming wave, and $Y_{\lambda\mu}(\hat{\mathbf{r}})_{\hat{\mathbf{R}}}$, a spherical harmonic referred to a coordinate frame with its polar axis along $\hat{\mathbf{R}}$. Although the angular momentum of the unbound electron is not a constant of the motion, its component along $\hat{\mathbf{R}}$ is conserved. Consequently, the good quantum number μ is related to Λ_I and Λ by the connection

$$\Lambda=\Lambda_I+\mu\ . \qquad (3.16)$$

The orthogonality constraints upon the continuum orbitals, together with the normalization conditions (3.10) and

$$\langle q\lambda\mu(\Lambda_I q_I)\mathbf{R}m\,|\,q'\lambda'\mu'(\Lambda_I q_I)\mathbf{R}m\,\rangle=\delta_{\lambda\lambda'}\delta_{\mu\mu'}\delta(q-q')\ , \qquad (3.17)$$

imply that

$$\langle\!\langle\Lambda cq\mathbf{R}\,|\,\Lambda' c' q'\mathbf{R}'\rangle\!\rangle=\delta_{\Lambda\Lambda'}\delta_{cc'}\delta(q-q')\delta(\mathbf{R}-\mathbf{R}')\ . \qquad (3.18)$$

These relationships are, in turn, sufficient to ensure that the objects

$$C_p=\sum_{\lambda,\mu}\int dq\int d\mathbf{R}\,\,|\,\Lambda cq\mathbf{R}\rangle\!\rangle\langle\!\langle\Lambda cq\mathbf{R}\,|\ ,\quad p=(\Lambda_I q_I) \qquad (3.19)$$

satisfy the conditions

$$C_pC_{p'}=C_{p'}C_p=\delta_{pp'}C_p \qquad (3.20)$$

(with $\delta_{pp'}=\delta_{\Lambda_I\Lambda_I'}\delta_{q_Iq_I'}$) required of projection operators onto the singly ionized N-electron configurations associated with specifically designated states of the AB^+ diatomic ion.

The approximation we make is to replace the exact complement of the bound-state projection operator

$$\begin{aligned}&Q=\sum_q P_q\ ,\\&P_q\equiv\int d\mathbf{R}\,\,|\,\Lambda n\mathbf{R}\rangle\!\rangle\langle\!\langle\Lambda n\mathbf{R}\,|\ ,\quad q\equiv(\Lambda n)\end{aligned}\qquad (3.21)$$

with the projection operator

$$\begin{aligned}&P=\sum_p C_p\ ,\\&C_p=\sum_{\lambda,\mu}\int dq\int d\mathbf{R}\,\,|\,\Lambda cq\mathbf{R}\rangle\!\rangle\langle\!\langle\Lambda cq\mathbf{R}\,|\ ,\quad p\equiv(\Lambda_I q_I)\end{aligned}\qquad (3.22)$$

onto a set of singly-ionized frozen-core states. To complete the prescription for these states we define the continuum orbitals of the frozen-core basis to be those which satisfy the equations

$$\langle\Lambda_I q_I\mathbf{R}1\,|\,H_{\text{el}}-E(\Lambda cq;R)\,|\,\Lambda cq\mathbf{R}\rangle=0\ , \qquad (3.23)$$

with

$$E(\Lambda cq;R)=E^I_{\Lambda_I n_I}(R)+\hbar^2q^2/2m_e\ .$$

To aid in the interpretation of this prescription we observe [from the definitions (3.19) and (3.22)] that

$$PH_{\text{el}}P \mid \Lambda cq\mathbf{R}\rangle\rangle = \left[\sum_{p'}\sum_{p''} C_{p'}H_{\text{el}}C_{p''}\right] \mid \Lambda cq\mathbf{R}\rangle\rangle = \sum_{\Lambda'c'} \int dq' \mid \Lambda'c'q'\mathbf{R}\rangle\rangle\langle \Lambda'c'q'\mathbf{R} \mid H_{\text{el}} \mid \Lambda cq\mathbf{R}\rangle \ . \tag{3.24}$$

Consequently, (3.23) is equivalent to the requirement,

$$[H_{\text{FC}} - E(\Lambda cq;R)] \mid \Lambda cq\mathbf{R}\rangle\rangle = 0 \ , \tag{3.25}$$

that $\mid \Lambda cq\mathbf{R}\rangle\rangle$ be an eigenket of

$$H_{\text{FC}} = (PH_{\text{el}}P)_d = \sum_{p} C_pH_{\text{el}}C_p \ , \tag{3.26}$$

the frozen-core, diagonal fragment of the operator $PH_{\text{el}}P$. This operator H_{FC} is the part of $PH_{\text{el}}P$ that is diagonal in the polarization couplings; in other words, it is the part of $PH_{\text{el}}P$ to which the ionic wave functions are invariant.

The defining equations (3.23) or (3.25) can be written in the alternative forms

$$\left[-\frac{\hbar^2}{2m_e}\nabla_r^2 - [E - E^I_{\Lambda_I q_I}(R)] + V_{\Lambda_I q_I}(\mathbf{r} \mid \mathbf{R})\right]\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\mathbf{r} \mid \mathbf{R}) + \int d\mathbf{r}' K_{\Lambda_I q_I}(\mathbf{r},\mathbf{r}';\mathbf{R})\phi^{(\Lambda_\text{I} \text{q}_\text{I})}_{\text{q}\lambda\mu}(\mathbf{r}' \mid \mathbf{R}) = 0 \ , \tag{3.27}$$

which closely resemble Hartree-Fock equations. Here $E - E^I_{\Lambda_I q_I}(R) = \hbar^2 q^2/2m_e$ is the kinetic energy of the unbound electron, and $V_{\Lambda_I q_I} \equiv V_{\Lambda_I q_I, \Lambda_I q_I}$ and $K_{\Lambda_I q_I} \equiv K_{\Lambda_I q_I, \Lambda_I q_I}$ are diagonal elements of the Coulombic and exchange operators

$$V_{tt'}(\mathbf{r}_1 \mid \mathbf{R}) = \int d\mathbf{r}(1)[\phi_t(\mathbf{r}(1) \mid \mathbf{R})]^* \, U_1\phi_{t'}(\mathbf{r}(1) \mid \mathbf{R}) \tag{3.28}$$

and

$$K_{tt'}(\mathbf{r}_1,\mathbf{r}'_1 \mid \mathbf{R}) = -(N-1)\int d\mathbf{r}(1)\{[\phi_t(\mathbf{r}(1) \mid \mathbf{R})]^* H_{\text{el}}\phi_{t'}(\mathbf{r}(2) \mid \mathbf{R})\}\delta(\mathbf{r}_2 - \mathbf{r}'_1) \ , \tag{3.29}$$

respectively. [Recall that $d\mathbf{r}(1) = d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N$.] In these expressions

$$t = (\Lambda_I, q_I) \ ,$$

$$\phi_{\Lambda_I q_I}(\mathbf{r}(m) \mid \mathbf{R}) = \langle \mathbf{r}(m) \mid \Lambda_I q_I \mathbf{R} m\rangle \ ,$$

and

$$U_1 = \sum_{m=2}^{N} \frac{e^2}{|\xi_1 - \xi_m|} - \frac{Z_A e^2}{|\xi_1 - \hat{\mathbf{R}}R_A|} - \frac{Z_B e^2}{|\xi_1 + \hat{\mathbf{R}}R_B|} \ , \tag{3.30}$$

with $R_A = R(M_A/M_N)$ and $R_B = R(M_B/M_N)$.

The first term of (3.27) is descriptive of an unbound electron interacting with an AB^+ ion in the state $\phi^I_{\Lambda_I n_I}(\mathbf{r}(1) \mid \mathbf{R})$. The exchange term arises from the indistinguishability of the free electron from those that are bound. According to (3.27) the wave function of the unbound electron will be very small at separations r for which the effective potential energy is positive and greater than $\hbar^2 q^2/2m_e$; when the orbital angular momentum of this electron is large, the centrifugal barrier $\hbar^2\lambda(\lambda+1)/2m_e r^2$ prevents it from drawing near to the ion. Indeed, because the other energy operators appearing in (3.27) are short-ranged potentials and exchange interactions, the potential energy of the unbound electron is dominated for large values of λ by the centrifugal and Coulombic terms. Therefore, $\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\mathbf{r} \mid \mathbf{R})$ will be small whenever r is less than the critical value r^* defined by

$$\frac{\hbar^2\lambda(\lambda+1)}{2m_e r^{*2}} - \frac{e^2}{r^*} = \frac{\hbar^2 q^2}{2m_e} \ . \tag{3.31}$$

By rearranging this we obtain for r^* the formula[11]

$$r^* = q^{-1}\{-(a_0 q)^{-1} + [(a_0 q)^{-2} + \lambda(\lambda+1)]^{1/2}\} \ . \tag{3.32}$$

For modest values of the electronic energy, e.g., $\hbar^2 q^2/2m_e \lesssim 0.5$ eV, r^* is greater than molecular dimensions, e.g., 3 Å, even for values of λ as small as 3. This means that the wave function $\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\mathbf{r} \mid \mathbf{R})$ will be large in the immediate vicinity of the ion only if the value of λ is very small, namely, 0, 1, and 2. Conclusions that can be drawn from this observation will be discussed in Sec. V.

The boundary condition (3.15), the normalization condition (3.17), and the requirement of regularity at the origin combine with Eqs. (3.27) to fully specify the continuum orbitals of the frozen-core model. The "incoming wave" included in the asymptotic boundary condition (3.5) is determined in the course of solving the wave equation (3.27).[12] This term will involve a number of spherical harmonics, $Y_{\lambda\mu}(\hat{\mathbf{r}})_{\hat{\mathbf{R}}}$, because the angular momentum of an electron subject to the noncentral field of the diatomic ion is not a constant of the motion. A procedure for generating solutions to equations of the type (3.27) has been given (in the exchange-free approximation) by Itikawa,[12] and he and his collaborators have performed a number of calculations using this scheme.[12,13] A Coulomb wave is the solution of the equation obtained from (3.27) by discarding the exchange operator $K_{\Lambda_I q_I}$ and replacing $V_{\Lambda_I q_I}$ with the Coulombic potential characteristic of a single point charge. This is the approximation which has been used in virtually all calculations of the rates of chemi-ionization processes.

Combining the three equations (3.11), (3.12), and (3.13), we obtain the formula

$$\begin{aligned} |\Lambda c q \mathbf{R}\rangle\rangle &= \int d\mathbf{r}\, |\mathbf{r},\mathbf{R}\rangle\rangle\, A[\phi^{I}_{\Lambda_I q_I}(\mathbf{r}(m)\,|\,\mathbf{R})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\mathbf{r}_m\,|\,\mathbf{R})] \\ &= \int d\boldsymbol{\xi}\, |\boldsymbol{\xi},\mathbf{R}\rangle\rangle\, A[\phi^{I}_{\Lambda_I q_I}(\boldsymbol{\xi}(m)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\boldsymbol{\xi}_m\,|\,R\hat{\mathbf{z}})] \\ &= A\int d\mathbf{r}_m \int d\boldsymbol{\xi}(m)\, |\boldsymbol{\xi}(m),\mathbf{r}_m\rangle\, |\mathbf{R}\rangle \phi^{I}_{\Lambda_I q_I}(\boldsymbol{\xi}(m)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\mathbf{r}_m\,|\,\mathbf{R})\,, \end{aligned} \tag{3.33}$$

with

$$\phi^{I}_{\Lambda_I q_I}(\mathbf{r}(m)\,|\,\mathbf{R}) = \sum_{M_{SI},M_e} \langle S_I M_{SI} \tfrac{1}{2} M_e \,|\, S M_S\rangle \times \phi^{I}_{\Lambda_I n_I}(\mathbf{r}(m)\,|\,\mathbf{R})\chi_{(1/2)M_e}(\sigma_m)\,, \tag{3.34}$$

and where $\chi_{(1/2)M_e}(\sigma_m) = \langle \sigma_m \,|\, \frac{1}{2} M_e m\rangle$ denotes the spin wave function of the unbound electron. Here and elsewhere in this paper we suppress the spin coordinates of bound electrons. In its first appearance in (3.33), $\mathbf{R}$ is "conjugate"[10] to the nuclear angular momentum, in the second it is conjugate to $\mathbf{K}$, and in the third it is conjugate to $\mathbf{K}(m)$.

