Molecular-state close-coupling theory including continuum states. I. Derivation of close-coupled equations

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We formulate a close-coupling theory of slow ion-atom collisions based on molecular (adiabatic) electronic states, and including the electronic continuum. The continuum is represented by *packet states* spanning it locally and constructed explicitly from exact continuum states. Particular attention is given to two fundamental questions: (1) Unbound electrons can escape from the local region spanned by the packet states. We derive close-coupled integral equations correctly including the escape effects; the "propagator" generated by these integral equations does not conserve probability within the close-coupled basis. Previous molecular-state formulations including the continuum give no account of escape effects. (2) Nonadiabatic couplings of adiabatic continuum states with the same energy are singular, reflecting the fact that an adiabatic description of continuum behavior is not valid outside a local region. We treat these singularities explicitly and show that an accurate representation of nonadiabatic couplings within the local region spanned by a set of packet states is well behaved. Hence an adiabatic basis-set description can be used to describe close coupling to the continuum in a local "interaction region," provided the effects of escape are included. In principle, the formulation developed here can be extended to a large class of model problems involving many-electron systems and including models for Penning ionization and collisional detachment processes. However, we restrict specific attention here to the simpler problem of collisional (impact) ionization in one-electron systems (e.g., proton–hydrogen-atom collisions) and some results have been proved rigorously only for those systems.

I. INTRODUCTION

This work develops a close-coupling theory of ion-atom collisions at low to intermediate energies, based on a molecular (i.e., *adiabatic* or *near-adiabatic*) description of the coupled channel states, and including close coupling to the electronic continuum. We restrict attention here to a very simple class of problems, in which a single dynamical electron is excited to the continuum from bound electronic states lying entirely below it and there are no quasibound levels embedded in the continuum. The formulation is directly applicable to impact ionization in one-electron collision systems and we use the proton–hydrogen-atom system as a prototype in computational applications made in following papers.

With this simplification we can focus directly on three basic problems related to continuum excitation in slow collisions: (1) limitations of an adiabatic description of the continuum, (2) implications of a discretized representation of the continuum, and (3) bipolarity of collision system and its effects on the spatial distribution of ejected electrons.

The theory is based on a *classical trajectory* treatment[1] of the nuclear motion: For each impact parameter b and collision energy E, the trajectory $\mathbf{R}(t)$ is specified and the electronic system evolves according to the time-dependent Schrödinger equation, subject to suitable boundary conditions:

$$\iota(\partial/\partial t)\Psi(\mathbf{r};t)=H_e(\mathbf{r};\mathbf{R}(t))\Psi(\mathbf{r};t)\ . \tag{1.1}$$

Molecular or *adiabatic* electronic states are eigenfunctions of the electronic Hamiltonian $H_e(\mathbf{r};\mathbf{R})$ at each nuclear configuration $\mathbf{R}(t)$. If the continuum is included, these states form a complete set at each $\mathbf{R}$, and provide a valid formal basis for solving the Schrödinger equation. Close-coupling formalisms based on this fact and including the continuum have been given in the literature[2] and used as a framework for computations.[3,4] While our formulation has the same formal starting point, major modifications arise from consideration of the basic problems mentioned above.

It is obvious that an adiabatic expansion cannot offer a practical description of the electronic continuum throughout all time and space. An electron far from the nuclei certainly cannot follow their motion as the adiabatic continuum states do. There are singularities in the "nonadiabatic couplings" among adiabatic continuum states which arise from this fact. On the other hand, an adiabatic state description, including continuum components, should offer a valid description of electrons in the vicinity of slowly moving nuclei. We show here that a discretized set of adiabatic continuum *packet states* forms an appropriate basis for treating close-coupling *within a finite subspace spanning a suitably chosen interaction region.* The size and characteristics of this region are not evident at the outset and may depend strongly on the mechanism of excitation and resulting continuum electronic energy distribution.

Even if there were no inherent difficulties in an adiabatic description of continuum states, there are important physical consequences of any mathematical procedure which replaces the formal integrations over con-

tinuum energies appearing in an exact equation of motion by a discrete sampling scheme. In effect, such a discretization always replaces the part of Hilbert space spanned by the true continuum with a truncated subspace. As a result, certain operators in the equations of motion cannot be fully represented, and unless great care is taken they may not even be accurately represented within the truncated subspace. This is true in particular for the (zeroth-order) propagator itself. This point has been made earlier by Reading and Ford[5] in a paper treating close coupling in ion-atom collisions but using atomic-state basis expansions. They showed that if a discretization of the continuum is introduced (in their case, with a basis of L^2-type pseudostates), such a truncation necessarily restricts the description given by the close-coupled wave function to a finite region of configuration space. But since the propagator for continuum electrons must describe their *escape* from any such region, then, in contrast to the exact close-coupled equations, the close-coupled equations for the wave function in the truncated subspace are *necessarily nonunitary*, i.e., they should *not* conserve probability. Reading and Ford derived coupled integral equations with the required nonunitary character and discussed methods for their solution. However, their work was mainly concerned with collisions at intermediate and high energies, where the collision time is comparable to or shorter than the time required for an electron to escape from the local region described by the truncated pseudostate basis. We might expect escape effects to be more important in *slow* collisions. In the adiabatic close-coupling treatments cited above,[2-4] discretizations of the continuum are introduced, but escape effects are not accounted for. Here we develop the theory showing that the correct close-coupled equations in a discretized basis are not probability conserving and escape effects are included. In fundamental respects our derivation is similar to that of Reading and Ford,[5] but differs from theirs in that (a) we derive the integral equations in the truncated subspace by projection on packet states constructed explicitly from the exact continuum states and (b) we use an *adiabatic* zeroth-order basis description, with resulting additional complications arising from the singularities in the nonadiabatic couplings.

In Sec. II we present a version of the adiabatic close-coupling formalism, in the form of an integral equation for the unitary propagator, based on the *adiabatic* unitary propagator as the zeroth-order approximation. This serves to introduce the problems in adiabatic descriptions and provides a formal starting point for the close-coupling scheme eventually developed. In Sec. III we discretize the exact continuum using packet states, and derive some important results from the construction; in particular, we show that a representation of the adiabatic propagator within the packet-state subspace contains effects of escape by unbound electrons from the local region spanned by that basis. In Sec. IV we construct a subspace representation of the nonadiabatic coupling operator and derive integral equations for the evolution of the subspace state vector; as expected, probability is not conserved within the subspace. A following paper[6] contains illustrative computational results for the proton–H-atom system. Later papers will present results of close-coupling studies on this system based on the formulation.

II. ADIABATIC CLOSE-COUPLING FORMALISM

A. Molecular (adiabatic) eigenstates

At each nuclear configuration $\mathbf{R}$ the solutions of the electronic stationary state problem,

$$H_e(\mathbf{r};\mathbf{R})\phi_k(\mathbf{r};\mathbf{R})=\epsilon_k(R)\phi_k(\mathbf{r};\mathbf{R}) , \tag{2.1}$$

define a complete orthogonal set of molecular (adiabatic) eigenstates. The set $\{\phi_k(\mathbf{r};\mathbf{R})\}$ includes both discrete and continuum states and the general index k subsumes a more complete specification of quantum numbers appropriate to each system. The prototype one-electron, two-nucleus systems are separable in prolate spheroidal coordinates and eigenstates are labeled by two more quantum numbers (μ,λ), in addition to the energy. λ is the component of orbital angular momentum on the $\mathbf{R}$ axis; the index μ labels a constant of the motion $A_{\mu\lambda}$ associated in the united-atom limit $R\to 0$ with the angular momentum $A_{\mu\lambda}\to\mu(\mu+1)$, $\mu=|\lambda|$, $|\lambda|+1$, etc. μ,λ are thus analogous to spherical polar quantum numbers l,m but should not be confused with them. Bound states are denoted $\{\phi(n\mu\lambda;\mathbf{r};\mathbf{R})\}$, with energy eigenvalues $\epsilon(n\mu\lambda;R)<0$, and continuum states $\{\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R})\}$ with continuous eigenvalues $\epsilon>0$. At each $\mathbf{R}$ these eigenstates satisfy the orthogonality relations

$$\begin{aligned}
&\langle\phi(n'\mu'\lambda';\mathbf{R})\,|\,\phi(n\mu\lambda;\mathbf{R})\rangle=\delta_{n'n}\delta_{\mu'\mu}\delta_{\lambda'\lambda} ,\\
&\langle\phi(\epsilon'\mu'\lambda';\mathbf{R})\,|\,\phi(n\mu\lambda;\mathbf{R})\rangle=0 ,\\
&\langle\phi(\epsilon'\mu'\lambda';\mathbf{R})\,|\,\phi(\epsilon\mu\lambda;\mathbf{R})\rangle=\delta(\epsilon'-\epsilon)\delta_{\mu'\mu}\delta_{\lambda'\lambda} .
\end{aligned} \tag{2.2}$$

Assuming that $H_e(\mathbf{r};\mathbf{R})$ and its eigenfunctions can be continued analytically as functions of $\mathbf{R}$, then for the discrete states, as $\mathbf{R}\to\mathbf{R}'$, there is a one-to-one mapping,

$$\phi(n\mu\lambda;\mathbf{r};\mathbf{R})\to\phi(n\mu\lambda;\mathbf{r};\mathbf{R}'),\quad \epsilon(n\mu\lambda;R)\to\epsilon(n\mu\lambda;R') ; \tag{2.3a}$$

for the continuum states, we *define* the mapping so that

$$\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R})\to\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R}') , \tag{2.3b}$$

i.e., the continuum energy ϵ is independent of R. This mapping simplifies the problems associated with the one-electron type of continuum and the properties of the associated nonadiabatic couplings.

This work assumes that the electronic continuum basis states are "simple" in certain ways. Certainly the continua of the one-electron prototypes are simple in the required sense, and we use them here to illustrate what is intended by the term. We have specifically excluded adiabatic continua which contain embedded quasibound levels. The essential requirement is that the continuum wave functions vary smoothly without displaying any "fine structure" of the sort associated with Feshbach resonances (and arising from mixing with specific alterna-

tive physical configurations). Our results are strictly valid only for the one-electron prototype problems, but the general assumptions may be extended to a large class of approximate model problems; in general we may assume that continua of systems with a single active electron, described within an independent-particle model, are also simple in the required sense, and therefore the general framework presented here can be extended to them as well.[7]

B. Nonadiabatic couplings

If the solution $\Psi(\mathbf{r};t)$ to the Schrödinger equation (1.1) is expanded in the basis states $\{\phi_k[\mathbf{r};\mathbf{R}(t)]\}$ at each configuration $\mathbf{R}(t)$, transitions arise from *nonadiabatic couplings,* whose matrix elements are given *formally* by

$$-\iota\langle\phi_{k'}\,|\,(\partial/\partial t)\,|\,\phi_k\rangle=-\iota\mathbf{v}\cdot\langle\phi_{k'}\,|\,\nabla_R\,|\,\phi_k\rangle\ , \quad (2.4a)$$

where $\mathbf{v}\equiv(d\mathbf{R}/dt)$. The physical meaning is that transitions result from the finite rates of deformation of the adiabatic states as the nuclei move along $\mathbf{R}(t)$, with a coupling strength proportional to the local collision velocity $\mathbf{v}$. However, a rigorously correct definition of this operator and its matrix elements requires careful consideration of several points.

(1) Nonadiabatic couplings must be *gauge invariant*, i.e., their matrix elements cannot depend on the inertial reference frame chosen for electron coordinates, and they must also be defined consistently with correct asymptotic boundary conditions for the molecular-state channels. These requirements lead to *electron translation factor* (ETF) corrections to nonadiabatic couplings (cf. Sec. II B 2 below).

(2) The nonadiabatic coupling operator is not like an ordinary finite-range potential operator $\hat{V}(t)$. Its matrix elements among continuum components have singularities which reflect fundamental limitations of an adiabatic description of the continuum. We discuss the structure of these singularities in Sec. II C.

1. Radial and angular couplings

The trajectory $\mathbf{R}(t)$ is confined to a plane and is specified by magnitude $R(t)$ and angle $\vartheta(t)$; $\mathbf{v}$ then has radial and tangential components $v_R=(dR/dt)$, $v_\vartheta=R(d\vartheta/dt)=-bv_0/R$, where v_0 is the asymptotic collision speed, and hence

$$-\iota\mathbf{v}\cdot\langle\phi_{k'}\,|\,\nabla_R\,|\,\phi_k\rangle=-\iota v_R\langle\phi_{k'}\,|\,(\partial/\partial R)\,|\,\phi_k\rangle -\iota(v_\vartheta/R)\langle k'\,|\,(\partial/\partial\vartheta)\,|\,\phi_k\rangle\ . \quad (2.4b)$$

The gradient in Eq. (2.4) is taken keeping electron coordinates $\mathbf{r}'$ fixed in a nonrotating frame; if as is usual the eigenstates $\phi_k(\mathbf{r};\mathbf{R})$ are described in coordinates $\mathbf{r}$ of a frame rotating with $\mathbf{R}$, the eigenstates $\phi_k(\mathbf{r};R)$ depend only on R and the nonadiabatic couplings then are written formally as

$$K_{k'k}(t)=-\iota\mathbf{v}\cdot\langle\phi_{k'}\,|\,\nabla_R\,|\,\phi_k\rangle=v_R P^R_{k'k}+v_\vartheta P^\vartheta_{k'k}\ , \quad (2.5)$$

where

$$P^R_{k'k}(R)=-\iota\langle\phi_{k'}\,|\,(\partial/\partial R)\,|\,\phi_k\rangle \quad (2.6a)$$

and

$$P^\vartheta_{k'k}=-(1/R)\langle\phi_{k'}\,|\,L_y\,|\,\phi_k\rangle\ , \quad (2.6b)$$

and L_y is the electronic orbital angular momentum component normal to the collision plane (z axis coincides with $\mathbf{R}$). Equations (2.6a) and (2.6b) define the *radial* and *angular* nonadiabatic coupling matrix elements, respectively.

Selection rules are as follows: Since $\{\phi_k(\mathbf{r};\mathbf{R})\}$ are eigenfunctions of the R-axis angular momentum component L_z, the radial couplings obey the selection rule $\lambda_{k'}=\lambda_k$ and angular couplings $\lambda_{k'}=\lambda_k\pm1$. In a centrosymmetric system like $H_2{}^+$, coupled states must also have the same parity (g or u).

2. Translational invariance and ETF corrections

The physical description given by Eq. (1.1) cannot depend on the reference origin chosen for electron coordinates; hence the couplings denoted formally above as $-\iota\langle\phi_{k'}\,|\,(\partial/\partial t\,|\,\phi_k\rangle$ and elaborated in Eqs. (2.4)–(2.6) must also be invariant to that choice. [We use the geometric center of the system (GC) as (conventional) reference origin.] It is easy to show, however, that the coupling matrix elements defined by Eqs. (2.6) do not have the required origin invariance. The inconsistency is resolved by the observation that due to nuclear motion any new origin is translating with respect to GC and transformation theory requires that wave functions described in the new frame differ from those in the GC frame in a manner representing the relative translation. When the Hamiltonian acts on the transformed wave functions in the new frame, additional coupling terms are generated which preserve translational invariance of the effective couplings.

The couplings computed using GC as reference origin must also be defined *correctly*, i.e., consistently with correct asymptotic description of channel basis states. *This cannot be done using only the adiabatic molecular eigenstates of* H_e. Seen from the origin GC, an electron bound to either nucleus is *translating* with it, that is, the "correct inertial reference frame" for an electron bound to nucleus A is at A, not at GC. It is impossible to choose a unique inertial reference frame for the active electron which resolves this problem; since the colliding nuclei move relative to each other with velocity $\mathbf{v}$, the correct inertial frames for electrons bound to each are different and this difference has to be included in the definition of the basis functions, even in a classical trajectory description. Since the Hamiltonian H_e contains no information about nuclear motion, this relative translation cannot appear in the eigenstates $\{\phi_k\}$ themselves but must be included as a modifying electron translation factor (ETF) in a correct description of basis states. Asymptotic definitions of these factors are easily found from transformation theory, but the problem is how to modify molecular-state basis functions and the

resulting couplings in a global way which (1) gives correct asymptotic behavior, (2) ensures translational invariance of couplings, and (3) forms an efficient basis set for rapidly convergent close-coupling calculations.

Several solutions to this problem have been proposed. Here we use the *molecular-state switching function* formalism of Thorson and Delos.[8-10] Several close-coupling calculations using this or a closely related scheme have been carried out,[11-14] though none so far has treated close-coupling to the continuum. The most important result of translation factors in a molecular-state description of ion-atom collisions is to correct the nonadiabatic coupling matrices.[15] With GC as reference origin, the radial and angular couplings formally given in Eqs. (2.5) and (2.6) are *explicitly* defined as follows:

$$\text{“}-\iota\langle\phi_{k'}\,|\,(\partial/\partial R)\,|\,\phi_k\rangle\text{”}=P^R_{k'k}+A^R_{k'k} \tag{2.7a}$$

and

$$\text{“}-(1/R)\langle\phi_{k'}\,|\,L_y\,|\,\phi_k\rangle\text{”}=P^{\vartheta}_{k'k}+A^{\vartheta}_{k'k}\ , \tag{2.7b}$$

where $P^R_{k'k}$ and $P^{\vartheta}_{k'k}$ are the nonadiabatic couplings defined explicitly by Eqs. (2.6a) and (2.6b) *with GC as reference origin,* and *the ETF correction matrix elements* are given by

$$A^R_{k'k}=(\iota/2)(\epsilon_{k'}-\epsilon_k)\langle\phi_{k'}\,|\,zf_k(\mathbf{r};R)\,|\,\phi_k\rangle \tag{2.8a}$$

and

$$A^{\vartheta}_{k'k}=(\iota/2)(\epsilon_{k'}-\epsilon_k)\langle\phi_{k'}\,|\,xf_k(\mathbf{r};R)\,|\,\phi_k\rangle\ , \tag{2.8b}$$

where $f_k(\mathbf{r};R)$ is the *switching function* for the eigenstate $\phi_k(\mathbf{r};\mathbf{R})$.[16] In effect, the switching function shifts the electronic reference origin from GC to one more locally appropriate. For bound states, the appropriate local origins asymptotically are the atomic nuclei (A,B) to which an electron is bound; hence $f_k(\mathbf{r};R)$ satisfies the boundary conditions

$$\lim_{R\to\infty} f_k(r;R)=+1, \quad |\,\mathbf{r}_B\,| \text{ finite}$$
$$=-1, \quad |\,\mathbf{r}_A\,| \text{ finite}\ ,$$

but the form of $f_k(\mathbf{r};R)$ for finite R is not fully determined. Efficiency and convergence of close-coupling calculations using the resulting basis set is a relevant criterion for choice.

This paper is not concerned directly with the study of ETF corrections to nonadiabatic couplings, but two concluding points do bear on present objectives.

(1) For the prototype one-electron systems,[6] the molecular continuum packet states are centered on GC (more generally, on the center of positive charge), and not on the atomic centers, and this is probably a general feature of molecular continua. The implication is that for these states, the GC (or center of charge) is itself the proper reference origin, i.e., there should be no ETF corrections to continuum-continuum couplings.

(2) In any case the ETF correction matrix elements defined by Eqs. (2.8) are at most finite and cannot affect the *singularities* in continuum-state couplings which mainly concern us; these arise entirely from the couplings $\underline{\mathbf{P}}^{\mathbf{R}}, \underline{\mathbf{P}}^{\vartheta}$.

C. Nonadiabatic couplings and the Hellmann-Feynman theorem

Nonadiabatic couplings $P^R_{k'k}, P^{\vartheta}_{k'k}$ between two molecular continuum states are singular when their energies $\epsilon_{k'}$ and ϵ_k are equal. As noted earlier, this reflects the fact that an unbound electron far from the nuclei cannot really follow their motion adiabatically. General considerations based on the adiabatic approximation[17] suggest such a result must always hold for continuum-continuum nonadiabatic couplings, but for the prototype one-electron systems we can derive the explicit form of these singularities by a generalization of the Hellmann-Feynman theorem.

1. Hellmann-Feynman theorem

If the Hamiltonian H_e and its eigenstates $\{\phi_k\}$ can be analytically continued as functions of a parameter ζ, then the Hellmann-Feynman theorem,

$$\langle\phi_{k'}\,|\,(\partial H_e/\partial\zeta)\,|\,\phi_k\rangle=(d\epsilon_k/d\zeta)\langle\phi_{k'}\,|\,\phi_k\rangle + (\epsilon_{k'}-\epsilon_k)\langle\phi_{k'}\,|\,(\partial/\partial\zeta)\,|\,\phi_k\rangle\ ,$$

holds, provided at least one of the eigenstates $\phi_{k'},\phi_k$ is of L^2 type. This relation is applicable to both radial and angular nonadiabatic couplings,

$$P^R_{k'k}=-\iota\langle\phi_{k'}\,|\,(\partial H_e/\partial R)_{\mathbf{r}}\,|\,\phi_k\rangle/[\epsilon_k(R)-\epsilon_{k'}(R)] \tag{2.9a}$$

and

$$P^{\vartheta}_{k'k}=-(1/R)\langle\phi_{k'}\,|\,[L_y,H_e]\,|\,\phi_k\rangle/[\epsilon_k(R)-\epsilon_{k'}(R)]\ , \tag{2.9b}$$

provided at least one of the coupled states is bound.

These relations imply that nonadiabatic couplings may be very large if the states coupled become degenerate. For the one-electron prototypes considered here the bound states lie below the continuum, so this point is not pertinent to bound-continuum couplings. For couplings of two bound states, two cases may occur.

(1) Avoided crossings. Two adiabatic bound states can have an avoided crossing at some internuclear separation R_x; the adiabatic eigenvalues obey the noncrossing rule but the difference $(\epsilon_k-\epsilon_{k'})$ may become very small near R_x. In such cases the radial coupling matrix element $P^R_{k'k}$ is not singular, but exhibits a resonant maximum near R_x.

(2) Real crossings. Adiabatic bound states with different λ, and, in the prototype one-electron systems, even with the same λ,[18] may have real crossings. However, in these cases the corresponding couplings are not singular; the commutator matrix elements in the numerators of Eqs. (2.9) are linearly proportional to

$(\epsilon_k-\epsilon_{k'})$ near R_x, and the couplings themselves are smooth, nonresonant functions of R near such crossings.

2. *Generalization for continuum states*

With appropriate definitions, and the mapping of continuum states versus **R** defined earlier, the Hellmann-Feynman relations may be extended to continuum-continuum nonadiabatic couplings. In particular, the following is true.

(1) The relations (2.9a) and (2.9b) hold without modification for two continuum states when $(\epsilon_k-\epsilon_{k'})\neq 0$.

(2) When $(\epsilon_k-\epsilon_{k'})\to 0$, nonadiabatic couplings $P^R_{k'k}$ and $P^\vartheta_{k'k}$ between two continuum states have the forms

$$P^R_{k'k}=M^R_{k'k}\delta(\epsilon_k-\epsilon_{k'})+\mathcal{P}\left[\frac{N^R_{k'k}}{(\epsilon_k-\epsilon_{k'})}\right] \tag{2.10a}$$

and

$$P^\vartheta_{k'k}=M^\vartheta_{k'k}\delta(\epsilon_k-\epsilon_{k'})+\mathcal{P}\left[\frac{N^\vartheta_{k'k}}{(\epsilon_k-\epsilon_{k'})}\right], \tag{2.10b}$$

where $\delta(x)$ is the Dirac δ function and $\mathcal{P}$ implies that the Cauchy principal value is taken in integrations over continuum energies ϵ_k and $\epsilon_{k'}$.

(3) The numerators $N^R_{k'k}$ and $N^\vartheta_{k'k}$ are given as expected by the analytic matrix elements

$$N^R_{k'k}=-\iota\langle\phi_{k'}\,|\,(\partial H_e/\partial R)_r\,|\,\phi_k\rangle \tag{2.10c}$$

and

$$N^\vartheta_{k'k}=-(1/R)\langle\phi_{k'}\,|\,[L_y,H_e]\,|\,\phi_k\rangle\ , \tag{2.10d}$$

and the analytic strength coefficients $M^R_{k'k}$ and $M^\vartheta_{k'k}$ of the singular terms are also directly related to these commutator matrix elements.

An outline of the proof of these results and the explicit expressions for the analytic coefficients $N^{R,\vartheta}_{k'k}$ and $M^{R,\vartheta}_{k'k}$ are given for the one-electron prototype systems in Appendix A.

3. *Summary of continuum nonadiabatic couplings*

In this and preceding subsections we have given more explicit definition to the nonadiabatic coupling operator $\hat{\underline{\mathbf{K}}}(t)$ and its matrix elements. We divided the couplings into radial and angular types,

$$\hat{\underline{\mathbf{K}}}(t)=\hat{\underline{\mathbf{K}}}^{\mathbf{R}}(t)+\hat{\underline{\mathbf{K}}}^{\vartheta}(t)\ ,$$

with their respective selection rules on λ; we introduced the ETF corrections $\underline{\mathbf{A}}^{\mathbf{R}}$ and $\underline{\mathbf{A}}^{\vartheta}$, and discussed their effects on nonadiabatic couplings; and finally we have used the generalization of the Hellmann-Feynman theorem for continuum states (Appendix A) to show that for the one-electron prototypes both radial and angular couplings have a common singular structure,

$$\langle\epsilon'\mu'\lambda'\,|\,K^{R,\vartheta}\,|\,\epsilon\mu\lambda\rangle=\left[\delta(\epsilon-\epsilon')\langle\epsilon\mu'\lambda'\,|\,\mathcal{M}^{R,\vartheta}\,|\,\epsilon\mu\lambda\rangle+\mathrm{P}\left[\frac{\langle\epsilon'\mu'\lambda'\,|\,\mathcal{N}^{R,\vartheta}\,|\,\epsilon\mu\lambda\rangle}{(\epsilon-\epsilon')}\right]\right]. \tag{2.11}$$

Matrix elements of the operators $\hat{\mathcal{M}}^R,\hat{\mathcal{M}}^\vartheta$ and $\hat{\mathcal{N}}^R,\hat{\mathcal{N}}^\vartheta$ are analytic functions of the energies ϵ,ϵ' [script notation for these operators indicates velocities v_R,v_ϑ are included as required by Eq. (2.5)].

D. Derivation of integral equation

Direct substitution of the formal adiabatic expansion

$$|\Psi(t)\rangle=\sum_k|\phi_k[\mathbf{R}(t)]\rangle b_k(t)\exp\left[-\iota\int^t\epsilon_k(t')dt'\right]$$

in the time-dependent Schrödinger equation (1.1) (where it is understood that the sum over k includes both discrete and continuum states and implies integration over continuum energies ϵ) leads directly to a system of coupled *differential* equations for the coefficients $\{b_k(t)\}$. While formally correct, these equations are not a useful starting point for our formulation, and we develop instead the equivalent formulation in terms of an *integral* equation for the unitary propagator $\hat{U}(t;t_0)$.

A solution $|\Psi(t)\rangle$ to Eq. (1.1) is generated from its precursor $|\Psi(t_0)\rangle$ at an (earlier) time t_0 by the unitary propagator $\hat{U}(t;t_0)$,

$$|\Psi(t)\rangle=\hat{U}(t;t_0)\,|\Psi(t_0)\rangle\ ;$$

$\hat{U}(t;t_0)$ also obeys the Schrödinger equation

$$\iota(\partial/\partial t)\hat{U}(t;t_0)=\hat{H}(t)\hat{U}(t;t_0)$$

with initial condition $\hat{U}(t_0;t_0)=1$, and unitarity of $\hat{U}$ ensures the conservation of probability,

$$\langle\Psi(t)\,|\,\Psi(t)\rangle=\langle\Psi(t_0)\,|\,\Psi(t_0)\rangle=1\ .$$

If the Hamiltonian for a system has the form $\hat{H}(t)=\hat{H}_0+\hat{V}(t)$, it is easy to show that $\hat{U}(t;t_0)$ is related to the zeroth-order propagator $\hat{U}_0(t;t_0)$ satisfying the equation

$$\iota(\partial/\partial t)\hat{U}_0(t;t_0)=\hat{H}_0\hat{U}_0(t;t_0)$$

by the well-known integral equation

$$\hat{U}(t;t_0)=\hat{U}_0(t;t_0)-\iota\int_{t_0}^t dt'\hat{U}_0(t;t')\hat{V}(t')\hat{U}(t';t_0)\ .$$

We derive here the analogous integral equation

$$\hat{U}(t;t_0)=\hat{\chi}(t;t_0)-\iota\int_{t_0}^t dt'\hat{\chi}(t;t')\hat{K}(t')\hat{U}(t';t_0)\ , \tag{2.12}$$

where the zeroth-order propagator $\hat{\chi}(t;t_0)$ is an *adiabatic* propagator and $\hat{K}(t)$ is the nonadiabatic coupling operator discussed earlier. In the derivation it must be

kept in mind that basis kets $|\phi_k[\mathbf{R}(t)]\rangle \equiv |k(t)\rangle$ as well as operators depend on the time t.

The operator

$$\hat{\chi}(t;t_0) \equiv \sum_k |k(t)\rangle \times \exp\left[-\iota \int_{t_0}^{t} \epsilon_k(t')dt'\right] \langle k(t_0)| \quad (2.13)$$

propagates any state vector adiabatically from t_0 to t. It satisfies the equation of motion

$$\iota(\partial/\partial t)\hat{\chi}(t;t_0) = \hat{H}(t)\hat{\chi}(t;t_0) - \hat{K}(t)\hat{\chi}(t;t_0) ,$$

where $\hat{K}(t)$ is the nonadiabatic coupling operator given formally by Eqs. (2.4) and defined more explicitly in earlier discussion.

In adiabatic representation the unitary propagator $\hat{U}(t;t_0)$ is given by

$$\hat{U}(t;t_0) = \sum_{k,k'} |k'(t)\rangle U_{k'k}(t;t_0)\langle k(t)| \ ;$$

if we define

$$\hat{U}^{A}(t;t_0) \equiv \hat{\chi}^{\dagger}(t;t_0)\hat{U}(t;t_0) = \sum_{k,k'} |k(t_0)\rangle \exp\left[-\iota \int_{t_0}^{t} \epsilon_k(t')dt'\right] \times \langle k(t_0)| ,$$

it satisfies the "adiabatic interaction picture" equation of motion

$$\iota(\partial/\partial t)\hat{U}^{A}(t;t_0) = [\hat{\chi}^{\dagger}(t;t_0)\hat{K}(t)\hat{\chi}(t;t_0)]\hat{U}^{A}(t;t_0) .$$

Since this equation is expressed in the fixed basis $\{|k(t_0)\rangle\}$ it can be integrated directly to yield

$$\hat{U}^{A}(t;t_0) = 1 - \iota \int_{t_0}^{t} dt'[\hat{\chi}^{\dagger}(t';t_0)]\hat{K}(t') \times \hat{\chi}(t';t_0)\hat{U}^{A}(t';t_0)$$

and multiplication by $\hat{\chi}(t;t_0)$ then gives Eq. (2.12).

1. *Generalization to partly diabatic bases*

An important generalization of the above integral equation is possible. If a Hamiltonian $\hat{H}(t)$ can be partitioned,

$$\hat{H}(t) = \hat{H}_0(t) + \hat{V}(t) ,$$

and $\{|k(t)\rangle\}$ are the eigenstates of the operator $\hat{H}_0(t)$, then the procedures used above lead to the generalized integral equation

$$\hat{U}(t;t_0) = \hat{\chi}(t;t_0) - \iota \int_{t_0}^{t} dt'\hat{\chi}(t;t')[\hat{K}(t') + \hat{V}(t')]\hat{U}(t';t_0) , \quad (2.14)$$

where $\hat{\chi}(t;t_0)$ is the adiabatic propagator for the zeroth-order Hamiltonian $\hat{H}_0(t)$, and $\hat{K}(t)$ the corresponding nonadiabatic coupling.

Equation (2.14) can form the basis for a treatment of problems in which quasibound levels are embedded in a continuum and are coupled to it, using a formulation similar to the one developed here. Suppose a model Hamiltonian $\hat{H}_0(t)$ can be devised for such a problem, which defines a set of quasibound states and a surrounding set of continuum states in which they are embedded, but such that the (partly adiabatic) continuum of $\hat{H}_0(t)$ contains no mixing with the embedded bound levels and is coupled to them *only* via the interaction potential $\hat{V}(t)$ (the quasibound levels and the continuum are then *diabatically* related to one another). If the continuum of $\hat{H}_0(t)$ is of the "simple" one-electron type exemplified here in the prototype systems, the assumptions required in the derivations of Secs. III and IV are met, and Eq. (2.14) then forms the basis for a model formulation in which the interaction $\hat{V}(t)$ is responsible for initiating transitions from the quasibound levels to the continuum and nonadiabatic couplings in the continuum manifold influence the subsequent propagation of the unbound electron. Such a model provides a scheme for including close coupling to the continuum in the treatment of more complex phenomena such as Penning ionization and collisional detachment from negative ions.[19]

III. ADIABATIC PACKET STATES AND THEIR PROPAGATION

In this section we discuss representation of the molecular electronic continuum by a discretized basis set of *packet states* which span the continuum in a local region of configuration space. The packet states are constructed explicitly from exact continuum states using suitably chosen spectral density functions. Any application of close-coupling methods to the continuum involves some such discretization—for example, the use of numerical quadrature to represent the integrals over continuum energies which appear in the equations for the propagator $\hat{U}(t;t_0)$ [Eqs. (2.12) and (2.14)] or equivalent differential equations. Such discretizations always entail a truncated representation of the full continuum, and their implications must be considered carefully.