It is worthy of notice that ionic $(N-1)$-electron operators such as $\mathbf{L}(m)$, $\mathbf{S}_I^2(m)$, and $S_{Iz}(m)$ can be imbedded in the space of operators for N equivalent electrons. The quantum numbers of the frozen-core kets $|\Lambda c q \mathbf{R}\rangle\rangle$ then can be interpreted as pertaining to the bound electrons but not to any particular set of them such as $1,2,\ldots,N-1$. Thus, for example, $\hbar\Lambda_I$ can be identified as the eigenvalue of $|\Lambda c q \mathbf{R}\rangle\rangle$ associated with the N-electron operator

$$\hat{\mathbf{R}}\cdot\mathbf{L}_I = \hat{\mathbf{R}}\cdot \sum_{m=1}^{N} B(m)\mathbf{L}(m)B(m)\,. \tag{3.35}$$

This is defined in terms of projectors,

$$B(m) = \sum_{\Lambda,c} \int dq \int d\mathbf{R}\, |\Lambda c q \mathbf{R} m\rangle\rangle\langle\langle \Lambda c q \mathbf{R} m|\,, \tag{3.36}$$

onto the set of frozen-core continuum states

$$|\Lambda c q \mathbf{R} m\rangle\rangle = |\Lambda_I q_I \mathbf{R} m\rangle\rangle\, |q\lambda\mu(\Lambda_I q_I)\mathbf{R} m\rangle$$

with electron m unbound.

Our final task is to construct the continuum analog of the bound-state kets $|KM\Lambda n R\rangle\rangle$. These are related to the $|\Lambda c q \mathbf{R}\rangle\rangle$ by the formula

$$|KM\Lambda c q R\rangle\rangle = N_K \int d\hat{\mathbf{R}}\, D^{K}_{\Lambda M}(\hat{\mathbf{R}})\, |\Lambda c q \mathbf{R}\rangle\rangle\,. \tag{3.37}$$

With the help of (3.33) this can be rewritten in a form

$$|KM\Lambda c q R\rangle\rangle = N_K \int d\boldsymbol{\xi} \int d\hat{\mathbf{R}}\, |\boldsymbol{\xi},\mathbf{R}\rangle\rangle D^{K}_{\Lambda M}(\hat{\mathbf{R}}) A \times [\phi^{I}_{\Lambda_I q_I}(\boldsymbol{\xi}(m)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\boldsymbol{\xi}_m\,|\,R\hat{\mathbf{z}})]\,, \tag{3.38}$$

which is directly comparable to (3.7).

IV. FORMAL SCATTERING THEORY

Now that the necessary preliminaries have been established we can proceed with the construction of a scattering theory of associative ionization. This section deals mainly with formal matters; the construction of detailed, explicit formulas is deferred to Sec. V.

The fundamental object occurring in the theory of AI is the transition matrix element $\langle f\,|\,T\,|\,i\rangle$, an explicit integral representation of which is given by the expression

$$\langle f\,|\,T\,|\,i\rangle = \langle\langle \Phi^{-}(f\mathbf{q})\,|\,PHQ\,|\,\Psi^{+}(i\mathbf{k})\rangle\rangle\,. \tag{4.1}$$

This formula can be derived by the same methods used to obtain Eq. XIX.120 of Ref. 11. The kets $|\Psi^{+}(i\mathbf{k})\rangle\rangle$ and $|\Phi^{-}(f\mathbf{q})\rangle\rangle$ appearing in (4.1) are solutions of the equations

$$(H-E_T)\,|\Psi^{+}(i\mathbf{k})\rangle\rangle = 0,\quad [H \equiv (P+Q)H(P+Q)] \tag{4.2}$$

and

$$(H_{PP}-E_T)\,|\Phi^{-}(f\mathbf{q})\rangle\rangle = 0,\quad (H_{PP} \equiv PHP)\,, \tag{4.3}$$

respectively. Whenever it results in no confusion the symbols $|\Psi\rangle\rangle$ and $|\Phi\rangle\rangle$ will be used in place of $|\Psi^{+}(i\mathbf{k})\rangle\rangle$ and $|\Phi^{-}(f\mathbf{q})\rangle\rangle$. In (4.1)–(4.3) the $+$ $(-)$ superscript refers to the conventional outgoing (incoming) boundary condition of scattering theory. The composites i and f refer to the internal quantum numbers of the initial and final states, respectively, while $\mathbf{k}$ and $\mathbf{q}$ are the initial and final free-particle wave vectors. $P \equiv \sum_p C_p$ and $Q \equiv \sum_q P_q$ are the projection operators introduced in Sec. III; we recall that

$$PQ = QP = 0,\quad P^2 = P,\quad Q^2 = 0,\quad P+Q \equiv 1\,, \tag{4.4}$$

and that the sums over p and q are limited to configurations judged to be of importance to the particular collisional event under consideration.

The kets $|\Psi^{+}(i\mathbf{k})\rangle\rangle$ and $|\Phi^{-}(f\mathbf{q})\rangle\rangle$ soon will be more fully characterized. Indeed, much of the analysis will be concerned with how to construct $Q\,|\Psi\rangle\rangle$ and $|\Phi\rangle\rangle$, given the basis sets of Sec. III. The formal theory consists, in essence, of selecting an appropriate projection-operator scheme and then solving the associated equations. The particular scheme that we adopt associates an effective Hamiltonian operator with each channel. Inspection of these operators allows a number of qualitative predictions to be made without involvement in detailed numerical calculations.

The basic equations of the projection-operator formalism are obtained by applying Q and P to (4.2). In terms of the conventional notation, $QHQ \equiv H_{QQ}$, etc., these equations are

$$\begin{aligned}(H_{QQ}-E_T)Q\,|\Psi\rangle\rangle&=-H_{QP}P\,|\Psi\rangle\rangle\,,\\(H_{PP}-E_T)P\,|\Psi\rangle\rangle&=-H_{PQ}Q\,|\Psi\rangle\rangle\,.\end{aligned}\tag{4.5}$$

The solution of the second of (4.5) is given by the formula

$$P\,|\Psi\rangle\rangle=G_P^+H_{PQ}Q\,|\Psi\rangle\rangle\,,\tag{4.6}$$

wherein

$$G_P^+\equiv(E_T-H_{PP}+i\varepsilon)^{-1},\quad \varepsilon\to 0^+\,.\tag{4.7}$$

This solution satisfies the asymptotic boundary condition required of any inelastic channel, namely, that it consist exclusively of outgoing waves. By inserting the result (4.6) into the first of (4.5), we obtain the equation

$$(\mathcal{H}_{QQ}-E_T)Q\,|\Psi\rangle\rangle=0\,,\tag{4.8}$$

with

$$\mathcal{H}_{QQ}\equiv H_{QQ}+H_{QP}G_P^+H_{PQ}\,.\tag{4.9}$$

(4.8) is the governing equation for the projection of $|\Psi\rangle\rangle$ onto the Q subspace. The operators contained in $\mathcal{H}_{QQ}$ account for coupling between the bound and continuum electronic states. Because of this coupling the operator $\mathcal{H}_{QQ}$ is non-Hermitian and there is an associated, collision-induced flow of amplitude from Q space to P space.

To obtain equations describing the motion in a particular channel the projection-operator method must be applied again, this time to (4.8). Thus, by introducing the decomposition

$$Q\,|\Psi\rangle\rangle=P_i\,|\Psi\rangle\rangle+N_i\,|\Psi\rangle\rangle\,,\tag{4.10}$$

with N_i defined by the equation

$$N_i\equiv Q-P_i\,,\tag{4.11}$$

we obtain (in an obvious notation) the coupled equations

$$\begin{aligned}(\mathcal{H}_{ii}-E_T)P_i\,|\Psi\rangle\rangle&=-\mathcal{H}_{iN}N_i\,|\Psi\rangle\rangle\,,\\(\mathcal{H}_{NN}-E_T)N_i\,|\Psi\rangle\rangle&=-\mathcal{H}_{Ni}P_i\,|\Psi\rangle\rangle\,.\end{aligned}\tag{4.12}$$

From these it follows that

$$\Big(\mathcal{H}_{ii}-E_T+\sum_{m(\neq i)}\sum_{n(\neq i)}\mathcal{H}_{im}G_{mn}^+\mathcal{H}_{ni}\Big)P_i\,|\Psi\rangle\rangle=0\,,\tag{4.13}$$

and

$$P_j\,|\Psi\rangle\rangle=\sum_{l(\neq i)}G_{jl}^+\mathcal{H}_{li}P_i\,|\Psi\rangle\rangle,\quad j\neq i\tag{4.14}$$

with

$$G_{mn}^+\equiv P_m[N_i(E_T-\mathcal{H}_{QQ}+i\varepsilon)N_i]^{-1}P_n\,.\tag{4.15}$$

The formal solution to (4.13) is

$$\begin{aligned}&P_i\,|\Psi^+(i\mathbf{k})\rangle\rangle\\&\quad=\Big[1-G_i^+\sum_{j(\neq i)}\sum_{l(\neq i)}\mathcal{H}_{ij}G_{jl}^+\mathcal{H}_{li}\Big]^{-1}|\psi^+(i\mathbf{k})\rangle\rangle\,,\end{aligned}\tag{4.16}$$

with $G_i^+\equiv P_i(E_T-\mathcal{H}_{ii}+i\varepsilon)^{-1}P_i$. The ket $|\psi^+(i\mathbf{k})\rangle\rangle\equiv|\psi\rangle\rangle$ (note our use of a lower case psi) appearing here is a solution of the equation

$$(\mathcal{H}_{ii}-E_T)\,|\psi\rangle\rangle=0\,.\tag{4.17}$$

Equations (4.14) and (4.16) provide the desired formal prescription for determining the motion in each bound channel—expressed here in terms of the motion in the designated initial channel i. Several features of these results deserve comment. The operator $\mathcal{H}_{ii}$ is an effective Hamiltonian specific to a single, bound electronic state i that is coupled to a collection of continuum states (those of P space). The other operators, such as $\mathcal{H}_{im}G_{mn}^+\mathcal{H}_{ni}$, are contributions due to couplings between different bound states. Some of the strength of these couplings is attributable exclusively to the bound states but a part pertains to the continuum, cf. (4.15) and the definition (4.9). This projection-operator scheme is convenient for it allows us to handle the (possibly strong) bound-continuum coupling in a formally exact fashion. It also produces compact expressions for the presumably small corrections due to bound-bound transitions.

We now shift our attention to (4.3) and the associated electronic continuum final state. The procedure parallels that just used in our analysis of the bound channels. We denote by $p(f)$ the value of $p=(\Lambda_I q_I)$ connected with the selected final state f. The corresponding projection operator is $C_{p(f)}=C_f$ and its orthogonal complement within the space of continuum states is $N_f=P-C_f$. The equation satisfied by $C_f\,|\Phi^-(f\mathbf{q})\rangle\rangle$ can be obtained from (4.3). It is found to be

$$\Big[H_{ff}+\sum_{p(\neq f)}\sum_{q(\neq f)}H_{fp}g_{pq}^-H_{qf}-E_T\Big]C_f\,|\Phi^-(f\mathbf{q})\rangle\rangle=0\,,\tag{4.18}$$

with $H_{pq}=C_pHC_q$, $H_{fq}=H_{p(f)q}$, $H_{ff}=H_{p(f)p(f)}$, and

$$g_{pq}^-=C_p[N_f(E_T-H-i\varepsilon)N_f]^{-1}C_q\,.\tag{4.19}$$

The notation $p\neq f$ is an abbreviation for $p\neq p(f)$.