In particular, the propagation of a continuum wave packet is of direct interest, and we examine the behavior of a system which is in a packet state at time t_0, under the influence of the adiabatic propagator $\hat{\chi}(t;t_0)$. Since the packet states are not stationary states of the Hamiltonian $H_e(\mathbf{r};\mathbf{R})$, the wave packets evolving from them move away from the region spanned by the packet states, in accordance with the Ehrenfest theorem, and their projections on the original packet states decay with time in a manner consistent with this propagation.

From these considerations we can draw two conclusions. The first and most important is that if the full continuum is represented by truncation to a subspace spanned by a discrete set of packet states, a proper representation of the zeroth-order propagator $\hat{\chi}(t;t_0)$ must include the decay mentioned above, representing escape by an unbound electron from the subspace spanned by the packet states. The second conclusion is implicit, and concerns the validity of an *adiabatic* evolution for a

moving wave packet whose amplitude is far from the nuclei.

A. Construction of packet states

Representation of a continuum by a discrete set of "pseudostates" has been widely discussed, in a variety of contexts.[2,20,21] Given the difficulty of constructing exact continuum states for many problems, a major goal in much of the literature is the construction of pseudostates as eigenfunctions of the Hamiltonian (or a suitable pseudo-Hamiltonian) from basis sets of L^2-type functions.[20,21] In such cases the positive energy eigenvalue spectrum for such pseudostates emerges as a result of the basis set and/or boundary conditions and the model Hamiltonian, and a primary concern of the construction process is the accuracy with which various spectral moments of the true continuum can be represented using such pseudostate expansions.

However, it is also possible to construct discrete sets of pseudostates by a direct superposition of exact continuum states, assuming these are known. In particular, the construction of such *packet states* as discrete bases for close-coupling calculations has been discussed formally by Micha and Piacentini.[2] It is characteristic of this direct construction approach that the spectral distribution of packet amplitudes and the resulting mean energies and widths associated with the packet states is open to choice, and criteria for that choice must in turn be determined by the purpose of the construction: For example, the criterion that each packet state shall be localized approximately within some given bounded region of configuration space leads to a specification of the spectral distribution.

Here we use the continuum eigenstates of the prototype one-electron system (H_2^+ in particular) as a specific example for our discussion, and some features of derivation and notation are specific to that system. However, we emphasize that the major conclusions of the discussion are expected to apply more generally to packet states representing an electronic continuum. The prototype system H_2^+ retains the characteristic properties of a "simple" adiabatic eigenspectrum and the *bipolarity* inherent in a molecular problem. Simplification to a central potential problem, for example, even though it would display the essential points we wish to make about packet-state propagation, would cause the loss of these realistic features and hamper later discussion.

1. Continuum eigenstates for H_2^+

The one-electron two-center Coulomb problem is separable in prolate spheroidal coordinates (ξ,η,φ) and the continuum eigenfunctions $\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R})$ have the form[22,23]

$$\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R})=X(\epsilon\mu\lambda;\xi;R)S(\epsilon\mu\lambda;\eta;R)e^{i\lambda\varphi}/\sqrt{2\pi}\ ; \quad (3.1)$$

as $|\mathbf{r}|\to\infty$ for fixed R, the coordinates approach asymptotically closely to spherical polar coordinates, $(R/2)\xi\approx r$, $\eta\approx\cos\vartheta$, and we refer to $X(\epsilon\mu\lambda;\xi;R)$ as "radial" and $S(\epsilon\mu\lambda;\eta;R)e^{i\lambda\varphi}/\sqrt{2\pi}$ as "angular" functions. The angular functions can be expanded in spherical harmonics,

$$S(\epsilon\mu\lambda;\eta;R)e^{i\lambda\varphi}/\sqrt{2\pi}=\sum_{l=|\lambda|}^{\infty} B_{l\mu}^{|\lambda|}\,Y_{l\lambda}(\cos^{-1}\eta,\varphi)\ ; \quad (3.2)$$

the coefficients $\{B_{l\mu}^{|\lambda|}\}$ and associated eigenvalue $A_{\mu\lambda}$ depend on both ϵ and R in the general case, but for the homopolar systems (e.g., H_2^+) only on the parameter $c^2=(\epsilon R^2/2)$. The dependence of $S(\epsilon\mu\lambda;\eta;R)$ on ϵ is not rapid but in principle must be considered in constructing packet states.

The radial function has the asymptotic form[23]

$$X(\epsilon\mu\lambda;\xi;R)\approx\mathcal{C}(\xi^2-1)^{-1/2}\sin[c\xi+(q/2c)\ln(c\xi)+\delta(\epsilon\mu\lambda;R)]\ , \quad (3.3)$$

where $q=Z_TR$ and Z_T is the total nuclear charge. The constant $\mathcal{C}$ is chosen to satisfy Eqs. (2.2), i.e., the density of states is included in the normalization. Since $c=kR/2$, where $\epsilon=k^2/2$, we can express this in spherical polar coordinates as $|\mathbf{r}|\to\infty$,

$$X(\epsilon\mu\lambda;\xi;R)\approx(2/\pi k)^{1/2}r^{-1}\sin[kr+(Z_T/k)\ln(kr)+\delta(\epsilon\mu\lambda;R)]\ . \quad (3.4)$$

This is the standard form for a Coulomb radial function, but the phase shift $\delta(\epsilon\mu\lambda;R)$ differs from the standard Coulomb phase, due to the bipolar field. At *all* ξ the solutions can be represented in the *phase-amplitude* form[6]

$$X(\epsilon\mu\lambda;\xi;R)=\mathcal{C}[(\xi^2-1)p_r(\xi)]^{-1/2}\sin\theta(\epsilon\mu\lambda;\xi;R)\ , \quad (3.5)$$

where the *phase* $\theta(\epsilon\mu\lambda;\xi;R)$ given by

$$\theta(\epsilon\mu\lambda;\xi;R)=\int_1^{\xi}p_r(\epsilon\mu\lambda;\xi';R)d\xi' \quad (3.6)$$

and the *quantal momentum* p_r are easily computed, slowly varying functions of their arguments.[6] This representation of the radial functions makes it particularly easy to construct packet states and examine their properties.

Together with the bound states $\{|\phi(n\mu\lambda;\mathbf{R})\rangle\}$ the continuum states form a complete set,

$$\sum_{\mu,\lambda}\left[\sum_n|\phi(n\mu\lambda;\mathbf{R})\rangle\langle\phi(n\mu\lambda;\mathbf{R})|+\int_0^{\infty}d\epsilon\,|\phi(\epsilon\mu\lambda;\mathbf{R})\rangle\langle\phi(\epsilon\mu\lambda;\mathbf{R})|\right]=1\ . \quad (3.7)$$

2. Definition and properties of packet states

We define a discrete set of packet states $\{\tilde{\phi}(j\mu\lambda;\mathbf{r};\mathbf{R})\}$ by the integrals

$$\tilde{\phi}(j\mu\lambda;\mathbf{r};\mathbf{R})\equiv(\Delta_j)^{-1/2}\int_{\epsilon_j-\Delta_j/2}^{\epsilon_j+\Delta_j/2}d\epsilon\,\phi(\epsilon\mu\lambda;\mathbf{r};\mathbf{R})\ , \quad (3.8a)$$

where

$$\epsilon_{j+1}=\epsilon_j+\tfrac{1}{2}(\Delta_j+\Delta_{j+1}),\quad \epsilon_1=\tfrac{1}{2}\Delta_1 \tag{3.8b}$$

and the spectral widths Δ_j are not yet defined. From Eqs. (2.2) it follows that these functions are orthogonal and normalized to unity,

$$\langle\tilde{\phi}(j'\mu'\lambda';\mathbf{R})\,|\,\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle=\delta_{j'j}\delta_{\mu'\mu}\delta_{\lambda'\lambda}\ . \tag{3.9}$$

The packet states $|\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle$ are localized spatially in a fashion controlled by the widths Δ_j: From Eqs. (3.1) and (3.5) and making the approximations

$$\begin{aligned}
&S(\epsilon\mu\lambda;\eta;R)\approx S(\epsilon_j\mu\lambda;\eta;R)+\cdots\ ,\\
&[p_r(\epsilon\mu\lambda;\xi;R)]^{-1/2}\approx[p_r(\epsilon_j\mu\lambda;\xi;R)]^{-1/2}+\cdots\ ,\\
&\theta(\epsilon\mu\lambda;\xi;R)\approx\theta(\epsilon_j\mu\lambda;\xi;R)\\
&\qquad+(\epsilon-\epsilon_j)[\partial\theta(\epsilon\mu\lambda;\xi;R)/\partial\epsilon]_{\epsilon_j}+\cdots\ ,
\end{aligned} \tag{3.10}$$

in Eq. (3.8a), we obtain

$$\begin{aligned}
\tilde{\phi}(j\mu\lambda;\mathbf{r};\mathbf{R})\approx\Delta_j^{1/2}&\phi(\epsilon_j\mu\lambda;\mathbf{r};\mathbf{R})\\
&\times f(\tfrac{1}{2}\Delta_j[\partial\theta(\epsilon\mu\lambda;\xi;R)/\partial\epsilon]_{\epsilon_j})\ ,
\end{aligned} \tag{3.11}$$

where $f(x)=x^{-1}\sin x$. Since $(\partial\theta/\partial\epsilon)$ is a monotonically increasing function of ξ, the factor f is an envelope function which decreases to a small size for $\xi\geq\xi_0$ such that

$$\Delta_j[\partial\theta(\epsilon\mu\lambda;\xi_0;R)/\partial\epsilon]_{\epsilon_j}=2\pi\ . \tag{3.12}$$

[Asymptotically, $(\partial\theta/\partial\epsilon)_{\epsilon_j}\approx(r/v_j)$ where v_j is the electron speed for energy ϵ_j, and this result reduces to the condition $(\Delta_j r/v_j)\approx 2\pi$: The packet is localized in a region whose radius is the distance an electron with energy ϵ_j would travel in time $\tau_j=2\pi/\Delta_j$.] The packet width Δ_j thus fixes the packet's localization in a spatial region for given ϵ_j. Equations (3.12) and (3.8b) can be used to determine a set of packet widths $\{\Delta_j\}$ for a basis set of packet states localized within an interaction region of specified size $r_0=(R\xi_0/2)$; alternatively, an *a priori* specification of packet widths implies corresponding packet-state sizes.

In the paper following[6] we present the results of packet-state computations for the prototype system H_2^+, for various values of the interaction region size parameter r_0. The resulting widths $\{\Delta_j\}$ are found to be essentially independent of internuclear distance R and quantum numbers (μ,λ) for $r_0\geq 40.0$ a.u. The packet states [computed explicitly from Eqs. (3.8)] are localized as expected within the region bounded by r_0. A less expected result is that for all reasonable values of the quantum numbers (μ,λ) they are strongly localized at the *center of charge* and not on the nuclei as internuclear separation R increases. This is probably a general characteristic of molecular continuum states.

Since such a packet-state basis set clearly does not span the full continuum, the *approximate closure relation*

$$\sum_{\mu\lambda}\Big[\sum_n|\phi(n\mu\lambda;\mathbf{R})\rangle\langle\phi(n\mu\lambda;\mathbf{R})|+|\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle\langle\tilde{\phi}(j\mu\lambda;\mathbf{R})|\Big]\approx 1 \tag{3.13}$$

must be used with great caution. It is valid only for operators such as localized interaction potentials whose influence is confined to the interaction region spanned by the packet-state basis. For other operators, notably the adiabatic propagator $\hat{\mathcal{X}}(t;t_0)$ and the nonadiabatic coupling $\hat{K}(t)$, it is not valid, and their representations within the subspace spanned by the packet states must be computed very carefully.

B. Adiabatic propagation of moving packets

Now consider the actual behavior of a *moving wave packet* given by one of the packet states $\tilde{\phi}[j\mu\lambda;\mathbf{r};\mathbf{R}(t_0)]$ at some initial time t_0, but developing from t_0 to $t=t_0+\tau$ under the adiabatic propagator $\hat{\mathcal{X}}(t;t_0)$. This is given by the expression

$$\tilde{\phi}^{\tau}[j\mu\lambda;\mathbf{r};\mathbf{R}(t)]=(\Delta_j)^{-1/2}\int_{\epsilon_j-\Delta_j/2}^{\epsilon_j+\Delta_j/2}d\epsilon\, e^{-\iota\epsilon\tau}\phi[\epsilon\mu\lambda;\mathbf{r};\mathbf{R}(t)]\ . \tag{3.14}$$

These moving packet states are also orthogonal and normalized,

$$\langle\tilde{\phi}^{\tau}[j'\mu'\lambda';\mathbf{R}(t)]\,|\,\tilde{\phi}^{\tau}[j\mu\lambda;\mathbf{R}(t)]\rangle=\delta_{j'j}\delta_{\mu'\mu}\delta_{\lambda'\lambda}\ , \tag{3.15}$$

but for $|\tau|\gg 0$ they are no longer localized in the interaction region but outside it. With the same approximations previously used to obtain Eq. (3.11) one obtains the result

$$\begin{aligned}
\tilde{\phi}^{\tau}[j\mu\lambda;\mathbf{r};\mathbf{R}(t)]\approx(\mathscr{C}/2\iota)\Delta_j^{1/2}&\exp(-\iota\epsilon_j\tau)[S(\epsilon_j\mu\lambda;\eta;R)e^{-\iota\lambda\varphi}/\sqrt{2\pi}]\\
&\times[f(\zeta_+)e^{+\iota\theta(\epsilon_j\mu\lambda;\xi;R)}-f(\zeta_-)e^{-\iota\theta(\epsilon_j\mu\lambda;\xi;R)}]/[(\xi^2-1)p_r(\epsilon_j\mu\lambda;\xi;R)]^{1/2}\ ,
\end{aligned} \tag{3.16}$$

where

$$\zeta_{\pm}=(\Delta_j/2)[\pm(\partial\theta/\partial\epsilon)_{\epsilon_j}-\tau]$$

and $f(x)=x^{-1}\sin x$ as before. For asymptotically long times $\tau\gg 0$ (or $\tau\ll 0$) this corresponds to an outgoing (or incoming) wave packet centered at $r=|v_j\tau|$, i.e., the packet moves according to classical expectations for a particle of energy ϵ_j.

Consistent with this result, the moving packets are escaping for $|\tau| \gg 0$ to a portion of Hilbert space *not* spanned by the standing packet-state basis $\{|\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle\}$ at $t_0+\tau$. The overlap or correlation amplitude with the standing packet states is

$$\langle \tilde{\phi}^0[j'\mu'\lambda';\mathbf{r};\mathbf{R}(t_0+\tau)] \,|\, \tilde{\phi}^\tau[j\mu\lambda;\mathbf{R}(t_0+\tau)]\rangle = \langle \tilde{\phi}^0[j'\mu'\lambda';\mathbf{r};\mathbf{R}(t_0+\tau)] \,|\, \hat{\chi}(t_0+\tau;t_0) \,|\, \tilde{\phi}^0[j\mu\lambda;\mathbf{R}(t_0)]\rangle$$
$$= \delta_{j'j}\delta_{\mu'\mu}\delta_{\lambda'\lambda} f(\Delta_j \tau/2) \,, \tag{3.17}$$

where $f(x)$ is the same envelope function as before. The projection of the true adiabatically propagated moving packet on the corresponding standing adiabatic packet at the same time decays with time τ. Hence the correct packet basis representation for the continuum portion of the adiabatic propagator $\hat{\chi}(t;t_0)$ is *not* the simple result

$$\sum_{j\mu\lambda} |\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0+\tau)]\rangle \exp(-\iota\epsilon_j\tau)\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0)]| \;; \tag{3.18a}$$

instead one must use the expression

$$\sum_{j\mu\lambda} |\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0+\tau)]\rangle \exp(-\iota\epsilon_j\tau)[(\Delta_j\tau/2)^{-1}\sin(\Delta_j\tau/2)]\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0)]| \;. \tag{3.18b}$$

This is the result obtained by Reading and Ford[5] in a slightly different context: The subspace representation of the continuum propagator must exhibit *decay* due to escape of particles from the interaction region.

The same difficulties appear if one retains the formally correct integral equations (2.12) or (2.14) (or equivalent differential equations), with the full continuum as formal basis, and then attempts to implement them by doing integrals over continuum energies by numerical quadrature.[3,4] The point is that the propagator is a rapidly varying function of energy ϵ and it is this rapid variation which moves the wave packet $[\tilde{\phi}^\tau(j\mu\lambda;\mathbf{R})\rangle$ out of the subspace spanned by the packet-state basis $\{|\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle\}$. Unless the integrals are done very carefully, the correct physical behavior will not be obtained. In particular, if the quadrature points are spaced at intervals Δ_j, the neglect of escape effects is a serious source of error after times $\tau_j \approx \pi/\Delta_j$.

C. Failure of adiabatic description for escaping particles

These results illustrate a second point more clearly. The moving wave packet $|\tilde{\phi}^\tau[j\mu\lambda;\mathbf{R}(t_0+\tau)]\rangle$ propagated by $\hat{\chi}(t;t_0)$ from the initial packet state $|\tilde{\phi}^\tau[j\mu\lambda;\mathbf{R}(t_0)]\rangle$ is a superposition of continuum eigenstates of the Hamiltonian at time $t=t_0+\tau$, $H_e[\mathbf{r};\mathbf{R}(t_0+\tau)]$. Yet as shown by Eq. (3.16) this wave packet is located at this later time in a region of space increasingly remote from the interaction region. By what physical mechanism is such a packet able to adapt its shape *adiabatically* to the nuclear positions? Of course, no such mechanism exists: The zeroth-order description given by $\hat{\chi}(t;t_0)$ is unrealistic outside a local region. If in spite of this such a description is used, the price to be paid shows up in the effects of the nonadiabatic coupling $\hat{K}(t)$ with its singularities.

In Sec. IV we show that the nonadiabatic coupling operator $\hat{K}(t)$ can be represented within the truncated subspace spanned by a set of bound states plus a set of packet states with widths $\{\Delta_j\}$; the coupling matrix elements then have finite strengths, but the strength of couplings linking neighboring packets varies inversely as the packet widths. Choosing smaller packet widths implies spanning a larger spatial domain, as we have seen, but nonadiabatic couplings are then correspondingly stronger, and become singular in the limit as the widths $\{\Delta_j\}$ tend uniformly to zero. At some point the only practical solution of the problem is to abandon the whole idea of adiabatic propagation far from the nuclei; an adiabatic description can only be valid locally.

IV. SUBSPACE REPRESENTATION OF CLOSE-COUPLED EQUATIONS

A. Introduction

In Sec. II we derived the formally exact equations (2.12) for the unitary propagator $\hat{U}(t;t_0)$, with the adiabatic propagator $\hat{\chi}(t;t_0)$ as zeroth-order description and the nonadiabatic coupling $\hat{K}(t)$ as the operator causing transitions. Equation (2.12) is equivalent to the *differential* equations which have been used more commonly as a framework for close-coupling treatments.[2] Equation (2.14) provides an important generalization of Eq. (2.12) to *partly diabatic* descriptions of a system.

One must replace the true continuum with some discrete sampling procedure to realize these formalisms computationally. In Sec. III we introduced such discretization in the form of *packet states*; using numerical quadrature to do integrations over continuum energies is essentially an equivalent procedure. Using the prototype one-electron system as an example, we showed that a set of packet states can be constructed which describes the continuum states within a local *interaction region* whose size dictates the packet widths $\{\Delta_j\}$.

In this section we derive approximate representations of the exact close-coupled equations within the *truncated subspace* spanned by a suitable set of bound states and a set of such packet states. We denote this subspace by P and its complement by $Q=1-P$ (P may be divided into its bound and continuum parts, $P=P_D+P_C$). Again our derivation and specific notation are strictly valid only for the one-electron prototype systems, but general assumptions and results are applicable to a broader class of model systems.

The representation of operators such as finite-range potentials whose effects are localized in the region spanned by the P subspace is straightforward, since the approximate closure relation (3.13) may be used. Technically, we assume the packet states span the continuum adequately with respect to operators whose matrix elements vary slowly with continuum energy over the packet widths Δ_j. Representations for operators not meeting this criterion must be computed more carefully.

We showed in Sec. III that the adiabatic propagator $\hat{\chi}(t;t_0)$ [Eq. (2.13)] cannot be completely represented within the P_C subspace because it takes operands in that space into the complementary subspace Q outside the interaction region (escape). However, taking explicit account of the rapid variation of the factor $\exp[\iota\epsilon(t-t_0)]$ over a packet width Δ_j, we computed the accurate representation of $\hat{\chi}(t;t_0)$ *within* the P_C subspace [Eq. (3.18b)]. If the close-coupling basis spanning P at any nuclear configuration $\mathbf{R}$ consists of bound states $\{|\phi(n\mu\lambda;\mathbf{R})\rangle\}$ and the packet states $\{|\tilde{\phi}(j\mu\lambda;\mathbf{R})\rangle\}$, the subspace representation of the adiabatic propagator is given by

$$\hat{\chi}_{PP}(t;t_0)=\sum_{n\mu\lambda}|\phi[n\mu\lambda;\mathbf{R}(t)]\rangle\exp\left[-\iota\int_{t_0}^{t}\epsilon[n\mu\lambda;R(t')]dt'\right]\langle\phi[n\mu\lambda;\mathbf{R}(t_0)]| + \sum_{j\mu\lambda}|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t)]\rangle f(\Delta_j\tau/2)\exp(-\iota\epsilon_j\tau)\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0)]| \ , \tag{4.1}$$

where $\tau=t-t_0$ and $f(x)=x^{-1}\sin x$. It is evident that this operator is no longer unitary, i.e., *does not conserve probability,* because of the decaying amplitude factors $f(\Delta_j\tau/2)$ in the packet-state terms.

Similarly, the effects of the nonadiabatic coupling operator cannot be fully represented within the P space because of the rapid variation with energy given by Eq. (2.11) for the continuum-state couplings. As noted earlier, the singular structure near the energy shell $\epsilon'-\epsilon\approx 0$ shows that these couplings have infinite range and implies an adiabatic representation is not appropriate far from the nuclei. However, we are only concerned here with representing the effects of $\hat{K}(t)$ within a local region, and these are finite and well behaved. As in the case of the adiabatic propagator, we obtain more accurate P space representations of this and other "rapidly varying" operators by performing the implied integrals over continuum energy within a packet width, *including explicitly any energy dependences deemed to be rapid.*

In this section two approximate subspace representations of the integral equation (2.12) are derived. [We only need to consider Eq. (2.12), since Eq. (2.14) differs from it by the inclusion of a potential $\hat{V}(t)$ whose effects we assume to be local, i.e., $\hat{V}_{PP}\approx\hat{V}$.] The first equation, which we call the *disconnected* form, is

$$\hat{U}_{PP}(t;t_0)=\hat{\chi}_{PP}(t;t_0) - \iota\int_{t_0}^{t}dt'\hat{\chi}_{PP}(t;t')\hat{K}_{PP}(t')\times\hat{U}_{PP}(t';t_0) \ . \tag{4.2}$$

The second, *connected* form is

$$\hat{U}_{PP}(t;t_0)=\hat{\chi}_{PP}(t;t_0) - \iota\int_{t_0}^{t}dt'\hat{\mathcal{G}}_{PP}(t;t')\hat{U}_{PP}(t';t_0) \ , \tag{4.3a}$$

where

$$\mathcal{G}_{PP}(t;t')=[\hat{\chi}(t;t')\hat{K}(t')]_{PP} \tag{4.3b}$$

is a joint representation of the two juxtaposed rapidly varying operators appearing in Eq. (2.12). The intent of this paper is to propose Eq. (4.2) as a workable equation for close-coupling including the continuum. In principle, Eq. (4.3) is more accurate than Eq. (4.2), but is derived here mainly to show that Eq. (4.2) is a reasonable approximation.

The propagator $\hat{U}_{PP}(t;t_0)$ generated by Eq. (4.2) [or Eqs. (4.3)] is *approximate*, firstly because it cannot describe unbound electrons outside the interaction region, or the propagation of electrons from the P subspace into the complementary Q subspace; the best account of this $\hat{U}_{PP}(t;t_0)$ can give is in its nonunitary character, i.e., it exhibits time decay of packet amplitudes due to escape, but gives no description of the fate of the escaped flux. Secondly, Eqs. (4.2) or (4.3) are approximate in the more usual sense that they assume the adequacy of the P subspace basis, i.e., that sampling appropriate slowly varying matrix elements at the finite intervals Δ_j suffices to give a good description of local physical behavior. Whether the size of the "interaction region" entailed in a given choice for the packet widths $\{\Delta_j\}$ really is large enough to cover the significant physical behavior is, of course, a matter of judgment and experience.

1. *Operand structure assumption*

We thus assume at the outset that a P-subspace state vector $|\Psi_P(t')\rangle$ given by

$$|\Psi_P(t')\rangle=\hat{U}_{PP}(t';t_0)|\Psi_P(t_0)\rangle \tag{4.4a}$$

and having the discretized form

$$|\Psi_P(t')\rangle=\sum_{\mu,\lambda}\left[\sum_n|\phi[n\mu\lambda;\mathbf{R}(t')]\rangle b(n\mu\lambda;t') + \sum_j|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t')]\rangle\tilde{b}(j\mu\lambda;t')\right] \tag{4.4b}$$

can describe the system locally throughout the collision.

Formally, a complete wave function, which obeys the exact equation

$$|\Psi_T(t')\rangle = \hat{U}(t';t_0)\,|\Psi_T(t_0)\rangle \tag{4.5a}$$

and forms an operand in the exact integral equation (2.12), may be expanded in the complete basis,

$$|\Psi_T(t')\rangle = \sum_{\mu,\lambda}\left[\sum_n |\phi[n\mu\lambda;\mathbf{R}(t')]\rangle b(n\mu\lambda;t') + \int_0^\infty d\epsilon\,|\phi[\epsilon\mu\lambda;\mathbf{R}(t')]\rangle b(\epsilon\mu\lambda;t')\right], \tag{4.5b}$$

and is able to describe the state vector not only in the "interaction region" spanned by the P subspace, but also outside it. It is evident from Sec. III, however, that its capacity to do so arises *specifically* from *rapid* variations of the coefficients $b(\epsilon\mu\lambda;t')$ with energy ϵ. Insofar as these coefficients are slowly varying functions of ϵ, the wave function given by Eqs. (4.5) is contained wholly within the P subspace, and hence could be adequately approximated by Eqs. (4.4). At some points in the derivation of Eqs. (4.2) and (4.3) (cf. Appendix B) we make the formal assumption that a (hypothetical) operand for the exact continuum operators to be represented has the form (4.5) with coefficients $b(\epsilon\mu\lambda;t')$ which vary slowly with energy over a packet width.

2. *Normalization relations*

(a) Expansion coefficients. Given any state vector of the form (4.5b), with slowly varying coefficients $b(\epsilon\mu\lambda;t')$, corresponding coefficients $\tilde{b}(j\mu\lambda;t')$ of its P-space approximant (4.4b) are given by

$$\tilde{b}(j\mu\lambda;t') = \Delta_j^{1/2} b(\epsilon\mu\lambda;t')\ . \tag{4.6a}$$

(b) Matrix elements of slowly varying operators $\hat{O}$. Similarly, the matrix elements of an operator $\hat{O}_{PP}$ in the P subspace are related to the matrix elements of $\hat{O}$ among true continuum states, provided these vary slowly with energy over a packet width:

$$\langle n'\mu'\lambda'\,|\,\hat{O}\,|\,j\mu\lambda\rangle = \Delta_j^{1/2}\langle n'\mu'\lambda'\,|\,\hat{O}\,|\,\epsilon_j\mu\lambda\rangle \tag{4.6b}$$

and

$$\langle j'\mu'\lambda'\,|\,\hat{O}\,|\,j\mu\lambda\rangle = \Delta_{j'}^{1/2}\Delta_j^{1/2}\langle\epsilon_{j'}\mu'\lambda'\,|\,\hat{O}\,|\,\epsilon_j\mu\lambda\rangle\ . \tag{4.6c}$$

[Here and below we use shorthand notations " $|\,j\mu\lambda\rangle$" for the packet states $|\tilde{\phi}(j\mu\lambda)\rangle$, " $|\,n\mu\lambda\rangle$" for bound states $|\phi(n\mu\lambda)\rangle$, and " $|\,\epsilon_j\mu\lambda\rangle$" for exact continuum states $|\phi(\epsilon_j\mu\lambda)\rangle$.]

B. Disconnected form

Equation (4.2) is obtained from Eq. (2.12) if we assume the rapid energy dependence in $\hat{\chi}(t;t')$ is somehow separable from that in $\hat{K}(t')$. This may not seem very plausible but we will show that the results are not very different from those obtained if we do not disconnect them. Since $\hat{\chi}_{PP}(t;t')$ is given by Eq. (4.1) we need only to construct the P-space representation of $\hat{K}(t')$. $\hat{K}$ can be decomposed into four parts,

$$\hat{K} = \hat{K}_{DD} + \hat{K}_{DC} + \hat{K}_{CD} + \hat{K}_{CC}\ ,$$

and the bound-state couplings $\hat{K}_{DD}$ are already projected.

In this work we assume that the dominant dependence of nonadiabatic coupling matrix elements on continuum energy ϵ is displayed explicitly in the Hellmann-Feynman relations [Eqs. (2.9) for bound-continuum and Eqs. (2.10) for continuum-continuum couplings]. The commutators $[\partial H_e/\partial R]_r$ and $[L_y,H_e]$ are essentially local operators, and if the continuum states in addition are "simple" in the sense required here, they have no fine structure due to embedded resonances; hence the matrix elements of these operators will indeed be slowly varying functions of ϵ. In the prototype system H_2^+ this assumption is known to be valid for the bound-continuum couplings, and in Ref. 6 we present results showing it is also valid for both types of analytic matrix elements ($N^R_{k'k}, N^\vartheta_{k'k}$ and $M^R_{k'k}, M^\vartheta_{k'k}$) appearing in Eqs. (2.10) for the continuum coupling matrix elements.

1. *Bound-continuum couplings* $\hat{K}_{DC}, \hat{K}_{CD}$

Since the bound states lie completely below the continuum, the energy denominators in Eqs. (2.9) are not really "rapidly varying" unless the bound state is just below the ionization limit and the continuum packet in question is just above it. In any case it is easy to show (cf. Appendix B) that

$$(\hat{K}_{DC})_{PP} = \sum_{n',\mu',\lambda'}\sum_{j,\mu,\lambda} |\phi(n'\mu'\lambda')\rangle \frac{\langle n'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j\mu\lambda\rangle}{[\epsilon_j - \epsilon(n'\mu'\lambda')]} \times \kappa_{n'j}\langle\tilde{\phi}(j\mu\lambda)|\ , \tag{4.7a}$$

where the *effective strength factor* $\kappa_{n'j}$ is given by

$$\kappa_{n'j} \equiv \alpha_{jn'}^{-1}\ln[(1+\tfrac{1}{2}\alpha_{jn'})/(1-\tfrac{1}{2}\alpha_{jn'})] \tag{4.7b}$$

and

$$\alpha_{jn'} \equiv \Delta_j / |\,\epsilon_j - \epsilon(n'\mu'\lambda')\,|\ . \tag{4.7c}$$

For $\alpha_{jn'} \le 1$ this factor differs from 1 by at most 10%. Of course, in this case we really had no reason to be concerned about "rapid" variation of the energy denominator; this part of $\hat{K}$ is really "slowly varying." Similarly,

$$(\hat{K}_{CD})_{PP} = \sum_{n,\mu,\lambda}\sum_{j',\mu',\lambda'} |\tilde{\phi}(j'\mu'\lambda')\rangle \frac{\langle j'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,n\mu\lambda\rangle}{[\epsilon(n\mu\lambda) - \epsilon_{j'}]} \times \kappa_{nj'}\langle\phi(n\mu\lambda)|\ . \tag{4.7d}$$

[In Eqs. (4.7) as in Eq. (2.11) we have used script notation, $\hat{\mathcal{N}}$, to indicate the inclusion of collision velocities.]

2. *Continuum couplings* $\hat{K}_{CC}$

These are given by [cf. Eq. (2.11)]

$$\hat{K}_{CC}=\sum_{\mu',\lambda'}\sum_{\mu,\lambda}\int_0^\infty d\epsilon'\int_0^\infty d\epsilon\,|\,\phi(\epsilon'\mu'\lambda')\rangle\left[\mathcal{P}\left[\frac{\langle\epsilon'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon\mu\lambda\rangle}{\epsilon-\epsilon'}\right]+\delta(\epsilon-\epsilon')\langle\epsilon\mu'\lambda'\,|\,\hat{\mathcal{M}}\,|\,\epsilon\mu\lambda\rangle\right]\langle\phi(\epsilon\mu\lambda)\,| \tag{4.8}$$

and we treat the two parts separately.

(a) δ function part. This is easily found to be

$$[\hat{K}_{CC}(\delta)]_{PP}=\sum_{\mu',\lambda'}\sum_{\mu,\lambda}\sum_{j}|\,\tilde{\phi}(j\mu'\lambda')\rangle\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{M}}\,|\,\epsilon_j\mu\lambda\rangle\langle\tilde{\phi}(j\mu\lambda)\,| \tag{4.9}$$

(note that the matrix element is not renormalized). As shown in Appendix A, this coupling is strictly off-diagonal, i.e., it vanishes if $(\mu',\lambda')=(\mu,\lambda)$.