The solution of (4.18) is given by the formula

$$\begin{aligned}&C_f\,|\Phi^-(f\mathbf{q})\rangle\rangle\\&\quad=\Big[1-g_f^-\sum_{p(\neq f)}\sum_{q(\neq f)}H_{fp}g_{pq}^-H_{qf}\Big]^{-1}|\phi^-(f\mathbf{q})\rangle\rangle\,,\end{aligned}\tag{4.20}$$

with $g_f^-=[E_T-H_{ff}-i\varepsilon]^{-1}$ denoting the final-state propagator. The frozen-core scattering state $|\phi^-(f\mathbf{q})\rangle\rangle$ (note that this is indicated by a lower case symbol) is a solution of the equation

$$(H_{ff}-E_T)\,|\phi^-(f\mathbf{q})\rangle\rangle=0\,,\tag{4.21}$$

which satisfies the usual "collapsing-wave" boundary condition.

The remaining projections, $C_p\,|\Phi^-(f\mathbf{q})\rangle\rangle$ with $p\neq p(f)$, are given by the expressions

$$C_p\,|\Phi^-(f\mathbf{q})\rangle\rangle=\sum_{q(\neq f)}g_{pq}^-H_{qf}C_f\,|\Phi^-(f\mathbf{q})\rangle\rangle\,.\tag{4.22}$$

The two formulas (4.20) and (4.22) relate the dynamics in P space to that of the single final state $|\phi^{-}(f\mathbf{q})\rangle\rangle$.

We now can write detailed expressions for the transition matrix elements. The results of the previous paragraphs enable us to express each transition matrix element in a form that explicitly illustrates the various pathways by which the designated initial and final states are connected. From (4.1), (3.21), and (3.22) it follows that

$$\begin{aligned}\langle f \mid T \mid i \rangle &= \langle\langle \Phi^{-}(f\mathbf{q}) \mid PHQ \mid \Psi^{+}(i\mathbf{k}) \rangle\rangle \\ &= \sum_{p}\sum_{j} \langle\langle \Phi \mid C_p H P_j \mid \Psi \rangle\rangle \ . \end{aligned} \tag{4.23}$$

Equations (4.14) and (4.22) now can be used to eliminate from this expression all components of $|\Psi\rangle\rangle$ and $|\Phi\rangle\rangle$ except those corresponding to the designated pair of initial and final channels. The result of these manipulations can be written in the form

$$\langle f \mid T \mid i \rangle = \sum_{\alpha=1}^{4} \langle f \mid T_\alpha \mid i \rangle \ , \tag{4.24}$$

with

$$\langle f \mid T_1 \mid i \rangle = \langle\langle \Phi \mid C_f H P_i \mid \Psi \rangle\rangle \ , \tag{4.25a}$$

$$\langle f \mid T_2 \mid i \rangle = \sum_{j(\neq i)}\sum_{l(\neq i)} \langle\langle \Phi \mid C_f H_{fj} G_{jl}^{+} \mathcal{H}_{li} P_i \mid \Psi \rangle\rangle \ , \tag{4.25b}$$

$$\langle f \mid T_3 \mid i \rangle = \sum_{p(\neq f)}\sum_{q(\neq f)} \langle\langle \Phi \mid C_f H_{fp} g_{pq}^{+} H_{qi} P_i \mid \Psi \rangle\rangle \ , \tag{4.25c}$$

$$\langle f \mid T_4 \mid i \rangle = \sum_{j(\neq i)}\sum_{l(\neq i)}\sum_{p(\neq f)}\sum_{q(\neq f)} \langle\langle \Phi \mid C_f H_{fp} g_{pq}^{+} H_{qj} G_{jl}^{+} \mathcal{H}_{li} P_i \mid \Psi \rangle\rangle \ . \tag{4.25d}$$

These formulas involve only the two kets $P_i \mid \Psi\rangle\rangle$ and $C_f \mid \Phi\rangle\rangle$, which are solutions of (4.13) and (4.18), respectively. It should be noted that $\langle f \mid T_2 \mid i \rangle$ depends linearly on the operators $\mathcal{H}_{li}$, which take explicit account of Coriolis couplings between the selected initial state and other bound electronic states. The operators H_{fp} appearing in $\langle f \mid T_3 \mid i \rangle$ incorporate similar corrections to the frozen-core approximation.

The final objective of this section is to display the dependence of the transition matrix on Coriolis ($\mathcal{H}_{li}$) and final-state ($H_{pp'}$) interactions in a systematic, order-by-order format. To accomplish this we combine (4.16), (4.20), and (4.24) to obtain the formula

$$\langle f \mid T \mid i \rangle = \langle\langle \phi^{-}(f\mathbf{q}) \mid \tau_{fi} \mid \psi^{+}(i\mathbf{k}) \rangle\rangle \ , \tag{4.26}$$

with

$$\begin{aligned}\tau_{fi} = {} & \left[1 - \sum_{p(\neq f)}\sum_{q(\neq f)} H_{fp} g_{pq} H_{qf} g_f^{+}\right]^{-1} t_{fi} \\ & \times \left[1 - G_i^{+} \sum_{j(\neq i)}\sum_{l(\neq i)} \mathcal{H}_{ij} G_{jl}^{+} \mathcal{H}_{li}\right]^{-1} \end{aligned} \tag{4.27}$$

and

$$\begin{aligned} t_{fi} = H_{fi} & + \sum_{j(\neq i)}\sum_{l(\neq i)} H_{fj} G_{jl}^{+} \mathcal{H}_{li} \\ & + \sum_{p(\neq f)}\sum_{q(\neq f)} H_{fp} g_{pq}^{+} H_{qi} \\ & + \sum_{j(\neq i)}\sum_{l(\neq i)}\sum_{p(\neq f)}\sum_{q(\neq f)} H_{fp} g_{pq}^{+} H_{qj} G_{jl}^{+} \mathcal{H}_{li} \ . \end{aligned} \tag{4.28}$$

By using the identities

$$\begin{aligned} G_{jl}^{+} = {} & \delta_{jl} G_j^{+} - G_j^{+} \mathcal{H}_{jl} G_l^{+} (1 - \delta_{jl}) \\ & + G_j^{+} \left[\sum_{k(\neq j,l)} \mathcal{H}_{jk} G_k^{+} \mathcal{H}_{kl}\right] G_l^{+} + \cdots \end{aligned} \tag{4.29}$$

and

$$\begin{aligned} g_{pq}^{+} = {} & \delta_{pq} g_p^{+} - g_p^{+} H_{pq} g_q^{+} (1 - \delta_{pq}) \\ & + g_p^{+} \left[\sum_{r(\neq p,q)} H_{pr} g_r^{+} H_{rq}\right] g_q^{+} + \cdots \ , \end{aligned} \tag{4.30}$$

this formally exact expression can be written as an ordered sum of terms, $\tau_{fi}^{(r,s)}$, each with two superscripts, the first indicating the number of factors of H_{pq}, and the second indicating the number of $\mathcal{H}_{lk}$. The first few of these are

$$\begin{aligned} \tau_{fi}^{(1,0)} &= H_{fi} \ , \\ \tau_{fi}^{(2,0)} &= \sum_{p(\neq f)} H_{fp} g_p^{+} H_{pi} \ , \\ \tau_{fi}^{(1,1)} &= \sum_{j(\neq i)} H_{fp} g_p^{+} \mathcal{H}_{ji} \ , \\ \tau_{fi}^{(2,1)} &= \sum_{p(\neq f)}\sum_{j(\neq i)} H_{fp} g_p^{+} H_{pj} G_j^{+} \mathcal{H}_{ji} \ , \\ \tau_{fi}^{(3,0)} &= \sum_{p(\neq f)} H_{fp} g_p^{+} \left[H_{pf} g_f^{+} H_{fi} - \sum_{q(\neq f)} H_{pq} g_q^{+} H_{qi}\right] \ . \\ & \vdots \end{aligned} \tag{4.31}$$

Associated with the $\tau_{fi}^{(r,s)}$ are the transition matrix elements $T_{fi}^{(r,s)}$ defined by

$$T_{fi}^{(r,s)} = \langle\langle \phi^{-}(f\mathbf{q}) \mid \tau_{fi}^{(r,s)} \mid \psi^{+}(i\mathbf{k}) \rangle\rangle \ . \tag{4.32}$$

The objects $T_{fi}^{(r,s)}$ are straightforward to compute for small values of the indices r and s. Thus, we have a direct perturbative procedure for assessing the importance of polarization and Coriolis couplings. Many steps in the calculation of these contributions to the transition matrix can be performed analytically, using the basis sets introduced in Sec. II. It remains, however, to connect $|\psi\rangle\rangle$ and $|\phi\rangle\rangle$ with those basis sets. This is the first item attended to in Sec. V. The result is then used to produce a quite simple formula for $T_{fi}^{(1,0)}$, the "main" contribution to the scattering amplitude, as well as somewhat more complicated formulas for $T_{fi}^{(1,1)}$ and $T_{fi}^{(2,0)}$.

Finally, it should be noted that the operator τ_{fi} transforms as a scalar and is diagonal in the total-electronic-spin quantum numbers S and M_S as well as in the total electronic parity (provided that the last can be considered a good quantum number). These conclusions follow from the observation that τ_{fi} is an operator constructed from components, each of which commutes with $D(\alpha\beta\gamma)$, $\mathbf{S}^2$, S_z, and (in homonuclear systems) the electronic parity operator. These selection rules are equivalent to the physical requirements that the total orbital angular momentum, the total electronic spin, and the electronic parity (if any) be constants of the motion.

V. THE TRANSITION MATRIX

In this section, we obtain explicit formulas for three of the transition matrix contributions $T_{fi}^{(r,s)}$. The first of these, $T_{fi}^{(1,0)}$, is the "primary contributor" to which virtually all previous theories have been devoted. The two others, $T_{fi}^{(1,1)}$ and $T_{fi}^{(2,0)}$, are first-order corrections due to couplings between the prescribed initial and final electronic states and other bound and continuum states. The computation of higher-order terms in these couplings becomes progressively more complicated but involves nothing fundamentally different. The calculation of the $T_{fi}^{(r,s)}$'s is simplified by using the total angular momentum basis sets of Sec. II. Therefore, we begin this section by establishing the connections between the two objects $|\psi^+(i\mathbf{k})\rangle\rangle$ and $|\phi^-(f\mathbf{q})\rangle\rangle$ and the angular momentum eigenkets of Sec. II.

A. The entrance-channel ket, $|\psi^+(i\mathbf{k})\rangle\rangle$

This ket is a solution of the equation

$$(\mathcal{H}_{ii}-E_T)\,|\psi\rangle\rangle=0,\quad \mathcal{H}_{ii}\equiv H_{ii}+H_{iP}G_P^+H_{Pi}\ , \tag{5.1}$$

which satisfies a radiative, $(+)$ boundary condition. We shall obtain an expansion of $|\psi\rangle\rangle$ in terms of kets $|KMik\rangle\rangle$, labeled with the wave number k and the quantum numbers K, M, and $i=(\Lambda_i n_i)$. Each of these is a superposition,

$$\begin{aligned}|KMik\rangle\rangle&=\int_0^\infty dR\,RF_{KMi}(k,R)\,|KMiR\rangle\rangle\\&=N_K\int d\xi\int d\mathbf{R}\,|\xi,\mathbf{R}\rangle\rangle\\&\qquad\times[R^{-1}F_{KMi}(k,R)D_{\Lambda_iM}^{K}(\hat{\mathbf{R}})\\&\qquad\times\phi_i(\xi\,|\,R\hat{\mathbf{z}})]\ ,\end{aligned} \tag{5.2}$$

of the previously defined kets $|KMiR\rangle\rangle\equiv|KM\Lambda_in_iR\rangle\rangle$, cf. (3.7), and each satisfies the equation

$$[\mathcal{H}_{ii}-E(k)]\,|KMik\rangle\rangle=0\ , \tag{5.3}$$

with $E(k)=\hbar^2k^2/2\mu$. That $\mathcal{H}_{ii}$ has an eigenket of this form is an immediate consequence of the scalar character of this operator.