(b) Principal value parts. The principal value terms can be broken up into a double sum over packet cells j',j:

$$\hat{K}_{CC}(\mathcal{P})=\sum_{j',\mu',\lambda'}\sum_{j,\mu,\lambda}\mathcal{P}\int_{\epsilon_{j'}-\Delta_{j'}/2}^{\epsilon_{j'}+\Delta_{j'}/2}d\epsilon'\int_{\epsilon_j-\Delta_j/2}^{\epsilon_j+\Delta_j/2}d\epsilon\,|\,\phi(\epsilon'\mu'\lambda')\rangle\left[\frac{\langle\epsilon'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon\mu\lambda\rangle}{\epsilon-\epsilon'}\right]\langle\phi(\epsilon\mu\lambda)\,|\ , \tag{4.10}$$

we consider first the nonresonant terms $j'\neq j$ and then the resonant terms $j'=j$. In Appendix B we show that the nonresonant terms are given by

$$[\hat{K}_{CC}(\mathcal{P})]_{PP}^{NR}=\sum_{j\mu\lambda}\sum_{\substack{j'\mu'\lambda'\\(j'\neq j)}}|\,\tilde{\phi}(j'\mu'\lambda')\rangle\left[\frac{\langle j'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j'}}\kappa_{j'j}^{NR}\right]\langle\tilde{\phi}(j\mu\lambda)\,|\ , \tag{4.11a}$$

where the effective strength factor κ_{lj}^{NR} is given by

$$\begin{aligned}\kappa_{lj}^{NR}=(\alpha_{lj}\alpha_{jl})^{-1}\{&[1+\tfrac{1}{2}(\alpha_{jl}+\alpha_{lj})]\ln[1+\tfrac{1}{2}(\alpha_{jl}+\alpha_{lj})]+[1-\tfrac{1}{2}(\alpha_{jl}+\alpha_{lj})]\ln[1-\tfrac{1}{2}(\alpha_{jl}+\alpha_{lj})]\\&-[1+\tfrac{1}{2}(\alpha_{jl}-\alpha_{lj})]\ln[1+\tfrac{1}{2}(\alpha_{jl}-\alpha_{lj})]-[1-\tfrac{1}{2}(\alpha_{jl}-\alpha_{lj})]\ln[1-\tfrac{1}{2}(\alpha_{jl}-\alpha_{lj})]\}\end{aligned} \tag{4.11b}$$

and α_{jl} is defined

$$\alpha_{jl}\equiv\Delta_j/|\,\epsilon_j-\epsilon_l\,|\ . \tag{4.11c}$$

The factor κ_{lj}^{NR} differs from unity by less than 5% for $\alpha_{jl},\alpha_{lj}\leq 0.5$. For the "near-resonant" terms $j'=j\pm1$, Eq. (4.11b) becomes

$$\kappa_{j\pm1,j}^{NR}=\frac{(\Delta_j+\Delta_{j\pm1})}{2\Delta_j\Delta_{j\pm1}}\left[\Delta_j\ln\left[\frac{\Delta_j+\Delta_{j\pm1}}{\Delta_j}\right]+\Delta_{j\pm1}\ln\left[\frac{\Delta_j+\Delta_{j\pm1}}{\Delta_{j\pm1}}\right]\right] \tag{4.11d}$$

which has the value $2\ln 2$ for $\Delta_j=\Delta_{j\pm1}$.

Finally we also show in Appendix B that the effect of the resonant terms is an enhancement of the couplings between adjacent cells:

$$\begin{aligned}[K_{CC}(\mathcal{P})]_{PP}^{R}=\sum_{\mu',\lambda'}\sum_{\mu,\lambda}\sum_{j}\Bigg[&(\Delta_j/4\Delta_{j+1})\Bigg[|\,\tilde{\phi}(j\mu'\lambda')\rangle\frac{\langle j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j+1\mu\lambda\rangle}{\epsilon_{j+1}-\epsilon_j}\langle\tilde{\phi}(j+1\mu\lambda)\,|\\&+|\,\tilde{\phi}(j+1\mu'\lambda')\rangle\frac{\langle j+1\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j+1}}\langle\tilde{\phi}(j\mu\lambda)\,|\Bigg]\\&+(\Delta_j/4\Delta_{j-1})\Bigg[|\,\tilde{\phi}(j\mu'\lambda')\rangle\frac{\langle j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j-1\mu\lambda\rangle}{\epsilon_{j-1}-\epsilon_j}\langle\tilde{\phi}(j-1\mu\lambda)\,|\\&\times|\,\tilde{\phi}(j-1\mu'\lambda')\rangle\frac{\langle j-1\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j-1}}\langle\tilde{\phi}(j\mu\lambda)\,|\Bigg]\Bigg];\end{aligned} \tag{4.12a}$$

this amounts to an extra strength factor of

$$\kappa_{j,j\pm1}^{R}=(\Delta_j^2+\Delta_{j\pm1}^2)/4\Delta_j\Delta_{j\pm1}\ . \tag{4.12b}$$

(c) Summary of continuum couplings. The singular nonadiabatic coupling operator $\hat{K}_{CC}$ is therefore represented in the close-coupled basis by

$$(\hat{K}_{CC})_{PP}=\sum_{j\mu\lambda}\sum_{\substack{j'\mu'\lambda'\\(j'\neq j)}}|\tilde{\phi}(j'\mu'\lambda')\rangle\left[\frac{\langle j'\mu'\lambda'|\hat{\mathcal{N}}|j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j'}}\kappa_{j'j}\right]\langle\tilde{\phi}(j\mu\lambda)|$$
$$+\sum_{\mu',\lambda'}\sum_{\mu,\lambda}\sum_{j}|\tilde{\phi}(j\mu'\lambda')\rangle\langle\epsilon_j\mu'\lambda'|\hat{\mathcal{M}}|\epsilon_j\mu\lambda\rangle\langle\tilde{\phi}(j\mu\lambda)|\ , \tag{4.13}$$

where $\kappa_{j'j}$ is given by Eq. (4.11b) if $j'\neq j\pm1$, and by the sum of the two strengths (4.11d) and (4.12b) if $j'=j\pm1$. The second term, arising from the Dirac δ function singularities in $\hat{K}_{CC}$, is strictly off-diagonal, $[(\mu',\lambda')\neq(\mu,\lambda)]$, and the entire expression is nonsingular and retains the proper symmetries of the nonadiabatic coupling operator; the exact expression for $\hat{K}_{CC}$ is recovered in the limit when the widths Δ_j tend uniformly to zero.

The construction of $\hat{K}_{PP}$ completes the derivation of Eq. (4.2). Before discussing them we first derive the connected form, Eqs. (4.3).

C. Connected form

To derive Eqs. (4.3) we require a P-space representation of the joint operator $\hat{\mathcal{G}}(t;t')=\hat{\chi}(t;t')\hat{K}(t')$. As with $\hat{K}$ we decompose $\hat{\mathcal{G}}$ into four parts $\hat{\mathcal{G}}_{DD}$, $\hat{\mathcal{G}}_{DC}$, $\hat{\mathcal{G}}_{CD}$, and $\hat{\mathcal{G}}_{CC}$. Only the last two need be considered since $\hat{\mathcal{G}}_{DD}$ is already projected and

$$(\hat{\mathcal{G}}_{DC})_{PP}=\hat{\chi}_{PP}(t;t')[\hat{K}_{DC}(t')]_{PP}\ .$$

1. *Bound-continuum part*

By essentially the same procedure used to determine $(\hat{K}_{CD})_{PP}$, we find

$$[\hat{\mathcal{G}}_{CD}(t;t')]_{PP}=\sum_{j',\mu'\lambda'}\sum_{n,\mu,\lambda}|\tilde{\phi}(j'\mu'\lambda')\rangle\exp(-\iota\epsilon_{j'}\tau)g_{j'n}(\tau)\left[\frac{\langle j'\mu'\lambda'|\hat{\mathcal{N}}|n\mu\lambda\rangle}{[\epsilon(n\mu\lambda)-\epsilon_{j'}]}\kappa_{j'n}\right]\langle\phi(n\mu\lambda)|\ , \tag{4.14a}$$

where $\tau=t-t'$, $\kappa_{j'n}$ is the effective strength defined in Eq. (4.7b), and the function $g_{j'n}(\tau)$ is given by

$$g_{j'n}(\tau)\equiv\kappa_{j'n}^{-1}\int_{-1}^{1}\frac{\exp(-\iota\beta_{j'}u)du}{2(1+\frac{1}{2}\alpha_{j'n}u)}\ , \tag{4.14b}$$

with $\beta_{j'}=(\Delta_{j'}\tau/2)$ and $\alpha_{j'n}$ defined by Eq. (4.7c). For small $\alpha_{j'n}$ this is approximately equal to the decay factor $f(\beta_{j'})$ appearing in the corresponding terms of the disconnected approximation (cf. Appendix B).

2. *Continuum-continuum terms* $\hat{\mathcal{G}}_{CC}$

(a) δ-function parts. The terms in $\hat{\mathcal{G}}_{CC}$ arising from the δ-function terms in $\hat{K}_{CC}$ are just given by the product

$$[\hat{\mathcal{G}}_{CC}(\delta)]_{PP}=\hat{\chi}_{PP}(t;t')[\hat{K}_{CC}(\delta)]_{PP}\ . \tag{4.15a}$$

(b) Principal value parts. As with $\hat{K}_{CC}$ we can break up the principal-value integral into a double sum over cells j',j and then treat the nonresonant terms $(j'\neq j)$ and resonant terms $(j'=j)$ separately. For the nonresonant terms we obtain the result

$$[\hat{\mathcal{G}}_{CC}(\mathcal{P})]_{PP}^{NR}=\sum_{j,\mu,\lambda}\sum_{\substack{j',\mu',\lambda'\\(j'\neq j)}}|\tilde{\phi}(j'\mu'\boldsymbol{\lambda}')\rangle\exp(-\iota\epsilon_{j'}\tau)g_{j'j}^{NR}(\tau)\left[\frac{\langle j'\mu'\lambda'|\hat{\mathcal{N}}|j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j'}}\kappa_{j'j}^{NR}\right]\langle\tilde{\phi}(j\mu\lambda)|\ , \tag{4.15b}$$

where $\kappa_{j'j}^{NR}$ is the effective strength factor defined in Eq. (4.11b) and the time-decay factor $g_{j'j}^{NR}(\tau)$ is defined

$$g_{lj}^{NR}(\tau)\equiv\frac{(\epsilon_j-\epsilon_l)}{\kappa_{lj}^{NR}\Delta_j\Delta_l}\times\int_{-\Delta_l/2}^{+\Delta_l/2}dx'\,e^{-\iota x'\tau}\times\int_{-\Delta_j/2}^{+\Delta_j/2}\frac{dx}{(\epsilon_j-\epsilon_l+x-x')}\ . \tag{4.15c}$$

For $l\neq j\pm1$, where the parameters α_{jl} and α_{lj} are small compared to 1, this function is again well approximated by the simple decay factor $f(\beta_l)$. For the near-resonant case $l=j\pm1$, the isolated singularity at the boundary of neighboring cells leads to somewhat more significant modification; an explicit formula is given in Appendix B.

Calculation of the resonant contribution to the principal-value part is more difficult, but it is shown in Appendix B that a reasonable approximation again corresponds to an enhancement of the near-neighbor ($j\leftrightarrow j\pm1$) terms in $(\hat{\mathcal{G}}_{CC})_{PP}$, with a more complicated decay function.

(c) Summary. Comparing the results obtained for the connected propagator $[\hat{\mathcal{G}}_{PP}(t;t')]$ with those for the disconnected product $\hat{\chi}_{PP}(t;t')\hat{K}_{PP}(t')$ shows that the two differ negligibly except in the details of the decay functions and effective coupling strengths linking near-neighbor packets ($j\leftrightarrow j\pm1$), and even for these cases the differences are of quantitative rather than qualitative character. Since our purpose in this derivation was to show that the disconnected form of the integral equations [Eq. (4.2)] is a reasonable approximation to the more accurate version, we have not put much emphasis on these finer details. In what follows we work only with Eq. (4.2).

D. Nonconservation of probability

The propagator $\hat{U}_{PP}(t;t_0)$ obtained by solving the close-coupled integral equation (4.2) describes the evolution of the electronic system within the subspace (P) spanned by the bound states and the chosen set of packet states, from an initial state $|\Psi_P(t_0)\rangle$ contained in the subspace at time t_0, into that portion of the state vector which remains in the subspace at time t,

$$|\Psi_P(t)\rangle=\hat{U}_{PP}(t;t_0)\,|\Psi_P(t_0)\rangle\ . \tag{4.16}$$

However, the following restrictions are necessarily implied.

(a) The true state vector at t_0 must be described by $|\Psi_P(t_0)\rangle$ and, in particular, cannot contain continuum components; hence, t_0 must be an "initial time" before collision begins, when no excitation of continuum components has yet occurred; in this sense $t_0=\text{"}-\infty\text{."}$

(b) The true state vector at time t is not fully described by $|\Psi_P(t)\rangle$, but only that part of it remaining in the P subspace; part has escaped due to the decay factors $f(\Delta_j\tau/2)$ in Eq. (4.2).

(c) $\hat{U}_{PP}(t;t_0)$ is *not unitary;* its inverse is not defined, and, in particular, the relation

$$\hat{U}(t;t_0)=\hat{U}(t;t')\hat{U}(t';t_0)\ ,$$

satisfied by the exact unitary propagator, is *not* satisfied by $\hat{U}_{PP}(t;t_0)$.

(d) Hence it also follows that Eq. (4.2) cannot be converted into any equivalent close-coupled *differential* equation.

In particular, $\hat{U}_{PP}(t;t_0)$ does not satisfy the Schrödinger equation; an extra term arising from the time derivatives of the decay functions $f(\Delta_j\tau/2)$ appears, and we will show that it leads to a net change in probability with time.

Differentiating Eq. (4.2) with respect to time t yields

$$\iota(\partial/\partial t)\hat{U}_{PP}(t;t_0)=\iota(\partial/\partial t)\hat{\chi}_{PP}(t;t_0)+K_{PP}(t)\hat{U}_{PP}(t;t_0)-\iota\int_{t_0}^{t}dt'[\iota(\partial/\partial t)\hat{\chi}_{PP}(t;t')]\times K_{PP}(t')\hat{U}_{PP}(t';t_0)\ ,$$

but

$$\iota(\partial/\partial t)\hat{\chi}_{PP}(t;t')=-\hat{K}_{PP}(t')\hat{\chi}_{PP}(t;t')+\hat{H}_{PP}(t)\hat{\chi}_{PP}(t;t')+\iota\hat{\sigma}_{PP}(t;t')\ ,$$

where

$$\hat{H}_{PP}(t)\hat{\chi}_{PP}(t;t')\equiv\sum_{n,\mu,\lambda}|\phi[n\mu\lambda;\mathbf{R}(t)]\rangle\epsilon[n\mu\lambda;R(t)]\exp\left[-\iota\int_{t'}^{t}dt''\epsilon[n\mu\lambda;R(t'')]\right]\langle\phi[n\mu\lambda;\mathbf{R}(t')]|+\sum_{j,\mu,\lambda}|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t)]\rangle\epsilon_j\exp(-\iota\epsilon_j\tau)f(\Delta_j\tau/2)\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t')]|$$

and $\hat{\sigma}_{PP}(t;t')$ is defined

$$\hat{\sigma}_{PP}(t;t')\equiv\sum_{j,\mu,\lambda}|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t)]\rangle[(\Delta_j/2)f'(\Delta_j\tau/2)]\exp(-\iota\epsilon_j\tau)\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t')]\rangle\ , \tag{4.17}$$

where $\tau=t-t'$ and $f'(x)=d/dx(x^{-1}\sin x)=(1/x^2)(x\cos x-\sin x)$. Making the reasonable approximation

$$\hat{H}(t)\hat{\chi}_{PP}(t;t')\approx\hat{H}_{PP}(t)\hat{\chi}_{PP}(t;t')\ ,$$

we obtain the result

$$[\iota(\partial/\partial t)-\hat{H}(t)]\hat{U}_{PP}(t;t_0)=\iota\hat{\sigma}_{PP}(t;t_0)+\int_{t_0}^{t}dt'\hat{\sigma}_{PP}(t;t')\hat{K}_{PP}(t')\hat{U}_{PP}(t';t_0)\ ;$$

since $|\Psi_P(t_0)\rangle$ contains only bound states,

$$[\iota(\partial/\partial t)-\hat{H}(t)]\,|\Psi_P(t)\rangle=\int_{t_0}^{t}dt'\hat{\sigma}_{PP}(t;t')\hat{K}_{PP}(t')\,|\Psi_P(t')\rangle\ . \tag{4.18}$$

Now let $W_P(t)\equiv\langle\Psi_P(t)\,|\,\Psi_P(t)\rangle$ be the total probability in the P subspace at time t; we assume that $W_P(t_0)=W_P(-\infty)=1$. If we define

$$|D_P(t')\rangle\equiv\hat{K}_{PP}(t')\,|\Psi_P(t')\rangle=\sum_{j,\mu,\lambda}|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t')]\rangle D_P(j\mu\lambda;t')+\sum_{n\mu\lambda}|\phi[n\mu\lambda;\mathbf{R}(t')]\rangle D_P(n\mu\lambda;t')\ ,$$

then from Eq. (4.18) we find

$$dW_P(t)/dt=\sum_{j,\mu,\lambda}\int_{-\infty}^{t}dt'\int_{-\infty}^{t}dt''e^{\iota\epsilon_j(t'-t'')}D_P^*(j\mu\lambda;t'')D_P(j\mu\lambda;t')\frac{d}{dt}\{f[\Delta_j(t-t')/2]f(\Delta_j(t-t'')/2)\}\ .$$

Integration of this equation from $t_0=-\infty$ to $t\to+\infty$, and subsequent integration by parts, gives

$$W_P(+\infty)=1+\sum_{j,\mu,\lambda}\left|\int_{-\infty}^{t\to+\infty}dt'e^{\iota\epsilon j t'}D_P(j\mu\lambda;t')f(\Delta_j(t-t')/2)\right|^2$$
$$-2\,\mathrm{Re}\sum_{j,\mu,\lambda}\int_{-\infty}^{+\infty}dt\int_{-\infty}^{t}dt'e^{-\iota\epsilon_j(t-t')}D_P^*(j\mu\lambda;t)D_P(j\mu\lambda;t')f(\Delta_j(t-t')/2)\ .$$

However, the first sum vanishes in the limit $t\to+\infty$ because the amplitudes $D_P(t)$ tend to zero as $t\to\infty$, while the decay factors f are nonzero only for finite arguments. Hence the final probability is

$$W_P(+\infty)=1-2\,\mathrm{Re}\sum_{j,\mu,\lambda}\int_{-\infty}^{+\infty}dt\int_{0}^{\infty}d\tau D_P^*(j\mu\lambda;t)D_P(j\mu\lambda;t-\tau)e^{-\iota\epsilon_j\tau}f(\Delta_j\tau/2)\ . \tag{4.19}$$

We have not shown formally that $W_P(+\infty)\leq 1$ but it seems likely on physical grounds.