The radial amplitude $F_{KMi}(k,R)$ is required to vanish at the origin and to have the asymptotic form

$$F_{KMi}(k,R)\underset{R\to\infty}{\sim}(2/\pi)^{1/2}\sin(kR+\eta_{KMi})\ . \tag{5.4}$$

The phase shift η_{KMi} is complex valued, owing to the non-Hermiticity of $\mathcal{H}_{ii}$. Indeed, eigenkets of this operator corresponding to different values of k need not even be orthogonal; one only can assert that $|KMik\rangle\rangle$ will be "bi-orthogonal" to the "adjoint kets" $|KMik';\dagger\rangle\rangle$ which satisfy the equation

$$[\mathcal{H}_{ii}^{\dagger}-E(k')]\,|KMik';\dagger\rangle\rangle=0\ . \tag{5.5}$$

Here $\mathcal{H}_{ii}^{\dagger}=H_{ii}+H_{iP}G_P^-H_{Pi}$ signifies the adjoint of the operator $\mathcal{H}_{ii}$. The condition of bi-orthogonality implies that

$$\langle\langle KMik\,|\,K'M'i'k';\dagger\rangle\rangle=\delta_{KK'}\delta_{MM'}\delta_{ii'}\delta(k-k')\ , \tag{5.6}$$

and this, in turn, imposes the condition

$$\int_0^\infty dR\,F_{KMi}^{*}(k,R)F_{KMi}(k',R;\dagger)=\delta(k-k') \tag{5.7}$$

on the inner product of $F_{KMi}(k,R)$ and the analogously defined [cf. (5.2)] adjoint amplitude $F_{KMi}(k',R;\dagger)$.

By substituting (5.2) into (5.3) one obtains the following integrodifferential equations for the radial amplitudes:

$$\begin{aligned}&\Bigg[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2}{2\mu R^2}[K(K+1)-\Lambda_i^2]-[E(k)-E_i(R)]\\&\quad+\frac{\hbar^2}{2\mu}\left[\left\langle i\mathbf{R}\left|\frac{\mathbf{L}_\perp^2}{\hbar^2R^2}\right|i\mathbf{R}\right\rangle-\langle i\mathbf{R}\,|\,\partial_R^2\,|\,i\mathbf{R}\rangle-2\langle i\mathbf{R}\,|\,\partial_R\,|\,i\mathbf{R}\rangle\frac{d}{dR}\right]\Bigg]F_{KMi}(k,R)\\&\qquad=-\int_0^\infty dR'RR'\langle\langle KMiR\,|\,F^+\,|\,KMiR'\rangle\rangle F_{KMi}(k,R')\ ,\end{aligned} \tag{5.8}$$

with

$$\begin{aligned}&\langle\langle KMiR\,|\,F^+\,|\,KMiR'\rangle\rangle\\&\quad=N_K^2\int d\hat{\mathbf{R}}\int d\hat{\mathbf{R}}'D_{\Lambda_iM}^{K*}(\hat{\mathbf{R}})\left[\int d\xi\int d\xi'\phi_i(\xi\,|\,R\hat{\mathbf{z}})^*\langle\langle\xi,\mathbf{R}\,|\,F^+\,|\,\xi',\mathbf{R}'\rangle\rangle\phi_i(\xi'\,|\,R'\hat{\mathbf{z}})\right]D_{\Lambda_iM}^{K}(\hat{\mathbf{R}}')\ .\end{aligned} \tag{5.9}$$

Here $|i\mathbf{R}\rangle = |\Lambda_i n_i \mathbf{R}\rangle$, $E_i(R) = E_{\Lambda_i n_i}(R)$, $\mathbf{L}_1^2 = \mathbf{L}^2 - (\hat{\mathbf{R}}\cdot\mathbf{L})^2$, and $\phi_i(\xi\,|\,R\hat{\mathbf{z}}) = \langle \xi\,|\,i\mathbf{R}\rangle$. The symbol F^+ denotes the scalar operator $H_{QP}G_P^+H_{PQ}$. These equations (5.8) are closely analogous to (but distinctly different from) the equations obtained by Bieniek,[3] who based his analysis on the rigid-rotor, nuclear angular momentum representation instead of the total orbital angular momentum representation used here.

Because the kinetic energy operator $\mathbf{P}_R^2/2\mu = -(\hbar^2/2\mu)\nabla_R^2$ maps Q space onto itself (when Q is constructed according to the prescription given in Sec. III), the two Hamiltonians which appear explicitly in $F^+ = QHPG_P^+HQ$ may be replaced with electronic Hamiltonians H_{el}. The electronic matrix element which contributes to the integral operator $\langle KMiR\,|\,F^+\,|\,KMiR'\rangle\rangle$ then can be written in the more explicit form

$$\int d\xi \int d\xi' \phi_i(\xi\,|\,R\hat{\mathbf{z}})^* \langle\langle \xi,\mathbf{R}\,|\,F^+\,|\,\xi',\mathbf{R}'\rangle\rangle \phi_i(\xi'\,|\,R'\hat{\mathbf{z}}) = \sum_{p,p'} V^*_{\Lambda cq,i}(R)\langle\langle \Lambda cq\mathbf{R}\,|\,G_P^+\,|\,\Lambda'c'q'\mathbf{R}'\rangle\rangle V_{\Lambda'c'q',i}(R')\ , \tag{5.10}$$

wherein

$$\begin{aligned} V_{\Lambda cq,i}(R) &= \langle \Lambda cq\mathbf{R}\,|\,H_{\mathrm{el}}\,|\,i\mathbf{R}\rangle \\ &= \int d\xi\, A\,[\phi^I_{\Lambda_I q_I}(\xi(m)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\xi m\,\,|\,R\hat{\mathbf{z}})]^* H_{\mathrm{el}}\phi_i(\xi\,|\,R\hat{\mathbf{z}}) \\ &= N^{1/2} \int d\xi[\phi_{\Lambda_I q_I}(\xi(1)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\xi_1\,|\,R\hat{\mathbf{z}})]^* H_{\mathrm{el}}\phi_i(\xi_1,\xi(1)\,|\,R\hat{\mathbf{z}})\ . \end{aligned} \tag{5.11}$$

This electronic matrix element can differ from zero only if $\Lambda_i = \Lambda_I + \mu$, $S_i = S$, $M_{Si} = M_S$, and (for nuclei of equal charge) if the electronic parities of the bound and continuum states are the same.

It is virtually impossible to perform an exact evaluation of the Green function

$$\langle\langle \Lambda cq\mathbf{R}\,|\,G_P^+\,|\,\Lambda'c'q'\mathbf{R}'\rangle\rangle$$

and even if an explicit, nonlocal approximation were available the prospect of solving the corresponding set of integrodifferential equations (5.8) would not be appealing. Thus, it is usual (but see Ref. 14) to replace this Green function with the "local approximation,"[3,15,16]

$$-i\pi\delta_{\Lambda\Lambda'}\delta_{cc'}\delta(q-q')\delta(\mathbf{R}-\mathbf{R}')\delta(\varepsilon_q - \varepsilon(R))\ .$$

Here $\varepsilon_q \equiv \hbar^2 q^2/2m_e$ is the kinetic energy of the ejected electron and $\varepsilon(R) \equiv E_i(R) - E^I_{\Lambda_I n_I}(R)$ the vertical ionization energy specific to the internuclear separation R. The right-hand side of (5.8) then reduces to the product of $F_{KMi}(k,R)$ and an imaginary-valued potential $(i/2)\Gamma_{ii}(R)$ with

$$\Gamma_{ii}(R) = 2\pi \sum_{\Lambda,c} \int dq\,\,|\,V_{\Lambda cq,i}(R)\,|^2 \delta(\varepsilon_q - \varepsilon(R))\ , \tag{5.12}$$

which is proportional to the golden rule formula for the R-dependent rate of autoionization of the initial electronic state. With this approximation the task of computing the radial amplitudes $F_{KMi}(k,R)$ becomes quite manageable.

Now that the procedure for generating the kets $|\,KMik\,\rangle\rangle$ has been established, we can proceed to the expansion

$$|\,\psi^+(i\mathbf{k})\rangle\rangle = \sum_{KM} a_{KMi}(\hat{\mathbf{k}})\,|\,KMik\,\rangle\rangle\ . \tag{5.13}$$

The coefficients $a_{KM}(\hat{\mathbf{k}})$ are evaluated in the standard way,[17] that is, by requiring that the heavy-particle wave function $\langle\langle i\mathbf{R}\,|\,\psi^+(i\mathbf{k})\rangle\rangle$ be the sum of the plane wave $\exp(i\mathbf{k}\cdot\mathbf{R})$ and outgoing, expanding waves. The result of a short computation is the formula

$$a_{KMi}(\hat{\mathbf{k}}) = (8\pi^3)^{1/2} k^{-1} N_K D^K_{\Lambda_i M}(-\hat{\mathbf{k}}) e^{i\eta_{KMi}}\ . \tag{5.14}$$

B. The final-state continuum ket, $|\,\phi^-(f,\mathbf{q})\rangle\rangle$

Next, we turn our attention to the frozen-core electronic scattering states $|\,\phi^-(f,\mathbf{q})\rangle\rangle$ of (4.21) and their expansions in terms of the kets $|\,KM\Lambda cqR\,\rangle\rangle$ of Sec. III. The first step is to introduce electronic states $|\,\Lambda c\mathbf{q}\mathbf{R}-\,\rangle\rangle$, which are eigenkets of H_{FC} satisfying collapsing wave, "minus $(-)$" boundary conditions. These are related to the $|\,\Lambda cq\mathbf{R}\rangle\rangle$ by the well-known expansion[12]

$$|\,\Lambda_I q_I \mathbf{q} R - \rangle\rangle = \sum_{\lambda,\mu} [\,Y^*_{\lambda\mu}(\hat{\mathbf{q}})_{\hat{\mathbf{R}}} e^{-i\eta_{\lambda\mu}} i^{\lambda}]\,|\,\Lambda cq\mathbf{R}\rangle\rangle\ , \tag{5.15}$$

and are normalized in the manner

$$\begin{aligned} &\langle\langle \Lambda_I' q_I' \mathbf{q}'\mathbf{R}' -\,|\,\Lambda_I q_I \mathbf{q}\mathbf{R}-\,\rangle\rangle \\ &\qquad = \delta_{\Lambda_I'\Lambda_I}\delta_{q_I' q_I}\delta(\mathbf{R}-\mathbf{R}')[q^2\delta(\mathbf{q}-\mathbf{q}')]\ . \end{aligned} \tag{5.16}$$

In analogy with (3.37) we now form kets

$$\begin{aligned} |\,K_I M_I \Lambda_I q_I \mathbf{q} R - \rangle\rangle &= N_{K_I} \int d\hat{\mathbf{R}}\, D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}}) \\ &\qquad \times |\,\Lambda_I q_I \mathbf{q}\mathbf{R}-\,\rangle\rangle\ , \end{aligned} \tag{5.17}$$

which are eigenstates not only of H_{FC} but of $\mathbf{K}_I^2$, $\hat{\mathbf{z}}\cdot\mathbf{K}_I$, and $\hat{\mathbf{R}}\cdot\mathbf{L}_I$ as well. The frozen-core scattering states then can be defined by any of the equivalent forms,

$$\begin{aligned}|\phi^-(f\mathbf{q})\rangle\!\rangle &= \int_0^\infty dR\, R\mathcal{P}_{K_I\Lambda_I v}(R)\,|K_IM_I\Lambda_Iq_I\mathbf{q}R-\rangle\!\rangle \\ &= \int d\mathbf{R}[R^{-1}\mathcal{P}_{K_I\Lambda_I v}(R)N_{K_I}D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})]\sum_{\lambda,\mu}[Y^*_{\lambda\mu}(\hat{\mathbf{q}})_{\hat{\mathbf{R}}}e^{-i\eta_{\lambda\mu}}i^{\lambda}]\,|\Lambda c q\mathbf{R}\rangle\!\rangle \\ &= \int d\xi \int d\mathbf{R}\;|\xi,\mathbf{R}\rangle\!\rangle\, A\Bigg[R^{-1}\mathcal{P}_{K_I\Lambda_I v}(R)N_{K_I}D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})\phi^I_{\Lambda_I q_I}(\xi(m)\,|\,R\hat{\mathbf{z}}) \\ &\qquad\qquad \times\sum_{\lambda,\mu}[Y^*_{\lambda\mu}(\hat{\mathbf{q}})_{\hat{\mathbf{R}}}e^{-i\eta_{\lambda\mu}}i^{\lambda}]\phi^{(\Lambda_I q_I)}_{q\lambda\mu}(\xi_m\,|\,R\hat{\mathbf{z}})\Bigg]\;. \end{aligned} \tag{5.18}$$

The last of these three formulas expresses the scattering state as the antisymmetrized product of two factors, the first of which can be identified as the wave function of the product diatomic ion (aside from its inclusion [cf. (3.12)] of the N-electron spin state) and the second of which is the wave function of an unbound electron with momentum $\hbar\mathbf{q}$. From (5.16) and (5.17) it follows that

$$\langle\!\langle\phi^-(f'\mathbf{q}')\,|\,\phi^-(f\mathbf{q})\rangle\!\rangle=\delta_{K_I'K_I}\delta_{M_I'M_I}\delta_{\Lambda_I'\Lambda_I}\delta_{q_I'q_I}[q^2\delta(\mathbf{q}-\mathbf{q}')]\int_0^\infty dR\,\mathcal{P}^*_{K_I\Lambda_I v'}(R)\mathcal{P}_{K_I\Lambda_I v}(R)\;. \tag{5.19}$$

Using the expression (5.18) for $|\phi^-(f\mathbf{q})\rangle\!\rangle$ and the definition (3.19) for $C_f\equiv C_{p(f)}\equiv C_{\Lambda_I q_I}$, we find that

$$\begin{aligned}(C_fHC_f-E_T)\,|\phi^-(f\mathbf{q})\rangle\!\rangle = \int d\mathbf{R}\,N_{K_I}D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})R^{-1}\sum_{\lambda,\mu}[Y^*_{\lambda\mu}(\hat{\mathbf{q}})_{\hat{\mathbf{R}}}e^{-i\eta_{\lambda\mu}}i^{\lambda}] \\ \times\Bigg[\,|\Lambda_Iq_I\lambda\mu q\mathbf{R}\rangle\left[D_{\Lambda_I q_I}+\frac{\hbar^2q^2}{2m_e}-E_T\right] \\ +\sum_{\lambda',\mu'}\int dq'\,|\Lambda_Iq_I\lambda'\mu'q'\mathbf{R}\rangle B^{(\Lambda_I q_I)}_{c'q',cq}\Bigg]\mathcal{P}_{K_I\Lambda_I v}(R)\;, \end{aligned} \tag{5.20}$$

with

$$\begin{aligned}D_{\Lambda_I q_I}=-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2}{2\mu R^2}[K_I(K_I+1)-\Lambda_I^2]+E^I_{\Lambda_I n_I}(R)+\frac{\hbar^2}{2\mu}\Bigg[\left\langle I\mathbf{R}1\left|\frac{\mathbf{L}^2_{\perp(1)}}{\hbar^2R^2}\right|I\mathbf{R}1\right\rangle-\langle I\mathbf{R}1\,|\,\partial_R^2\,|\,I\mathbf{R}1\rangle \\ -2\langle I\mathbf{R}1\,|\,\partial_R\,|\,I\mathbf{R}1\rangle\frac{d}{dR}\Bigg]\;, \end{aligned} \tag{5.21}$$

$$\begin{aligned}B^{(\Lambda_I q_I)}_{c'q',cq}=-\frac{\hbar^2}{2\mu}\Bigg[\langle q'\lambda'\mu'(\Lambda_Iq_I)\mathbf{R}1\,|\,\partial_R^2\,|\,q\lambda\mu(\Lambda_Iq_I)\mathbf{R}1\rangle+2\langle q'\lambda'\mu'(\Lambda_Iq_I)\mathbf{R}1\,|\,\partial_R\,|\,q\lambda\mu(\Lambda_Iq_I)\mathbf{R}1\rangle \\ \times\left[\langle I\mathbf{R}\,|\,\partial_R\,|\,I\mathbf{R}\rangle+\frac{d}{dR}\right]\Bigg]\;, \end{aligned} \tag{5.22}$$

and where

$$\langle I\mathbf{R}1\,|\,f\,|\,I\mathbf{R}1\rangle=\langle\Lambda_In_I\mathbf{R}1\,|\,f(\xi(1))\,|\,\Lambda_In_I\mathbf{R}1\rangle\;. \tag{5.23}$$

The derivation of this result requires a use of the identity $\mathbf{K}-\mathbf{L}=\mathbf{K}(m)-\mathbf{L}(m)$ and of Eq. (3.25), recognizing that $C_fH_{\text{el}}C_f$ is a part of H_{FC}. It also depends critically upon the defining formulas [(3.11)–(3.13)] and orthonormality conditions satisfied by the frozen-core continuum kets.

If the one-electron continuum orbitals were independent of the internuclear separation R, as they are in the commonly used single-center Coulomb-wave approximation,[3,15,16] the radial Born-Oppenheimer terms $B^{(\Lambda_I q_I)}_{c'q',cq}$ would vanish identically. We see from (5.20) that when these presumably small terms are totally neglected, the equation

$$(C_fHC_f-E_T)\,|\phi^-(f\mathbf{q})\rangle\!\rangle=0$$

is satisfied by (5.18) *provided* that the nuclear wave functions $\mathcal{P}_{K_I\Lambda_I v}(R)$ are square-integrable solutions of the ordinary differential equation

$$(D_{\Lambda_I q_I}-E^{K_I}_{\Lambda_I n_I v})\mathcal{P}_{K_I\Lambda_I v}(R)=0\;, \tag{5.24}$$

which vanish at the origin *and* that the total energy is the sum, $E_T=\hbar^2q^2/2m_e+E^{K_I}_{\Lambda_I n_I v}$, of the energy of the free electron and that of the product ion. These conditions, in combination with (5.20)–(5.22), establish the physical significance of the frozen-core scattering ket $|\phi^-(f\mathbf{q})\rangle\!\rangle$. Because of the Hermiticity of the operator $D_{\Lambda_I q_I}$ the radial eigenfunctions can be orthonormalized according to the prescription [cf. (5.19)]

$$\int_0^\infty dR\, \mathcal{P}^*_{K_I\Lambda_I\nu'}(R)\mathcal{P}_{K_I\Lambda_I\nu}(R)=\delta_{\nu'\nu} \; . \tag{5.25}$$

Our final objective here is to obtain an expansion of $|\phi^-(f\mathbf{q})\rangle\rangle$ in terms of kets analogous to the $|KMik\rangle\rangle$ of (5.2). To reach this goal we begin with the second of the expressions (5.18) and use the identities (see Appendix C of Ref. 11)

$$Y^*_{\lambda\mu}(\hat{\mathbf{q}})_{\hat{\mathbf{R}}}=\sum_\eta Y^*_{\lambda\eta}(\hat{\mathbf{q}})D^\lambda_{\mu\eta}(\hat{\mathbf{R}}), \quad Y_{\lambda\eta}(\hat{\mathbf{q}})\equiv Y_{\lambda\eta}(\hat{\mathbf{q}})_{\hat{\mathbf{z}}} \tag{5.26}$$

and

$$D^\lambda_{\mu\eta}(\hat{\mathbf{R}})D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})=\sum_K (2K+1)(-1)^{\mu+\Lambda_I}(-1)^{-\eta-M_I}\begin{pmatrix}\lambda & K_I & K\\ \mu & \Lambda_I & -\mu-\Lambda_I\end{pmatrix}\begin{pmatrix}\lambda & K_I & K\\ \eta & M_I & -\eta-M_I\end{pmatrix}D^K_{\mu+\Lambda_I,\eta+M_I}(\hat{\mathbf{R}}) \; . \tag{5.27}$$

These manipulations lead directly to the formula

$$|\phi^-(f\mathbf{q})\rangle\rangle=\int_0^\infty dR\, R\mathcal{P}_{K_I\Lambda_I}(R)N_{K_I}\sum_{K,\eta}\sum_{\lambda,\mu}[Y^*_{\lambda\eta}(\hat{\mathbf{q}})e^{-i\eta_{\lambda\mu}}i^\lambda]C(K_IM_I\Lambda_I\lambda\mu;K\eta)\,|K,M_I+\eta,\Lambda_I+\mu,cqR\rangle\rangle \; , \tag{5.28}$$

with $|KM\Lambda cqR\rangle\rangle$ defined by (3.38) and where

$$C(K_IM_I\Lambda_I\lambda\mu;K\eta)=N_K^{-1}(2K+1)(-1)^{\Lambda_I+\mu}(-1)^{-M_I-\eta}\begin{pmatrix}\lambda & K_I & K\\ \mu & \Lambda_I & -\Lambda_I-\mu\end{pmatrix}\begin{pmatrix}\lambda & K_I & K\\ \eta & M_I & -M_I-\eta\end{pmatrix} \; . \tag{5.29}$$

The expression (5.28) can be written in the desired, alternative form

$$|\phi^-(f\mathbf{q})\rangle\rangle=\sum_{K,\eta}\sum_{\lambda,\mu}Y^*_{\lambda\eta}(\hat{\mathbf{q}})C(K_IM_I\Lambda_I\lambda\mu;K\eta)\,|K,M_I+\eta,\Lambda_I+\mu,K_Icq\rangle\rangle \; , \tag{5.30}$$

with $|K,M_I+\eta,\Lambda_I+\mu,K_Icq\rangle\rangle$ the analog of $|KMik\rangle\rangle$, cf. (5.2), defined by

$$\begin{aligned}|K,M_I+\eta,\Lambda_I+\mu,cq\rangle\rangle &= \int_0^\infty dR\, R\mathcal{P}_{K_I\Lambda_I\nu}(R)(N_{K_I}e^{-i\eta_{\lambda\mu}}i^\lambda\,|K,M_I+\eta,\Lambda_I+\mu,cqR\rangle\rangle)\\ &=N_K\int d\xi\int d\mathbf{R}\,|\xi,\mathbf{R}\rangle\rangle\{R^{-1}\mathcal{P}_{K_I\Lambda_I\nu}(R)(N_{K_I}e^{-i\eta_{\lambda\mu}}i^\lambda)D^K_{\Lambda_I+\mu,M_I+\eta}(\hat{\mathbf{R}})\\ &\quad\times A[\phi_{\Lambda_Iq_I}(\xi(m)\,|\,R\hat{\mathbf{z}})\phi^{(\Lambda_Iq_I)}_{q\lambda\mu}(\xi_m\,|\,R\hat{\mathbf{z}})]\} \; .\end{aligned} \tag{5.31}$$

C. Formula for $T^{(1,0)}_{fi}$

According to (4.31) and (4.32) the primary transition matrix element $T^{(1,0)}_{fi}$ is given by the formula

$$T^{(1,0)}_{fi}=\langle\langle\phi^-(f\mathbf{q})\,|\,PHQ\,|\,\psi^+(i\mathbf{k})\rangle\rangle \; . \tag{5.32}$$

It has been mentioned previously, in connection with the operator F^+ of (5.9) and (5.10), that the projection Q is so defined that $PHQ=PH_{\mathrm{el}}Q$. By using this fact and the expansions (5.13) and (5.30), we are led from (5.32) to the expression

$$T^{(1,0)}_{fi}=\sum_{K,M,\lambda,\mu}\sum_{K'\eta}a_{KMi}(\hat{\mathbf{k}})Y_{\lambda\eta}(\hat{\mathbf{q}})C(K_IM_I\Lambda_I\lambda\mu;K'\eta)\langle\langle K',M_I+\eta,\Lambda_I+\mu,cq\,|\,H_{\mathrm{el}}\,|\,KMik\rangle\rangle \; . \tag{5.33}$$

Because H_{el} is a scalar operator, the matrix elements appearing here are different from zero only if $K=K'$ and $M=M_I+\eta$.