E. Integro-differential equation related to conventional scheme

Coupled integro-differential equations more nearly analogous to the probability-conserving differential equations of conventional close-coupling theory can be derived from Eq. (4.2), and are probably more convenient as a computational form, especially if the effects of escape are deemed to be small in the application of interest.

We define a "decay-free" adiabatic P-subspace propagator $\Omega_{PP}(t;t')$:

$$\hat{\Omega}_{PP}(t;t')\equiv\sum_{n,\mu,\lambda}|\phi[n\mu\lambda;\mathbf{R}(t)]\rangle\exp\left[-\iota\int_{t'}^{t}dt''\epsilon[n\mu\lambda;R(t'')]\right]\langle\phi[n\mu\lambda;\mathbf{R}(t')]\,|$$
$$+\sum_{j,\mu,\lambda}|\tilde{\phi}[j\mu\lambda;\mathbf{R}(t)]\rangle\exp[-\iota\epsilon_j(t-t')]\langle\tilde{\phi}[j\mu\lambda;\mathbf{R}(t')]\,|\ , \tag{4.20}$$

in which the decay factors appearing in Eq. (4.1) are replaced by unity. Within the P subspace, $\hat{\Omega}_{PP}(t;t')$ is unitary, and

$$\hat{\Omega}_{PP}(t;t_0)=\hat{\Omega}_{PP}(t;t')\hat{\Omega}_{PP}(t';t_0)\ .$$

Then the "adiabatic interaction picture" propagator $\hat{U}^{I}_{PP}(t;t_0)$ defined by

$$\hat{U}^{I}_{PP}(t;t_0)\equiv\hat{\Omega}^{\dagger}_{PP}(t;t_0)\hat{U}_{PP}(t;t_0)$$

satisfies the integral equation

$$\hat{U}^{I}_{PP}(t;t_0)=\hat{\Omega}^{\dagger}_{PP}(t;t_0)\hat{\chi}_{PP}(t;t_0)-\iota\int_{t_0}^{t}dt'\hat{\Omega}^{\dagger}_{PP}(t';t_0)[\hat{\Omega}^{\dagger}_{PP}(t;t')\hat{\chi}_{PP}(t;t')]\hat{K}_{PP}(t')\hat{\Omega}_{PP}(t';t_0)\hat{U}^{I}_{PP}(t';t_0)$$

and this may be differentiated directly to yield

$$\iota(\partial/\partial t)\hat{U}^{I}_{PP}(t;t_0)=\iota\hat{\sigma}^{I}_{PP}(t;t_0)+[\hat{\Omega}^{\dagger}_{PP}(t;t_0)\hat{K}_{PP}(t)\hat{\Omega}_{PP}(t;t_0)]\hat{U}^{I}_{PP}(t;t_0)$$
$$+\int_{t_0}^{t}dt'\hat{\Omega}^{\dagger}_{PP}(t';t_0)\hat{\sigma}^{I}_{PP}(t;t')\hat{K}_{PP}(t')\hat{\Omega}_{PP}(t';t_0)\hat{U}^{I}_{PP}(t';t_0)\ , \tag{4.21}$$

where

$$\hat{\sigma}^{I}_{PP}(t;t')\equiv\hat{\Omega}^{\dagger}_{PP}(t;t')\hat{\sigma}_{PP}(t;t')$$

[cf. Eqs. (4.17)]. Equation (4.21) is the desired formal equation. The usual interaction picture expansion for the state vector $|\Psi_P(t)\rangle$ is

$$|\Psi_P(t)\rangle = \sum_{n,\mu,\lambda} |\phi[n\mu\lambda;\mathbf{R}(t)]\rangle \exp\left[-\iota \int_{t_0}^{t} dt' \epsilon[n\mu\lambda;R(t')]\right] a(n\mu\lambda;t)$$
$$+ \sum_{j,\mu,\lambda} |\tilde{\phi}[j\mu\lambda;\mathbf{R}(t)]\rangle \exp[-\iota\epsilon_j(t-t')]\bar{a}(j\mu\lambda;t) \ ;$$

hence the ket

$$|\Psi_P^I(t)\rangle = \Omega^{\dagger}_{PP}(t;t_0)|\Psi_P(t)\rangle = \hat{U}^I_{PP}(t;t_0)|\Psi_P(t_0)\rangle = \sum_{n,\mu,\lambda} |\phi[n\mu\lambda;\mathbf{R}(t_0)]\rangle a(n\mu\lambda;t) + \sum_{j,\mu,\lambda} |\tilde{\phi}[j\mu\lambda;\mathbf{R}(t_0)]\rangle \bar{a}(j\mu\lambda;t)$$

is the desired state vector. The explicit representative of Eq. (4.21) is therefore the set of close-coupled equations

$$\iota(d/dt)a(n\mu\lambda;t) = \sum_{k',\mu',\lambda'} \langle n\mu\lambda;\mathbf{R}(t)|\hat{K}_{PP}|k'\mu'\lambda';\mathbf{R}(t)\rangle a(k'\mu'\lambda';t)$$
$$\times \exp\left[-\iota \int_{t_0}^{t} dt' \{\epsilon[k'\mu'\lambda';R(t')] - \epsilon[n\mu\lambda;R(t')]\}\right] \tag{4.22a}$$

for the bound-state amplitudes and

$$\iota(d/dt)\bar{a}(j\mu\lambda;t) = \sum_{k',\mu',\lambda'} \langle j\mu\lambda;\mathbf{R}(t)|\hat{K}_{PP}|k'\mu'\lambda';\mathbf{R}(t)\rangle a(k'\mu'\lambda';t)$$
$$\times \exp\left[-\iota \int_{t_0}^{t} dt' \{\epsilon[k'\mu'\lambda';R(t')] - \epsilon_j\}\right]$$
$$+ \sum_{k',\mu',\lambda'} \int_{t_0}^{t} dt' [(\Delta_j/2)f'(\Delta_j\tau/2)] \langle j\mu\lambda;\mathbf{R}(t')|\hat{K}_{PP}|k'\mu'\lambda';\mathbf{R}(t')\rangle a(k'\mu'\lambda';t')$$
$$\times \exp\left[-\iota \int_{t_0}^{t'} dt'' \{\epsilon[k'\mu'\lambda';R(t'')] - \epsilon_j\}\right] \tag{4.22b}$$

for the continuum packet-state amplitudes. (In these equations we have used indices $k'\mu'\lambda'$ to indicate both bound states and packet states.) The conventional close-coupled differential equations are recovered when the integral terms in Eq. (4.22b) are neglected. If the widths $\{\Delta_j\}$ are small enough that escape effects are not large over the time intervals considered, an iterative method based on the back substitution of successive approximations to amplitudes $\{a(k'\mu'\lambda';t')\}$ in the integral terms, with the decay-free amplitudes as zeroth-order solution, can provide an efficient solution.

F. Discussion

We have shown that any attempt to include the continuum in a close-coupling computation involves some sort of discretization process, and that a proper account of the effects of such discretization leads to a nonunitary formulation which takes account of the effects of escape by unbound particles from the region spanned by the discretized representation. Since we are concerned with low-to-intermediate collision energies, we have used an adiabatic or near-adiabatic basis of *molecular states* with the resulting complications arising from the fact that an adiabatic description can never be a valid description of continuum evolution far from the nuclei. The integral equation (4.2) was obtained as a result; we showed that it does not conserve probability within the spanning basis, and we also derived the equivalent integro-differential equations (4.21) and (4.22) which show more clearly the relation between this more rigorous formulation of close-coupling theory for molecular-state descriptions and the conventional formulations[2] in terms of (probability-conserving) differential equations.

While the specific results derived have been rigorously *proven* only for the prototype one-electron systems, the general properties required to establish our major results are not restricted to those systems, but may be valid for a broad class of model problems. With this in mind we presented the generalized integral equation (2.14), and provided certain general conditions are satisfied by the continuum of the (partly diabatic) model Hamiltonian $\hat{H}_0(t)$, generalized close-coupling equations analogous to Eq. (4.2) and Eqs. (4.21) and (4.22) may be derived, which permit the discussion of more complicated problems involving coupling to a molecular electronic continuum. For the present, however, we restrict our attention to the simpler prototype problems.

Nothing in our formulation dictates the selection of widths $\{\Delta_j\}$ for the packet-state basis describing the continuum. Different interpretations or computational implementations of the formulation we have developed can be made, depending on the principles used to select these widths. It is useful to discuss two somewhat different approaches here, since they illustrate some practical aspects of the problem.

1. *"Convergence limit" approach*

By taking sufficiently small packet widths, the spatial region spanned by the corresponding packet states is made very large and the decay times $\tau_j = \pi/\Delta_j$ very

long. A calculation based on this approach could then follow the evolution of the system within the region spanned for a prolonged period, including the time evolution of the continuum electrons, either without including the escape effects or including them only in the "perturbative" fashion suggested by approximate solutions to Eqs. (4.21) and (4.22). If one interprets the amplitudes associated with these narrow adiabatic packets at "late" but still finite times as ionization amplitudes, an estimate of the total ionization probability and possibly also the final energy distribution of the ejected electrons can be obtained. Of course, the difficulty with this approach is the computational effort required; as pointed out in Sec. III, in addition to the rapidly increasing basis size resulting from smaller widths, the nonadiabatic couplings between neighboring close-coupled channels become much stronger. Ultimately, it is more practical to study the evolution of the continuum using a different zeroth-order description than is given by the adiabatic basis. Nevertheless, such studies, if feasible computationally, provide valuable insight about the actual physical mechanisms in specific problems.

2. *"Interaction region" approach*

A somewhat different interpretation of the theory is based on the idea that the physical processes involved in continuum excitation are localized in a certain *interaction region.* In this case the entire set of packet widths $\{\Delta_j\}$ to be used is dictated by the region size; in Ref. 6 we present tables of such widths for several choices of region size in the prototype H_2^+ system. This approach continues the viewpoint, almost implicit in close-coupling calculations with bound states, that excitation processes are localized (for example, the assumption that Rydberg states above a certain principal quantum number are not important). In applying the same idea to the continuum the focus of attention is on processes leading to continuum excitation, rather than attempting to follow the subsequent evolution of the continuum itself. While coupling among the continuum packet states is included, the fact that the widths $\{\Delta_j\}$ are typically larger means that (1) escape effects are relatively much more important and (2) the details of continuum evolution are not followed beyond the preliminary stages. Such a calculation by itself would permit an estimate of total ionization probability (from the loss due to escape) but offers no direct account of spectral energy distribution, angular distribution, etc. This method assumes that the detailed evolution of the continuum after the initial excitation process is a secondary process, to be followed using a different zeroth-order description from the adiabatic one. In work to be presented later we develop approaches to this secondary problem.

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APPENDIX A: NONADIABATIC COUPLINGS AND HELLMAN-FEYNMAN RELATIONS FOR CONTINUUM STATES

Nonadiabatic couplings between two degenerate continuum states are singular. For the one-electron prototype system the explicit structure of these couplings, including analytic coefficients of singular terms, can be derived by a generalization of the Hellmann-Feynman theorem.

1. Integral evaluations

Let $|\phi_1\rangle$ and $|\phi_2\rangle$ be two adiabatic continuum states of the one-electron prototype system,

$$|\phi_1\rangle \equiv |\phi(\epsilon\mu\lambda;\mathbf{R})\rangle \equiv X_1(\xi)S_1(\eta)e^{i\lambda\varphi}\sqrt{2\pi} ,$$

$$|\phi_2\rangle \equiv |\phi(\epsilon'\mu'\lambda';\mathbf{R})\rangle \equiv X_2(\xi)S_2(\eta)e^{i\lambda'\varphi}/\sqrt{2\pi} .$$

Matrix elements $\langle\phi_2|\hat{\mathcal{O}}|\phi_1\rangle$ for the operators $\hat{\mathcal{O}}$ of interest are defined using a convergence factor,

$$\langle\phi_2|\hat{\mathcal{O}}|\phi_1\rangle \equiv (R/2)^3 \lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi} \int_{-1}^{1} d\eta(\xi^2-\eta^2) \int_0^{2\pi} d\varphi/2\pi [X_2(\xi)S_2(\eta)e^{-i\lambda'\varphi}]\hat{\mathcal{O}}[X_1(\xi)S_1(\eta)e^{-i\lambda\varphi}] , \quad \text{(A1)}$$

where the limit $\alpha\to 0^+$ is taken after all integrations and other computational operations are done. Singularities in the integrals arise from infinite-range contributions to the integrals over ξ (and not, for example, from integrand singularities at $\xi=1$). Since the radial wave functions $X_j(\xi)$ have the phase-amplitude form [Eqs. (3.5a) and (3.5b)]

$$X_j(\xi) = \{2/[\pi R(\xi^2-1)]^{1/2}\}[p_{jr}(\xi)]^{-1/2}\sin\theta_j(\xi) ,$$

where $p_{jr}(\xi)$ and $\theta_j(\xi)$ are the corresponding quantal momentum and phase functions, all the required integrals can be reduced to terms which are *finite,* plus terms containing radial integrals of the form

$$\lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}\xi^{-k}[p_{2r}(\xi)p_{1r}(\xi)]^{-1/2} \times F_2(\xi)F_1(\xi)G(\xi) , \quad \text{(A2)}$$

where $k \geq 0$, $F_j(\xi) = \sin\theta_j(\xi)$ or $\cos\theta_j(\xi)$, and $G(\xi)$ is a function which tends to a constant as $\xi \to \infty$, and is such that the integrand is nonsingular for all ξ. The quantal momentum and phase functions have asymptotic forms

$$p_r(\xi) \simeq \tilde{p}_r(\xi) = c + (q/2c)\xi^{-1} + O(\xi^{-2}) ,$$
$$\theta(\xi) \simeq \tilde{\theta}(\xi) = c\xi + (q/2c)\ln(c\xi) + \delta(\epsilon\mu\lambda;R) + O(\xi^{-1}) ,$$

where $\delta(\epsilon\mu\lambda;R)$ is the phase shift, $c^2 \equiv \epsilon R^2/2$, and $q = (Z_A + Z_B)R$; also,

$$G(\xi) \simeq \tilde{G}(\xi) = G_0 + G_1/\xi + O(\xi^{-2}) ;$$

hence the integral (A2) differs from the asymptotic approximation

$$\lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}\xi^{-k}[\tilde{p}_{2r}(\xi)\tilde{p}_{1r}(\xi)]^{-1/2} \times \tilde{F}_2(\xi)\tilde{F}_1(\xi)\tilde{G}(\xi) \quad \text{(A3)}$$

by terms which are at most finite, since integrals of the forms

$$\lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}\xi^{-k'}\tilde{F}_2(\xi)\tilde{F}_1(\xi)$$

converge absolutely for $k' \geq 2$. We therefore have the possibly singular integrals

$$\lim_{\alpha\to 0^+} \int_1^\infty d\xi \exp[-\alpha\xi + \iota(\tilde{\theta}_2 \pm \tilde{\theta}_1)]\xi^{-k} ,$$

where $k \geq 0$. Since

$$\tilde{\theta}_2 \pm \tilde{\theta}_1 = \beta_\pm\xi \pm \gamma\beta_\pm \ln\xi + \Delta_\pm ,$$

where

$$\beta_\pm = c_2 \pm c_1, \quad \gamma = q/2c_1c_2 ,$$

and

$$\Delta_\pm = (\delta_2 \pm \delta_1) + [(q/2c_2)\ln_2 \pm (q/2c_1)\ln c_1] ,$$

these integrals reduce to

$$\lim_{\alpha\to 0^+} \int_1^\infty d\xi \exp[-\alpha\xi + \iota(\tilde{\theta}_2 \pm \tilde{\theta}_1)]\xi^{-k} = \exp(\iota\Delta_\pm)\mathcal{J}_k(\beta_\pm; \pm\gamma\beta_\pm) ,$$

where

$$\mathcal{J}_k(\beta; \pm\gamma\beta) = \lim_{\alpha\to 0^+} \int_1^\infty d\xi \exp[-(\alpha - \iota\beta)\xi](\xi)^{-k \pm \iota\gamma\beta}$$
$$= \lim_{\alpha\to 0^+} [(\alpha - \iota\beta)^{k-1 \mp \iota\gamma\beta} e^{-(\alpha-\iota\beta)} \times U(k \mp \iota\gamma\beta, k \mp \iota\gamma\beta; \alpha - \iota\beta)] \quad \text{(A4)}$$

and $U(a,b;x)$ is the confluent hypergeometric function.[24] From the known properties of this function under suitable limiting conditions, we may then obtain the following results.