At this point it is convenient to select a laboratory frame with its $\hat{\mathbf{z}}$ axis coincident with the direction $\hat{\mathbf{k}}$, in which case[6]

$$a_{KMi}(\hat{\mathbf{z}})=(8\pi^3)^{1/2}k^{-1}N_K\delta_{\Lambda_i,-M}(-1)^Ke^{i\eta_{KMi}} \; . \tag{5.34}$$

Then, by using (3.7), (5.31), and the selection rule $\Lambda_i=\Lambda_I+\mu$ of H_{el}, we are able to rewrite (5.33) in the more explicit form

$$\begin{aligned}T^{(1,0)}_{fi}&=(8\pi^3)^{1/2}k^{-1}\sum_{K,\lambda}N_{K_I}N_K[(-1)^Ke^{i\eta_{K,-\Lambda_i,i}}]C(K_I,M_I,\Lambda_I,\lambda,\Lambda_i-\Lambda_I;K,-\Lambda_i-M_I)\\ &\quad\times[Y^*_{\lambda,-\Lambda_i-M_I}(\hat{\mathbf{q}})e^{-i\eta_{\lambda,\Lambda_i-\Lambda_I}}i^\lambda]^*\int_0^\infty dR\,\mathcal{P}^*_{K_I\Lambda_I\nu}(R)V_{\Lambda cq,i}(R)F_{K,-\Lambda_i,i}(k,R) \; ,\end{aligned} \tag{5.35}$$

with $V_{\Lambda cq,i}(R)$ denoting the electronic matrix element defined by (5.11).

The expression (5.35) is similar in structure to formulas for the AI transition matrix element derived by Miller *et al.*[15] and Bieniek,[3] but it is different owing to the choice of basis sets employed here. For example, because we treat the angular momenta without approximation, the formula (5.35) is exact—to the prescribed, zero order in the Coriolis couplings. In contrast to this, the theory of Ref. 3 "neglects the coupling of the angular momenta of the bound electronic states with that of the free particles." Because of this Bieniek[3] found it necessary to restrict his analysis to the case of $\mu=\Lambda_i-\Lambda_I=0$. This same problem also was encountered by Hickman and Morgner.[18]

The formula (5.35) can be simplified further, for as we now shall show, the sums over K and λ extend over only a few terms. This demonstration hinges upon the observation that when the energy of the ejected electron is less than 0.5 eV the values of the matrix elements $V_{\Lambda cq,i}(R)$ are relatively small for λ in excess of 2 or 3. To see why this is so, we recall from Sec. III that for $\lambda \gtrsim 3$ the amplitude of the continuum orbital $\phi_{q\lambda\mu}^{(\Lambda_I q_I)}(\xi_m \mid R\hat{\mathbf{z}})$ is very small for $\mid \xi_m \mid \lesssim 3$ Å. Since this is about the same as the range of the bound electronic wave function $\phi_i(\xi \mid R\hat{\mathbf{z}})$, there will be little overlap between the initial- and final-state wave functions for $\lambda \gtrsim 3$ and so the associated matrix elements will be correspondingly small.

From this observation and the formula (5.29) for $C(K_I M_I \Lambda_I \lambda\mu; K\eta)$, we see that the ranges of K and λ in (5.35) are limited by the two constraints

$$\mid K_I-\lambda \mid \le K \le \mid K_I+\lambda \mid \tag{5.36a}$$

and

$$\lambda \lesssim 3 \; . \tag{5.36b}$$

Furthermore, because $\mid \eta \mid \equiv \mid \Lambda_i+M_I \mid \le \lambda$ [cf. the spherical harmonic appearing in (5.35)], the second of these constraints implies that

$$\mid M_I \mid \lesssim \mid \Lambda_i+3 \mid \; . \tag{5.37}$$

These conclusions, (5.36) and (5.37), have experimentally verifiable consequences. First of all, since the relevant values of $\mid \Lambda_i \mid$ are invariably 0, 1, or 2, the projection quantum number $\mid M_I \mid$ of the product diatomic ion rarely will exceed 3 or 4. This number is to be compared with K_I, which according to (5.36) differs from K by no more than 3. Finally, since it is expected that the number of contributing nuclear partial waves will be rather large (25 or so for thermal Na-Na collisions), the mean values of K and K_I should fall within the range of 15–20. From these considerations we conclude that when the ejected electrons are not too energetic the angular momenta of the product diatomic ions will be very nearly perpendicular to the incident $\hat{\mathbf{k}}$ axis; this phenomenon has in fact been observed experimentally.[19]

D. *T*-matrix and cross-section selection rules

We turn now to a discussion of several selection rules associated with AI scattering. First, it is clear that the initial and final states connected by $\tau_{fi}^{(1,0)}$ must have identical total-electronic-spin quantum numbers. Second, the single-state and interference cross sections[1]

$$\sigma_{ij}=\left[\frac{m_e}{2\pi\hbar^2}\right]^2 \frac{\mu q}{m_e k} \int d\hat{\mathbf{q}}\, T_{fi}^{(1,0)} T_{fj}^{(1,0)*} \tag{5.38}$$

are proportional to $\delta_{\Lambda_i,\Lambda_j}$ and to δ_{π_i,π_j}, with π_i denoting the total electronic parity of the initial state (when this is a good quantum number). This statement can be verified by evaluating the integral over $\hat{\mathbf{q}}$ appearing in (5.38), with the help of (5.35). The result of the integration is a sum of terms each proportional to the product of

$$\left[\int_0^\infty dR\, \mathcal{P}^*_{K_I\Lambda_I\nu}(R) V_{\Lambda cq,i}(R) F_{K,-\Lambda_i,i}(R) \right] \left[\int_0^\infty dR\, \mathcal{P}^*_{K_I\Lambda_I\nu}(R) V_{\Lambda c'q,j}(R) F_{K',-\Lambda_j,j}(R) \right]^*$$

and

$$\int d\hat{\mathbf{q}}\, Y_{\lambda,-\Lambda_i-M_I}(\hat{\mathbf{q}}) Y^*_{\lambda',-\Lambda_j-M_I}(\hat{\mathbf{q}})=\delta_{\lambda,\lambda'}\delta_{\Lambda_i,\Lambda_j} \; .$$

The $\Lambda_i=\Lambda_j$ "selection rule" follows from the second of these, while the "π rule" can be deduced from the observation that $V_{\Lambda cq,k}(R)$ is proportional to the Kronecker delta

$$\delta(\pi_I(-1)^\lambda,\pi_k) \; ,$$

with π_I the electronic parity of the free ion, $(-1)^\lambda$ that of the unbound electron, and π_k that of an N-electron bound state.

These selection rules have been proved here for the particular T-matrix elements $T_{fi}^{(1,0)}$ and $T_{fj}^{(1,0)}$ but they are valid in general. The reason for this is that any of the quantities $T_{fi}^{(r,s)}$ could be written in the form (5.33) but with H_{el} replaced with a different, more complicated operator. However, in every case this operator would be a scalar and it would be diagonal in the quantum numbers associated with electronic spin and parity. Therefore, the selection rules may be summarized as follows:

$$\langle\langle f\mathbf{q} \mid T \mid i\mathbf{k} \rangle \propto \delta_{S_f,S_i}\delta_{M_{Sf},M_{Si}} \tag{5.39}$$

and

$$\int d\hat{\mathbf{q}} \langle\langle f\mathbf{q} \mid T \mid i\mathbf{k} \rangle\rangle \langle\langle f\mathbf{q} \mid T \mid j\mathbf{k} \rangle\rangle \propto \delta_{\Lambda_i,\Lambda_j}\delta_{\pi_i,\pi_j} \; , \tag{5.40}$$

with S and M_S denoting the total electronic spin quantum numbers. The only restriction upon the validity of these is our assumption that spin-orbit coupling can be neglected.

There are two additional and weaker selection rules which deserve mention. The first of these is a consequence of the selection rule, $\mu=\Lambda_I-\Lambda_i$, satisfied by the electronic-matrix element $V_{\Lambda cq,i}(R)$ and to which the transition matrix element $T_{fi}^{(1,0)}$ is therefore subject. This rule dictates that when the initial electronic state *and* that of the product ion are both Σ states, the axial projection of the free-electron orbital angular momentum must be equal to zero. Let us now denote by σ_i the quantum number (equal to ± 1) associated with reflection of the initial-state electronic wave function in a plane containing the internuclear axis. σ_I is the analogously defined quantum number of the electronic state of the product diatomic ion. Because the projection quantum number μ is zero for $\Sigma \rightarrow \Sigma$ transitions, the reflection quantum number of the unbound electron equals unity. Then, because the electronic Hamiltonian is invariant with respect to this reflection operation, it follows that σ_i and σ_I must equal one another and that consequently $T_{fi}^{(1,0)} \propto \delta_{\sigma_i,\sigma_I}$. From this we conclude that when $\Lambda_i = \Lambda_j = \Lambda_I = 0$, the approximation to the AI cross section given by (5.38) will differ from zero only if $\sigma_i = \sigma_j = \sigma_I$. To this approximation, collisions beginning in quasimolecular Σ^- states cannot produce Σ^+ diatomic ions. The axial symmetry of the system is broken by the Coriolis forces that are incorporated within the contributions to the exact transition matrix associated with terms $T_{fi}^{(r,s)}$ with $s > 0$ and/or $r > 1$. Therefore, the selection rule just stated is valid only to the extent that Coriolis corrections to the cross section are of negligible magnitude.

The second of the two "weaker" selection rules can be obtained by treating the heavy-particle motion semiclassically.[20] This is appropriate when the collisions are sufficiently energetic that the de Broglie wavelength associated with the relative motion of the two atoms is much less than atomic dimensions. Considerations of stationary phase then lead one to conclude that an ionizing (AI) transition can occur only if there is one or more internuclear separations R^* for which

$$E_i(R^*) = E^I_{\Lambda_I n_I}(R^*) + \hbar^2 q^2/2m_e \ . \tag{5.41}$$

Here $\hbar^2 q^2/2m_e > 0$ is the energy of the ejected electron, E_i is that of the electronic initial state, and $E^I_{\Lambda_I n_I}$ is that of the product ion. The familiar implication of this Franck-Condon condition is that autoionization of the colliding pair of atoms only can occur at internuclear separations at which the BO energy curve of the (quasi) bound electronic initial state lies embedded within the continuum associated with the electronic configuration $AB^+ + e^-$.

E. Formula for $T_{fi}^{(1,1)}$

This contribution to the transition matrix is of first order in the Coriolis couplings. It is given by the formula

$$T_{fi}^{(1,1)} = \sum_{j(\neq i)} \langle\langle \phi^-(f\mathbf{q}) \,|\, H_{fj} G_j^+ \mathcal{H}_{ji} \,|\, \psi^+(i\mathbf{k}) \rangle\rangle \ , \tag{5.42}$$

with $H_{fj} G_j^+ \mathcal{H}_{ji} = C_f HQP_j (E_T^+ - \mathcal{H}_{jj})^{-1} \mathcal{H}_{ji}$ and $\mathcal{H}_{ji} = H_{ji} + P_j F^+ P_i$, with $F^+ = QHPG_P^+ PHQ$ and $E_T^+ = E_T + i\varepsilon$. As before [see comments immediately following (5.32)], the H operators appearing explicitly in these two factors may be replaced with electronic energy operators $H_{\rm el}$. Then using (3.21) and (3.33) we find that

$$P_j F^+ P_i = \int d\mathbf{R} \int d\mathbf{R}' \,|\, j\mathbf{R} \rangle\rangle \left[\sum_{p,p'} V^*_{\Lambda cq,j}(R) \langle\langle \Lambda cq\mathbf{R} \,|\, G_P^+ \,|\, \Lambda' c' q' \mathbf{R}' \rangle\rangle V_{\Lambda' c' q',i}(R') \right] \langle\langle i\mathbf{R}' \,| \ . \tag{5.43}$$

The local approximation [see remarks in connection with (5.12)] to this is given by the formula

$$P_j F^+ P_i \doteq -\frac{i}{2} \int d\mathbf{R} \,|\, j\mathbf{R} \rangle\rangle \Gamma_{ji}(R) \langle\langle i\mathbf{R} \,| \ , \tag{5.44}$$

with

$$\Gamma_{ji}(R) = 2\pi \sum_{\Lambda,c} \int dq \; V^*_{\Lambda cq,j}(R) V_{\Lambda cq,i}(R) \delta[\varepsilon_q - \bar{\varepsilon}(R)] = 2\pi \langle j\mathbf{R} \,|\, H_{\rm el} \rho_{ij}(\mathbf{R}) H_{\rm el} \,|\, i\mathbf{R} \rangle \ . \tag{5.45}$$

The objects $\bar{\varepsilon}(R)$ and $\rho_{ji}(\mathbf{R})$ appearing in these formulas are defined by $\bar{\varepsilon}(R) = \frac{1}{2}[E_i(R) + E_j(R)] - E^I_{\Lambda_I n_I}(R)$ and

$$\rho_{ji}(\mathbf{R}) = \sum_{\Lambda,c} \int dq \;\, |\, \Lambda cq,\mathbf{R} \rangle \delta[\bar{\varepsilon}_q - \varepsilon(R)] \langle \Lambda cq,\mathbf{R} \,| \ , \tag{5.46}$$

respectively. It follows from its definition that $\Gamma_{ji}(R)$ can differ from zero only if both of the kets $H_{\rm el} \,|\, i\mathbf{R} \rangle$ and $H_{\rm el} \,|\, j\mathbf{R} \rangle$ have projections onto the electronic continuum.

When $\mathcal{H}_{ji}$ and $\mathcal{H}_{jj}$ are replaced with the corresponding "local approximations" $\mathcal{H}_{ji}^{(L)} = H_{ji} - (i/2)\Gamma_{ji}$ and $\mathcal{H}_{jj}^{(L)} = H_{jj} - (i/2)\Gamma_{jj}$, the formula (5.42) becomes

$$T_{fi}^{(1,1)} = \sum_{j(\neq i)} \int d\mathbf{R} \sum_{\lambda,\mu} \int dq' \langle\langle \Lambda c q' \mathbf{R} \,|\, \phi^-(f\mathbf{q}) \rangle\rangle^* V_{\Lambda cq',j}(R) (E_T^+ - \mathcal{H}_{jj}^{(L)})^{-1} \mathcal{H}_{ji}^{(L)} \langle\langle i\mathbf{R} \,|\, \psi^+(i\mathbf{k}) \rangle\rangle \ . \tag{5.47}$$

Using (5.13), (5.15), and (5.18) we can rewrite this in either of two equivalent forms

$$\begin{aligned} T_{fi}^{(1,1)} &= \sum_{j(\neq i)} \int d\mathbf{R} [R^{-1} \mathcal{P}_{K_I \Lambda_I \nu}(R) N_{K_I} D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})]^* \langle \Lambda_I q_I \mathbf{q}\mathbf{R} - \,|\, H_{\rm el} \,|\, j\mathbf{R} \rangle [E_T^+ - \mathcal{H}_{jj}^{(L)}]^{-1} \mathcal{H}_{ji}^{(L)} \psi^+(i\mathbf{k} \,|\, \mathbf{R}) \\ &= \frac{i}{\hbar} \sum_{j(\neq i)} \int_0^\infty dt \, e^{-iE_T^+ t/\hbar} \int d\mathbf{R} [R^{-1} \mathcal{P}_{K_I \Lambda_I \nu}(R) N_{K_I} D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})]^* \langle \Lambda_I q_I \mathbf{q}\mathbf{R} - \,|\, H_{\rm el} \,|\, j\mathbf{R} \rangle e^{i\mathcal{H}_{jj}^{(L)} t/\hbar} [\mathcal{H}_{ji}^{(L)} \psi^+(i\mathbf{k} \,|\, \mathbf{R})] \ , \end{aligned} \tag{5.48}$$

wherein

$$\psi^+(i\mathbf{k}\,|\,\mathbf{R})\equiv\langle\langle i\mathbf{R}\,|\,\psi^+(i\mathbf{k})\rangle\rangle$$
$$=\sum_{KM}a_{KMi}(\hat{\mathbf{k}})[R^{-1}F_{KMi}(k,R)N_K D^K_{\Lambda_i}(\hat{\mathbf{R}})] \tag{5.49}$$

denotes the wave function descriptive of the heavy-particle motion in the channel associated with the initial electronic state. The object

$$R^{-1}\mathcal{P}_{K_I\Lambda_I\nu}(R)N_K D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})$$

is, of course, the final-state heavy-particle wave function and $\langle\Lambda_I q_I\mathbf{q}\mathbf{R}-\,|\,H_{\text{el}}\,|\,j\mathbf{R}\rangle$ is the matrix element connecting the electronic final state (consisting of a diatomic ion and an ionized electron with momentum $\hbar\mathbf{q}$) to the bound electronic "intermediate" state $|\,j\mathbf{R}\rangle$. The second of the expressions (5.48) is analogous to the formula derived by Lee and Heller[21] for the amplitude of a Raman scattering event and it can be similarly interpreted. Thus, the "wave function" $\chi_i(0)\equiv\mathcal{H}^{(L)}_{ji}\psi^+(i\mathbf{k}\,|\,\mathbf{R})$ is the product of an electronic $i\rightarrow j$ transition operator and the initial-state "wave function" ψ^+. Each term of (5.47) is the overlap between a propagated value of this function

$$\chi_i(t)\equiv\exp[-i(E_T^+-\mathcal{H}^{(L)}_{jj})t/\hbar]\chi_i(0)$$

and the unpropagated final-state wave function

$$\chi_f=[R^{-1}\mathcal{P}_{K_I\Lambda_I\nu}(R)N_{K_I}D^{K_I}_{\Lambda_I M_I}(\hat{\mathbf{R}})]$$
$$\times\langle j\mathbf{R}\,|\,H_{\text{el}}\,|\,\Lambda_I q_I\mathbf{q}\mathbf{R}-\rangle\ .$$

The propagator consists of a "phase factor" $\exp[-i(E_T^+-H_{jj})t/\hbar]$ characteristic of the intermediate j state and a "decay factor" $\exp[-\Gamma_{jj}t/2\hbar]$. In the Lee-Heller theory of Raman scattering the rate of decay of the initial state is governed by a phenomenological coefficient, whereas here it is given in terms of the R dependent rate of autoionization $\Gamma_{jj}/2\hbar$.

To compute the action of $\mathcal{H}^{(L)}_{ji}$ we use the formula[22]

$$HD^K_{\Lambda N}(\hat{\mathbf{R}})\chi^K_\Lambda(\xi,R\hat{\mathbf{z}})=D^K_{\Lambda M}\left[\frac{p_R^2}{2\mu}+\frac{\hbar^2}{2\mu R^2}[K(K+1)-\Lambda^2]+\frac{\mathbf{L}_\perp^2}{2\mu R^2}+H_{\text{el}}\right]\chi^K_\Lambda$$
$$+D^K_{\Lambda+1,M}\left[-\frac{\lambda_+(K\Lambda)}{2\mu R^2}(L^B_+\chi^K_\Lambda)\right]+D^K_{\Lambda-1,M}\left[-\frac{\lambda_-(K\Lambda)}{2\mu R^2}(L^B_-\chi^K_\Lambda)\right]\ . \tag{5.50}$$

Here, as in the Introduction, the mass-polarization term has been discarded. The quantities $\lambda_\pm$ are defined by $\lambda_\pm(K\Lambda)=[K(K+1)-\Lambda(\Lambda\pm1)]^{1/2}$ and $L^B_\pm$ are the ladder operators associated with the electronic orbital angular momentum referred to the body (B) frame. From (5.50) it can be shown that

$$\mathcal{H}^{(L)}_{ji}[R^{-1}F_{KMi}(k,R)N_K D^K_{\Lambda_i M}(\hat{\mathbf{R}})]$$
$$=[R^{-1}N_K D^K_{\Lambda_j M}(\hat{\mathbf{R}})]\left[\sum_{m=0,\pm1}\delta_{\Lambda_j,\Lambda_i+m}H^{(m)ji}_{K\Lambda_i}\right]$$
$$\times F_{KMi}(k,R)\ , \tag{5.51}$$

wherein

$$H^{(0)ji}_{K\Lambda_i}=-\frac{\hbar^2}{2\mu}(\langle j\mathbf{R}\,|\,\partial_R^2\,|\,i\mathbf{R}\rangle+2\langle j\mathbf{R}\,|\,\partial_R\,|\,i\mathbf{R}\rangle\partial_R)$$
$$+\left\langle j\mathbf{R}\left|\frac{\mathbf{L}_\perp^2}{2\mu R^2}-\frac{i}{2}2\pi H_{\text{el}}\rho_{ji}H_{\text{el}}\right|i\mathbf{R}\right\rangle$$
$$+\delta_{ji}\left[-\frac{\hbar^2}{2\mu}\partial_R^2+\frac{\hbar^2}{2\mu R^2}[K(K+1)-\Lambda_i^2]\right.$$
$$\left.+E_i(R)\right]\ , \tag{5.52a}$$

and

$$H^{(\pm1)ji}_{K\Lambda_i}=-\frac{\lambda_\pm(K\Lambda_i)}{2\mu R^2}\langle j\mathbf{R}\,|\,L^B_\pm\,|\,i\mathbf{R}\rangle\ . \tag{5.52b}$$

Then choosing the $\hat{\mathbf{z}}$ axis of the laboratory frame to lie in the direction of $\hat{\mathbf{k}}$ [cf. (5.34)] we find that

$$T^{(1,1)}_{fi}=(8\pi^3)^{1/2}k^{-1}\sum_{j(\neq i)}\sum_{K,\lambda}N_K N_{K_I}[(-1)^K e^{i\eta_{K,-\Lambda_i,i}}]C(K_I,M_I,\Lambda_I,\lambda,\Lambda_j-\Lambda_I;K,-\Lambda_i-M_I)$$
$$\times[Y^*_{\lambda,-\Lambda_i-M_I}(\hat{\mathbf{q}})e^{-i\eta_{\lambda,\Lambda_j-\Lambda_I}}i^\lambda]^*$$
$$\times\int_0^\infty dR\,\mathcal{P}^*_{K_I\Lambda_I\nu}(R)V_{\Lambda cq,j}(R)(E_T^+-H^{(0)jj}_{K,\Lambda_j})^{-1}\left[\sum_{m=0,\pm1}\delta_{\Lambda_j,\Lambda_i+m}H^{(m)ji}_{K,\Lambda_i}\right]F_{K,-\Lambda_i,i}(k,R)\ . \tag{5.53}$$

There is a striking similarity between this and the formula (5.35) for $T_{fi}^{(1,0)}$. Indeed, except for some (critical) indicial alterations, the most noticeable distinction between the two is that the radial integrals of (5.53) are augmented by the intermediate-state propagators $(E_T^+ - H_{K,\Lambda_i}^{(0)jj})^{-1}$ and the channel-mixing operators $H_{K,\Lambda_i}^{(m)ji}$. Because the summation does not include the initial state i, the operator $H_{K,\Lambda_i}^{(0)ji}$ occurring in (5.53) consists only of the radial BO operator

$$-(\hbar^2/2\mu)(\langle j\mathbf{R} \mid \partial_R^2 \mid i\mathbf{R}\rangle + 2\langle j\mathbf{R} \mid \partial_R \mid i\mathbf{R}\rangle\partial_R)$$

and

$$\langle j\mathbf{R} \mid \mathbf{L}_\perp^2/2\mu R^2 - (i/2)2\pi H_{\text{el}}\rho_{ji}H_{\text{el}} \mid i\mathbf{R}\rangle \ .$$

The more interesting Coriolis couplings are associated with the terms $H_{K,\Lambda_i}^{(\pm1)ji}$.