(1) For $\beta \neq 0$, the integrals $\mathcal{J}_k(\beta; \pm\gamma\beta)$ are finite for all $k \geq 0$. Since $\beta_+ = (c_2 + c_1) \neq 0$ in any case, and $\beta_- = (c_2 - c_1) \to 0$ only when $(\epsilon_2 - \epsilon_1) \to 0$, all the required integrals are finite if $\epsilon_2 \neq \epsilon_1$.

(2) For $k \geq 2$, it is easily shown that $\mathcal{J}_k(0;0) = 1/(k-1)$.

(3) $k = 0$. In this case the limiting singularity in $\mathcal{J}_0$ is just $(\alpha - \iota\beta)^{-1}$ and hence in the neighborhood of the singular point $\epsilon_2 = \epsilon_1 = \epsilon$,

$$\mathcal{J}_0[c_2 - c_1; -\gamma(c_2 - c_1)] = (4c/R^2)\{\pi\delta(\epsilon_1 - \epsilon_2) - \iota\mathcal{P}[1/(\epsilon_1 - \epsilon_2)]\} , \quad \text{(A5)}$$

where $\delta(x)$ is the Dirac δ function and $\mathcal{P}(1/x)$ means the Cauchy principal value is taken in integrations over the singular point.

(4) Case $k = 1$. $\mathcal{J}_1(\beta; -\gamma\beta)$ has a logarithmic singularity at the isolated point $\beta = 0$. The "strength" of this singularity can be defined in comparison with the Dirac δ function, as the integral under the singular function in an infinitesimal neighborhood $-h \leq \beta \leq +h$ of the point $\beta = 0$; this is proportional to $(h \ln h)$ and tends to zero in the limit. Hence the strength of this singularity is *zero*, and we can discard contributions from integrals of type $\mathcal{J}_1$ to singularities at degeneracy.

2. Singular couplings

Using these results we can derive explicit formulas for the singular nonadiabatic couplings between degenerate continuum states. For *radial couplings,*

$$(\partial/\partial R)_r = (\partial/\partial R)_{\xi,\eta} - [R(\xi^2 - \eta^2)]^{-1}[\xi(\xi^2 - 1)\partial/\partial\xi + \eta(1 - \eta^2)\partial/\partial\eta] ;$$

hence

$$\langle \phi_2 | (\partial/\partial R)_r | \phi_1 \rangle = \delta_{\lambda'\lambda}\left[\left[\int_{-1}^{1} d\eta\, S_2(\eta)S_1(\eta)\right] RX0 + \left[\int_{-1}^{1} d\eta\, S_2(\eta)[\partial S_1(\eta)/\partial R]_\eta\right] \cdot RX1 + \cdots \right] ,$$

where $\cdots$ represents finite terms,

$$RX0 \equiv (R^2/2\pi) \lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}[p_{2r}(\xi)p_{1r}(\xi)]^{-1/2} \sin\theta_2(\xi)\cos\theta_1(\xi)[(\partial\theta_1/\partial R)_\xi - (\xi/R)(\partial\theta_1/\partial\xi)] ,$$

and

$$RX1 \equiv (R^2/2\pi) \lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}[p_{2r}(\xi)p_{1r}(\xi)]^{-1/2} \sin\theta_2(\xi)\sin\theta_1(\xi) .$$

Both these integrals have the form (A2) with $k=0$ and are singular if $\epsilon'=\epsilon$. We therefore find, as $(\epsilon-\epsilon')\to 0$,

$$\langle \phi(\epsilon'\mu'\lambda;\mathbf{R}) \mid (\partial/\partial R)_r \mid \phi(\epsilon\mu\lambda;\mathbf{R})\rangle = [(1-\delta_{\mu'\mu})\mathcal{S}^R_{\mu'\mu}\cos\Delta^R_{\mu'\mu}]\delta(\epsilon-\epsilon') + (1/\pi)\{(1-\delta_{\mu'\mu})\mathcal{S}^R_{\mu'\mu}\sin\Delta^R_{\mu'\mu} - \delta_{\mu'\mu}[\partial\delta(\epsilon\mu\lambda;R)/\partial R]\}\mathcal{P}[1/(\epsilon-\epsilon')] , \tag{A6a}$$

where $\delta(\epsilon\mu\lambda;R)$ is the scattering phase shift for state $|\phi(\epsilon\mu\lambda;\mathbf{R})\rangle$,

$$\Delta^R_{\mu'\mu} \equiv [\delta(\epsilon\mu'\lambda;R) - \delta(\epsilon\mu\lambda;R)] , \tag{A6b}$$

and

$$\mathcal{S}^R_{\mu'\mu} \equiv \int_{-1}^{1} d\eta\, S(\epsilon\mu'\lambda;\eta)[\partial S(\epsilon\mu\lambda;\eta)/\partial R]_\eta ; \tag{A6c}$$

note that this vanishes if $\mu'=\mu$. The integrals $\mathcal{S}^R_{\mu'\mu}$ are easily computed using the relation

$$\mathcal{S}^R_{\mu'\mu} = [\epsilon R/(A_{\mu\lambda} - A_{\mu'\lambda})] \int_{-1}^{1} d\eta\, S(\epsilon\mu'\lambda;\eta)\eta^2 S(\epsilon\mu\lambda;\eta) . \tag{A6d}$$

For *angular couplings,*

$$\langle \phi(\epsilon'\mu'\lambda\pm 1;\mathbf{R}) \mid L_\pm \mid \phi(\epsilon\mu\lambda;\mathbf{R})\rangle = (R/2)^3 \lim_{\alpha\to 0^+} \left[\left[\int_1^\infty d\xi\, e^{-\alpha\xi}\xi(\xi^2-1)^{1/2}X_2(\xi)X_1(\xi)\right] \times \left[\int_{-1}^{1} d\eta\, S_2(\eta)L^\eta_\pm(\lambda)S_1(\eta)\right] + \left[\int_1^\infty d\xi\, e^{-\alpha\xi}X_2(\xi)L^\xi_\pm(\lambda)X_1(\xi)\right] \times \left[\int_{-1}^{1} d\eta\, \eta(1-\eta^2)^{1/2}S_2(\eta)S_1(n)\right]\right] ,$$

where

$$L^\eta_\pm(\lambda) \equiv \mp(1-\eta^2)^{1/2}[(\partial/\partial\eta) \pm \lambda\eta(1-\eta^2)]$$

and

$$L^\xi_\pm(\lambda) \equiv \pm(\xi^2-1)^{1/2}[(\partial/\partial\xi) \mp \lambda\xi/(\xi^2-1)] .$$

As $(\epsilon-\epsilon')\to 0$,

$$\langle \phi(\epsilon'\mu'\lambda\pm 1;\mathbf{R}) \mid L_\pm \mid \phi(\epsilon\mu\lambda;\mathbf{R})\rangle = \left[\left[\int_{-1}^{1} d\eta\, S_2(\eta)L^\eta_\pm(\lambda)S_1(\eta)\right] AX0 + \left[\int_{-1}^{1} d\eta\, \eta(1-\eta^2)S_2(\eta)S_1(\eta)\right] AX1 + \cdots\right] ,$$

where $\cdots$ represents finite terms,

$$AX0 \equiv (R^2/2\pi) \lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}[p_{2r}(\xi)p_{1r}(\xi)]^{-1/2} \times \sin\theta_2(\xi)\sin\theta_1(\xi) ,$$

and

$$AX1 \equiv (R^2/2\pi) \lim_{\alpha\to 0^+} \int_1^\infty d\xi\, e^{-\alpha\xi}\xi^{-1}[p_{2r}(\xi)p_{1r}(\xi)]^{-1/2} \times \sin\theta_2(\xi)\cos\theta_1(\xi)(\partial\theta_1/\partial\xi) ,$$

and these again have the form (A2) with $k=0$ and $k=1$, respectively. Hence we obtain the result

$$\langle \phi(\epsilon'\mu'\lambda\pm 1;\mathbf{R}) \mid L_\pm \mid \phi(\epsilon\mu\lambda;\mathbf{R})\rangle = \mathcal{S}^\pm_{\mu'\mu}\{\cos\Delta^\pm_{\mu'\mu}\delta(\epsilon-\epsilon') + (1/\pi)\sin\Delta^\pm_{\mu'\mu}\mathcal{P}[1/(\epsilon-\epsilon')]\} , \tag{A7a}$$

where

$$\Delta^\pm_{\mu'\mu} \equiv \delta(\epsilon\mu'\lambda\pm 1;R) - \delta(\epsilon\mu\lambda;R) \tag{A7b}$$

and

$$\mathcal{S}^\pm_{\mu'\mu} \equiv \int_{-1}^{1} d\eta\, S(\epsilon\mu'\lambda\pm 1;\eta)L^\eta_\pm(\lambda)S(\epsilon\mu\lambda;\eta) . \tag{A7c}$$

3. Generalized Hellmann-Feynman relation

If $|\phi_1\rangle$, $|\phi_2\rangle$ are two continuum states and $\hat{\mathcal{O}}$ is one of the coupling operators $(\partial/\partial R)_r, L_\pm$,

$$\langle \phi_2 \mid [\hat{\mathcal{O}}, H_e] \mid \phi_1\rangle = (\epsilon-\epsilon')\langle \phi_2 \mid \hat{\mathcal{O}} \mid \phi_1\rangle + \{\langle H_e\phi_2 \mid \hat{\mathcal{O}} \mid \phi_1\rangle - \langle \phi_2 \mid H_e\hat{\mathcal{O}} \mid \phi_1\rangle\} ,$$

where integral norms are defined as in Eq. (A1). It follows that the Hellmann-Feynman relations, Eqs. (2.9a) and (2.9b), may be extended to two continuum states if $(\epsilon-\epsilon')\neq 0$ and the expression in curly brackets above vanishes, i.e., if the Hamiltonian H_e is Hermitian with respect to the kets $|\phi_2\rangle$, $|\hat{\mathcal{O}}\phi_1\rangle$. When $(\epsilon-\epsilon')=0$, the first term in the above equation vanishes, but the term in curly brackets is finite, and yields a connection between the commutator matrix elements and analytic coefficients of the principal-value terms in Eqs. (A6) and (A7).

The term in curly brackets can be reduced to the expression

$$-(R/4)\lim_{\alpha\to 0^+}\left[\alpha\int_1^\infty d\xi\, e^{-\alpha\xi}\int_{-1}^{1}d\eta\int_0^{2\pi}(d\varphi/2\pi)[(\partial\phi_2^*/\partial\xi)(\hat{\mathcal{O}}\phi_1)-\phi_2^*\partial/\partial\xi(\hat{\mathcal{O}}\phi_1)]\right].$$

Except for the additional inserted factor of α, the integrals in this expression again have the form of Eq. (A2). Since all such integrals converge to finite values when $(\epsilon-\epsilon')\neq 0$, the above expression vanishes in the limit and the usual Hellmann-Feynman formulas (2.9a) and (2.9b) are valid for couplings of nondegenerate continuum states. When $(\epsilon-\epsilon')\to 0$, the only terms in the above expression which do not vanish are those which would yield a Dirac δ function if the factor α were not present, and these now give a finite factor $(1/\pi)$ instead. We find, as $(\epsilon-\epsilon')\to 0$,

$$\langle\phi(\epsilon\mu'\lambda;\mathbf{R})\,(\partial H_e/\partial R)_r\,|\,\phi(\epsilon\mu\lambda;\mathbf{R})\rangle = (1/\pi)\{(1-\delta_{\mu'\mu})\mathcal{S}^R_{\mu'\mu}\sin\Delta^R_{\mu'\mu} - \delta_{\mu'\mu}[\partial\delta(\epsilon\mu\lambda;R)/\partial R]\} \quad \text{(A8)}$$

for radial couplings, and

$$\langle\phi(\epsilon\mu'\lambda\pm 1;\mathbf{R})\,|\,[L_\pm,H_e]\,|\,\phi(\epsilon\mu\lambda;\mathbf{R})\rangle = (1/\pi)\mathcal{S}^\pm_{\mu'\mu}\sin\Delta^\pm_{\mu'\mu} \quad \text{(A9)}$$

for angular couplings. This proves Eqs. (2.10), since these are just the coefficients of the principal-value terms in Eqs. (A6) and (A7).

APPENDIX B: REPRESENTATION OF RAPIDLY VARYING CONTINUUM OPERATORS

Here we given representative details of some results cited in Sec. IV for P-subspace representations of operators $\hat{K}(t)$ and $\hat{\mathcal{G}}(t;t')$, which vary rapidly with energy over a packet width Δ_j.

1. Nonresonant terms in $\hat{K}_{CC}$

As in Eq. (4.10) we break up the principal-value integrals into contributions associated with cells j',j and consider the nonresonant terms $(j'\neq j)$; the contribution for a particular pair $(j'\mu'\lambda',j\mu\lambda)$ is then given by

$$\mathcal{P}\int_{-\Delta_{j'}/2}^{+\Delta_{j'}/2}dx'\int_{-\Delta_j/2}^{+\Delta_j/2}dx\;|\,\phi(\epsilon_{j'}+x',\mu',\lambda')\rangle\left[\frac{\langle\epsilon_{j'}+x',\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+x,\mu\lambda\rangle}{(\epsilon_j-\epsilon_{j'})+(x-x')}\right]\langle\phi(\epsilon_j+x,\mu\lambda)\,|\;.$$

In this expression, we approximate the slowly varying matrix element by its value at the packet centers and, assuming that operands to left and right are also "slowly varying," we insert the P-subspace projector on both left and right; the result is then

$$|\,\tilde{\phi}(j'\mu'\lambda')\rangle\left[\frac{\langle j'\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j'}}\right]\kappa^{NR}_{j'j}\langle\tilde{\phi}(j\mu\lambda)\,|\;,$$

where we have "renormalized" the matrix element as in Eqs. (4.6) and

$$\kappa^{NR}_{lj}\equiv\left[\frac{\epsilon_j-\epsilon_l}{\Delta_j\Delta_l}\right]\mathcal{P}\int_{-\Delta_l/2}^{+\Delta_l/2}\int_{-\Delta_j/2}^{+\Delta_j/2}dx[(\epsilon_j-\epsilon_l)+(x-x')]^{-1}, \quad \text{(B1)}$$

the principal value being taken at any singularities. Evaluation of this integral leads to Eqs. (4.11). A similar method leads to the results cited in Eqs. (4.7).