Because the same spherical harmonic with argument $\hat{\mathbf{q}}$ appears in both (5.35) and (5.53), the integral $\int d\hat{\mathbf{q}}(T_{fi}^{(1,0)}+T_{fi}^{(1,1)})(T_{fj}^{(1,0)}+T_{fj}^{(1,1)})^*$ is proportional to $\delta_{\Lambda_i,\Lambda_j}$. A similar argument applies to the parities of the two states $\mid i\mathbf{R}\rangle$ and $\mid j\mathbf{R}\rangle$. These specific observations are examples of our general conclusion (5.40).

F. The transition matrix contribution $T_{fi}^{(2,0)}$

The computation of this quantity,

$$T_{fi}^{(2,0)} = \sum_{p(\neq f)} \langle\langle \phi^-(f\mathbf{q}) \mid H_{fp}g^+H_{pi} \mid \psi^+(i\mathbf{k})\rangle\rangle \ , \tag{5.54}$$

involves manipulations closely resembling those just described in connection with $T_{fi}^{(1,1)}$. Consequently, we simply report the result of our calculation, namely,

$$\begin{aligned} T_{fi}^{(2,0)} = {} & (8\pi^3)^{1/2}k^{-1} \\ & \times \sum_{\Lambda_I' q_I'(\neq \Lambda_I q_I)} \sum_{K,\lambda} N_K N_{K_I}[(-1)^K e^{i\eta_{K,-\Lambda_i,i}}] C(K_I,M_I,\Lambda_I',\lambda,\Lambda_i-\Lambda_I';K,-\Lambda_i-M_I)(Y_{\lambda,-\Lambda_i-M_I}^*(\hat{\mathbf{q}})e^{-i\eta_{\lambda,\Lambda_i-\Lambda_I'}} i^\lambda)^* \\ & \times \sum_{\lambda,\mu',\mu} \delta_{\mu',\mu}\delta_{\mu,\Lambda_i-\Lambda_I'} \int dq' \int_0^\infty dR \left[\left| E_T - D_{\Lambda_I'q_I'} - \frac{\hbar^2 q^2}{2m_e} \right|^{-1} \right. \\ & \times \left. \left[\sum_{m=0,\pm1} \delta_{\Lambda_I',\Lambda_I+m} H_{\Lambda'c'q',\Lambda cq}^{(l)} \mathcal{P}_{K_I\Lambda_I v}(R) \right] \right]^* V_{\Lambda'c'q',i}(R) \\ & \times F_{K,-\Lambda_i,i}(k,R) \ . \end{aligned} \tag{5.55}$$

Here $D_{\Lambda'q'}$ is the operator defined by (5.21) and the $H^{(l)}$'s are defined as follows:

$$\begin{aligned} H_{\Lambda'c'q',\Lambda cq}^{(0)} = {} & \delta_{\lambda'\lambda}\delta(q'-q) \left[-\frac{\hbar^2}{2\mu}(\langle I'\mathbf{R}1 \mid \partial_R^2 \mid I\mathbf{R}1\rangle + 2\langle I'\mathbf{R}1 \mid \partial_R \mid I\mathbf{R}1\rangle\partial_R) + \left\langle I'\mathbf{R}1 \left| \frac{\mathbf{L}_\perp^2(1)}{2\mu R^2} \right| I\mathbf{R}1 \right\rangle \right] \\ & - \frac{\hbar^2}{2\mu}[2\langle I\mathbf{R}1 \mid \partial_R \mid I\mathbf{R}1\rangle\langle q'\lambda'\mu(\Lambda_I q_I')\mathbf{R}1 \mid \partial_R \mid q\lambda m(\Lambda_I q_I)\mathbf{R}1\rangle] \\ & + \int d\xi_1 \int d\xi_2 \phi_{q'\lambda'\mu}^{(\Lambda_I q_I')^*}(\xi_1 \mid R\hat{\mathbf{z}}) K_{\Lambda_I q_I',\Lambda_I q_I}(\xi_1,\xi_2 \mid R\hat{\mathbf{z}}) \phi_{q\lambda\mu}^{(\Lambda_I q_I)}(\xi_2 \mid R\hat{\mathbf{z}}) \end{aligned} \tag{5.56a}$$

and

$$\begin{aligned} H_{\Lambda'c'q',\Lambda cq}^{(\pm1)} = {} & \delta_{\lambda'\lambda}\delta(q'-q) \\ & \times \left[-\frac{\lambda_\pm(K_I\Lambda_I')}{2\mu R^2}\langle I'\mathbf{R}1 \mid L_\pm^B(1) \mid I\mathbf{R}1\rangle \right] \ . \end{aligned} \tag{5.56b}$$

Our previous conclusions about the cross-section (Λ and parity) selection rules associated with the approximate T matrix $T_{fi}^{(1,0)}+T_{fi}^{(1,1)}$ apply to $T_{fi}^{(1,0)}+T_{fi}^{(1,1)}+T_{fi}^{(2,0)}$ as well. The only approximation we used in progressing from (5.54) to (5.55) was to neglect (in the propagator) the same continuum-orbital BO couplings as we did previously in obtaining (5.24). This should be of little significance numerically and has no bearing on the T-matrix or cross-section selection rules.

VI. CONCLUDING REMARKS

Associative ionization takes place in large measure through the collision-induced interaction of bound and continuum electronic configurations. Previous theories of AI have concentrated solely on this contribution and there is little reason to doubt the validity of numerical computations based on these formalisms. However, the issues that concern us are best treated by an alternative approach. In particular, the discussion of selection rules and the treatment of corrections to the "main" mechanism of AI are both facilitated by introducing a "symmetric-top" basis in place of the more conventional "rigid rotor" basis.

Our original motivation for modifying the existing theories of AI was a desire to fully understand and, if possible, to physically interpret the sum and selection rules presented in Sec. V. These rules play a central role in the analysis of polarization-dependent AI collision processes and had only been demonstrated approximately (and somewhat artificially) using a Bieniek-like theory.[5] The observation[1] that at least one of these rules depends critically on the conservation of total orbital angular momentum is sufficient to motivate the current approach. However, other (initially unanticipated) advantages are evident. The relative ease with which the above-mentioned rules can be derived and the relative simplicity of the final scattering amplitude formulas [cf. (5.35), (5.53), and (5.55)] both have their origin in the use of a symmetric top basis set (labeled by total angular momentum quantum numbers), in combination with the physical requirement that the transition operator be a scalar.

Insofar as the derivation of scattering amplitude formulas is concerned, our goal has been to derive simple expressions for both the main contribution to AI and for corrections to that contribution due to alternative mechanisms for ionization. Here, the use of a projection-operator formalism allows all of the wave functions appearing in our final results to be interpreted as eigenfunctions of effective, single-channel Hamiltonians. This permits one to adopt the same physical intuition in interpreting complex systems as has been used to understand "two-state" (one bound plus continuum) systems. The projection-operator formalism can be used to construct simple expressions for AI scattering amplitudes, including corrections due to Born-Oppenheimer and "final-state" couplings. The corrections are only slightly more difficult to evaluate numerically than the main (Bieniek-like) contribution and this, in turn, is given by a rigorous expression no more complicated than the approximations previously reported. Two examples of these corrections ($T^{(1,1)}$ and $T^{(2,0)}$) have been given in Sec. V. These are the first-order modifications to the AI scattering amplitude due to Born-Oppenheimer and final-state couplings, respectively. Thus, it is a straightforward matter, once $T^{(1,0)}$ is known, to evaluate corrections due to Born-Oppenheimer couplings and perhaps, more importantly, due to the frozen-core approximation used to make the free-electron wave function calculationally tractable.

ACKNOWLEDGMENT

This research was supported by a grant from the National Science Foundation.

---

[*] Present address: Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003.

[†] Author to whom correspondence should be addressed.

[1] D. M. Jones and J. S. Dahler, Phys. Rev. A **35**, 3688 (1987).

[2] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[3] R. J. Bieniek, Phys. Rev. A **18**, 392 (1978).

[4] V. Hoffman and H. Morgner, J. Phys. B **12**, 2587 (1979). These authors have used a total orbital angular momentum basis to treat several special cases of Penning ionization.

[5] D. M. Jones and J. S. Dahler, Phys. Rev. A **31**, 210 (1985).

[6] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd revised ed. (Princeton University Press, Princeton, NJ, 1968).

[7] J. H. van Vleck, Rev. Mod. Phys. **23**, 213 (1951).

[8] S. E. Nielsen and J. S. Dahler, J. Chem. Phys. **45**, 4060 (1966).

[9] This is the convention employed by Edmonds; it is to be distinguished from the convention of "active" rotations used in Ref. 1.

[10] What we mean by this is that the angle $\phi_i(i=x,y,z)$ specifying the orientation of $\hat{\mathbf{R}}$ with respect to a clockwise rotation about the laboratory axis i, is conjugate to the angular momentum component N_i. Similar remarks apply to $\hat{\mathbf{R}}$ and $\mathbf{K}$ if $\hat{\mathbf{R}}$ specifies the orientation of the quasimolecule rather than that of the internuclear axis.

[11] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1962), Appendix B. This formula is identical to the equation appearing after (B.40).

[12] Y. Itikawa, Chem. Phys. **28**, 461 (1978); **30**, 109 (1978); **37**, 401 (1979).

[13] H. Takagi and H. Nakamura, J. Phys. B **11**, L675 (1978); Y. Itikawa, H. Takagi, H. Nakamura, and H. Sato, Phys. Rev. A **27**, 1319 (1983).

[14] K.-S. Lam and T. F. George, Phys. Rev. A **29**, 492 (1984).

[15] W. H. Miller, C. A. Slocomb, and H. F. Schaefer III, J. Chem. Phys. **56**, 1347 (1972).

[16] H. P. Saha, J. S. Dahler, and S. E. Nielsen, Phys. Rev. A **28**, 1487 (1983).

[17] For example, see Chap. X of Ref. 11.

[18] A. P. Hickman and H. Morgner, J. Phys. B **9**, 1765 (1976); the assumption of $\mu=0$ is relaxed in Ref. 4.

[19] M.-X. Wang, M. S. deVries, and J. Weiner, Phys. Rev. A **34**, 1869 (1986).

[20] See, for example, W. H. Miller, J. Chem. Phys. **52**, 3563 (1970); H. P. Saha, J. S. Dahler, and D. M. Jones, Phys. Rev. A **30**, 1345 (1984).

[21] Soo-Y. Lee and E. J. Heller, J. Chem. Phys. **71**, 4777 (1979).

[22] For example, see R. T Pack and J. O. Hirschfelder, J. Chem. Phys. **52**, 521 (1970).