2. Resonant terms in $\hat{K}_{CC}$

The contribution of a given resonant term $(j\mu'\lambda',j\mu\lambda)$ in the principal-value part of $\hat{K}_{CC}$ amounts to an enhancement of the effective coupling between neighboring cells. To prove this, we introduce explicitly the (hypothetical) slowly varying operands which appear to left and right of this part of $\hat{K}_{CC}$; then the effect of such a resonant term is given by an expression like

$$\mathcal{P}\int_{-\Delta_j/2}^{+\Delta_j/2}\int_{-\Delta_j/2}^{+\Delta_j/2}dx\left[c^*(\epsilon_j+x',\mu'\lambda')\frac{\langle\epsilon_j+x',\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+x,\mu\lambda\rangle}{(x-x')}b(\epsilon_j+x,\mu\lambda)\right],$$

where $c^*(\epsilon'\mu'\lambda')$ and $b(\epsilon\mu\lambda)$ are the expansion coefficients in these operands. To evaluate the integral set $z=(x+x')/2$ and $y=(x-x')/2$; the Jacobian of the transformation is 2 and the double integral over the cell j (for given indices $\mu'\lambda',\mu\lambda$) is given by

$$\left[\mathcal{P}\int_0^{+\Delta_j/2}dz\int_{-(\Delta_j/2-z)}^{+(\Delta_j/2-z)}dy(1/y)[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)] + \mathcal{P}\int_{-\Delta_j/2}^{0}dz\int_{-(\Delta_j/2+z)}^{+(\Delta_j/2+z)}dy(1/y)[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right],$$

where indices not referring to energy have been suppressed. Now we expand the slowly varying numerator in each integrand in a Taylor series about $y=0$ and do the principal-value integrals, with the result (to lowest order)

$$2\left[\int_0^{+\Delta_j/2} dz(\Delta_j/2-z)\left[\frac{d}{dy}[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right]_{y=0}\right.$$
$$\left.+\int_{-\Delta_j/2}^0 dz(\Delta_j/2+z)\left[\frac{d}{dy}[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right]_{y=0}\right];$$

the result of the integrations over z is

$$\tfrac{1}{4}\Delta_j^2\left[\left[\frac{d}{dy}[c^*(\epsilon_j+\bar{z}-y)\langle\epsilon_j+\bar{z}-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+\bar{z}+y\rangle b(\epsilon_j+\bar{z}+y)]\right]_{y=0}\right.$$
$$\left.+\left[\frac{d}{dy}[c^*(\epsilon_j-\bar{z}-y)\langle\epsilon_j-\bar{z}-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j-\bar{z}+y\rangle b(\epsilon_j-\bar{z}+y)]\right]_{y=0}\right],$$

where the z-dependent derivative has been replaced in each integrand by an appropriate mean value.

It remains to interpret these derivatives. A reasonable estimate of the derivative at "$+\bar{z}$" is given by

$$(\epsilon_{j+1}-\epsilon_j)^{-1}[c^*(\epsilon_j\mu'\lambda')\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_{j+1}\mu\lambda\rangle b(\epsilon_{j+1}\mu\lambda)-c^*(\epsilon_j\mu'\lambda')\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\mu\lambda\rangle b(\epsilon_j\mu\lambda)]$$
$$-(\epsilon_{j+1}-\epsilon_j)^{-1}[c^*(\epsilon_{j+1}\mu'\lambda')\langle\epsilon_{j+1}\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\mu\lambda\rangle b(\epsilon_j\mu\lambda)-c^*(\epsilon_j\mu'\lambda')\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\mu\lambda\rangle b(\epsilon_j\mu\lambda)]$$
$$=(\epsilon_{j+1}-\epsilon_j)^{-1}[c^*(\epsilon_j\mu'\lambda')\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_{j+1}\mu\lambda\rangle b(\epsilon_{j+1}\mu\lambda)]$$
$$+(\epsilon_j-\epsilon_{j+1})^{-1}[c^*(\epsilon_{j+1}\mu'\lambda')\langle\epsilon_{j+1}\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\mu\lambda\rangle b(\epsilon_j\mu\lambda)]\,. \quad \text{(B2a)}$$

and, similarly, that at "$-\bar{z}$" is equal to

$$(\epsilon_j-\epsilon_{j-1})^{-1}[c^*(\epsilon_{j-1}\mu'\lambda')\langle\epsilon_{j-1}\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\mu\lambda\rangle b(\epsilon_j\mu\lambda)]+(\epsilon_{j-1}-\epsilon_j)^{-1}[c^*(\epsilon_j\mu'\lambda')\langle\epsilon_j\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_{j-1}\mu\lambda\rangle b(\epsilon_{j-1}\mu\lambda)]\,. \quad \text{(B2b)}$$

Using the normalization rules to interpret both the coefficients and the matrix elements in terms of their subspace equivalents, we find the resulting contribution of resonant terms is represented by Eqs. (4.12).

3. Decay factor $g_{j'n}(\tau)$ for $[\hat{\mathcal{G}}_{CD}(t;t')]_{PP}$

The same procedures as are used above to obtain results for nonresonant terms in $\hat{K}_{CC}$ and $\hat{K}_{CD}$ lead to Eq. (4.14a), with $g_{j'n}(\tau)$ given explicitly by

$$g_{j'n}(\tau)\equiv(\kappa_{j'n})^{-1}\left[\frac{\epsilon(n\mu\lambda)-\epsilon_{j'}}{\Delta_{j'}}\right]\int_{-\Delta_j/2}^{+\Delta_j/2} dx\frac{e^{-\iota x\tau}}{[\epsilon(n\mu\lambda)-\epsilon_{j'}-x]}$$

and Eq. (4.14b) results from the substitutions $\beta_{j'}=\Delta_{j'}\tau/2$ and $\alpha_{j'n}$ defined by Eq. (4.7c). The integral can be expressed in closed form in terms of the cosine and sine integrals, but a more useful formula is

$$g_{j'n}(\tau)=\kappa_{j'n}^{-1}\sum_{k=0}^{\infty}(-\iota\alpha_{j'n}/2)^k f_k(\beta_{j'})\,, \quad \text{(B3a)}$$

where

$$f_k(\beta)\equiv(d/d\beta)^k\left[\frac{\sin\beta}{\beta}\right]; \quad \text{(B3b)}$$

in general, this function decays more slowly than the usual function $f_0(\beta)=(\sin\beta)/\beta$, but reduces to it when $\alpha_{j'n}\ll 1$.

4. Decay factors for nonresonant terms in $\hat{\mathcal{G}}_{CC}(t;t')$

The function $g_{lj}^{NR}(\tau)$ given explicitly by Eq. (4.15c) can be expressed as follows. Defining $\beta_l=\Delta_l\tau/2$, $\alpha_{jl}\equiv\Delta_j/|\epsilon_j-\epsilon_l|$, $\alpha_{lj}\equiv\Delta_l/|\epsilon_j-\epsilon_l|$, we find for $l\neq j\pm1$ (where α_{jl} and α_{lj} are both small compared to 1)

$$g_{lj}^{NR}(\tau)=(\kappa_{lj}^{NR})^{-1}\left[\alpha_{jl}^{-1}\ln[(1+\alpha_{jl}/2)/(1-\alpha_{jl}/2)]f_0(\beta_l)\right.$$
$$\left.+\sum_{k=1}^{\infty}(1/k)[\pm\iota\alpha_{lj}/2]^k[(1+\alpha_{jl}/2)^{-k}-(1-\alpha_{jl}/2)^{-k}]f_k(\beta_l)\right], \quad \text{(B4a)}$$

where $f_k(\beta)$ was defined above. For the near-resonant terms $l=j\pm1$, the formula resulting is

$$g^{NR}_{j\pm1,j}(\tau)=\left[\frac{\Delta_j+\Delta_{j\pm1}}{2\Delta_j\kappa^{NR}_{j\pm1,j}}\right]\left[\ln\left[\frac{2\Delta_j+\Delta_{j\pm1}}{2\Delta_{j\pm1}}\right]f_0(\beta)+(1/2\beta)\{\cos\beta\,\mathrm{Si}(2\beta)-\sin\beta\,\overline{\mathrm{Ci}}(2\beta)\pm\iota[\cos\beta\,\overline{\mathrm{Ci}}(2\beta)+\sin\beta\,\mathrm{Si}(2\beta)]\}\right.$$
$$\left.+\sum_{k=1}^{\infty}(1/k)[\mp\iota\Delta_{j\pm1}/(2\Delta_j+\Delta_{j\pm1}0)]^k f_k(\beta)\right], \tag{B4b}$$

where "β"$=\beta_{j\pm1}$ and $\mathrm{Si}(x),\overline{\mathrm{Ci}}(x)$ are the standard functions

$$\mathrm{Si}(x)\equiv\int_0^x\frac{\sin t}{t}dt,\quad\overline{\mathrm{Ci}}(x)\equiv\int_0^x\frac{(\cos t-1)}{t}dt\ .$$

5. Resonant terms in $\hat{\mathcal{G}}_{CC}$

Following the same procedure as was used to study the resonant terms in $\hat{K}_{CC}$, we now find the effect of the term for given $(j,\mu'\lambda',\mu\lambda)$ is given by

$$\mathcal{P}\int_{-\Delta_j/2}^{+\Delta_j/2}\int_{-\Delta_j/2}^{+\Delta_j/2}dx\,\exp[-\iota(\epsilon_j+x')\tau]\left[c^*(\epsilon_j+x',\mu'\lambda')\frac{\langle\epsilon_j+x',\mu'\lambda'\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+x,\mu\lambda\rangle}{(x-x')}b(\epsilon_j+x,\mu\lambda)\right];$$

after transforming to the new variables $z=(x+x')/2$, $y=(x-x')/2$ as before, this becomes

$$e^{-\iota\epsilon_j\tau}\left[\mathcal{P}\int_0^{+\Delta_j/2}dz\,e^{-\iota z\tau}\int_{-(\Delta_j/2-z)}^{+(\Delta_j/2-z)}dy(e^{\iota y\tau}/y)[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right.$$
$$\left.+\mathcal{P}\int_{-\Delta_j/2}^{0}dz\,e^{-\iota z\tau}\int_{-(\Delta_j/2+z)}^{+(\Delta_j/2+z)}dy(e^{\iota y\tau}/y)[c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right],$$

where, as before, indices not referring to energy are suppressed. Strictly, we should retain the exponential factor $\exp(\iota y\tau)$ as a "rapidly varying factor" in the integrations over y, but for our present purpose this much detail is not justified. A reasonably good first approximation is obtained if we include the exponential factor in the y integral as part of the "slowly varying" factors in its integrand. The rest of the derivation is then quite similar to that for the resonant part of $\hat{K}_{CC}$; the result of the y integrations is

$$2e^{-\iota\epsilon_j\tau}\left[\int_0^{+\Delta_j/2}dz(\Delta_j/2-z)e^{-\iota z\tau}D_y(z;0)=\int_{-\Delta_j/2}^{0}dz(\Delta_j/2+z)e^{-\iota z\tau}D_y(z;0)\right],$$

where $D_y(z;0)$ is the derivative of the "slowly varying" part of the integrands.

$$D_y(z;0)\equiv\left[\frac{\partial}{\partial y}[e^{\iota y\tau}c^*(\epsilon_j+z-y)\langle\epsilon_j+z-y\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j+z+y\rangle b(\epsilon_j+z+y)]\right]_{y=0}.$$

Approximating $D_y(z;0)$ in each of the two terms by a suitable mean value, we do the z integrations and obtain the result

$$\tfrac{1}{4}\Delta_j^2e^{-\iota\epsilon_j\tau}[f_-(\beta_j)D_y(\bar{z};0)+f_+(\beta_j)D_y(-\bar{z};0)],$$

where the new decay functions $f_\pm(\beta)$ are defined

$$f_\pm(\beta)\equiv2\int_0^1du(1-u)e^{\pm\iota\beta u}=(2/\beta^2)[(1-\cos\beta)\pm\iota(\beta-\sin\beta)] \tag{B5}$$

and, as before, $\beta_j=\Delta_j\tau/2$. By analogy with the computation for $\hat{K}_{CC}$, the derivatives $D_y(\pm\bar{z};0)$ are given by

$$D_y(\bar{z};0)=\frac{c^*(\epsilon_j)\langle\epsilon_j\,|\,\hat{\mathcal{N}}\,|\,\epsilon_{j+1}\rangle b(\epsilon_{j+1})}{\epsilon_{j+1}-\epsilon_j}+e^{-\iota(\epsilon_{j+1}-\epsilon_j)\tau}\frac{c^*(\epsilon_{j+1})\langle\epsilon_{j+1}\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\rangle b(\epsilon_j)}{\epsilon_j-\epsilon_{j+1}}$$

and

$$D_y(-\bar{z};0)=\frac{c^*(\epsilon_j)\langle\epsilon_j\,|\,\hat{\mathcal{N}}\,|\,\epsilon_{j-1}\rangle b(\epsilon_{j-1})}{\epsilon_{j-1}-\epsilon_j}+e^{-\iota(\epsilon_{j-1}-\epsilon_j)\tau}\frac{c^*(\epsilon_{j-1})\langle\epsilon_{j-1}\,|\,\hat{\mathcal{N}}\,|\,\epsilon_j\rangle b(\epsilon_j)}{\epsilon_j-\epsilon_{j-1}}\ .$$

After introducing packet states and their normalized matrix elements, the result can be represented as the matrix elements of the operator

$$\sum \left[\left[\frac{\Delta_j^2 f_-(\beta_j)+\Delta_{j+1}^2 f_+(\beta_j)}{8\Delta_j\Delta_{j+1}} \right] \left[|\tilde{\phi}(j\mu'\lambda')\rangle e^{-\iota\epsilon_j\tau} \frac{\langle j\mu'\lambda' | \hat{\mathcal{N}} | j+1\mu\lambda\rangle}{\epsilon_{j+1}-\epsilon_j} \langle \tilde{\phi}(j+1\mu\lambda)| \right.\right.$$
$$\left.\left. + |\tilde{\phi}(j+1\mu'\lambda')\rangle e^{-\iota\epsilon_{j+1}\tau} \frac{\langle j+1\mu'\lambda' | \hat{\mathcal{N}} | j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j+1}} \langle \tilde{\phi}(j\mu\lambda)| \right] \right.$$
$$+ \left[\frac{\Delta_j^2 f_+(\beta_j)+\Delta_{j-1}^2 f_-(\beta_j)}{8\Delta_j\Delta_{j-1}} \right] \left[|\tilde{\phi}(j\mu'\lambda')\rangle e^{-\iota\epsilon_j\tau} \frac{\langle j\mu'\lambda' | \hat{\mathcal{N}} | j-1\mu\lambda\rangle}{\epsilon_{j-1}-\epsilon_j} \langle \tilde{\phi}(j-1\mu\lambda)| \right.$$
$$\left. \left. + |\tilde{\phi}(j-1\mu'\lambda')\rangle e^{-\iota\epsilon_{j-1}\tau} \frac{\langle j-1\mu'\lambda' | \hat{\mathcal{N}} | j\mu\lambda\rangle}{\epsilon_j-\epsilon_{j-1}} \langle \tilde{\phi}(j\mu\lambda)| \right] \right]$$

(indices in the sum run over all $j,\mu\lambda,\mu'\lambda'$). But this is simply an enhancement of the near-neighbor ($j\leftrightarrow j\pm1$) terms in $\hat{\mathcal{Q}}_{PP}$.

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[1]This approximation is widely used for the study of ion-atom collisions; except at very low collision energies ($E \lesssim 50-100$ eV/amu) it is valid for this problem. See, for example, J. B. Delos, Rev. Mod. Phys. **53**, 287 (1981) or M. S. Child, Adv. At. Mol. Phys. **14**, 225 (1978).

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[7]Within an independent-particle description, the continuum states for a many-electron system with a single active electron may be treated in essentially the same way as is done here for the one-electron system. The first ionization potential is taken as the zero of energy for the continuum at each internuclear distance R, and the mapping of the continuum states vs R is defined as one which keeps the energy ϵ of the continuum state fixed with respect to that zero. This entails no difficulty since the actual dependence of the "core" binding energy upon internuclear distance merely plays the role of a potential energy for the heavy particle motion. Provided that the continuum states contain no "fine structure" of the sort we have specifically excluded here, due to embedded quasibound levels, it should be possible to extend the methods used here to such model problems; in effect, we would assume that any continuum whose eigenfunctions are the solutions to a potential scattering problem is "simple" in the same way as the prototype one-electron continuum.

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[15]At higher collision energies ($E \gtrsim 7-10$ keV/amu) the nonadiabatic coupling matrices become velocity dependent because the translation factors should be included in the basis states [they have been omitted from the matrix elements defined in Eqs. (2.6)–(2.8)]. Therre are also other, much smaller effects of translation factors, but a classical trajectory description entails approximations comparable to neglecting these.

[16]There is some dispute about whether switching functions need to be state specific (different f_k for each ϕ_k) or a common switching function can be used. A common choice is much simpler formally, and arguments have been given for a "universal" switching function [cf. J. Vaaben and K. Taulbjerg, J. Phys. B **14**, 1815 (1981)]; however, calculations using such forms have so far dealt only with total charge-transfer cross sections using limited basis sets and continuum couplings or transitions were not considered. More detailed studies such as those reported in Refs. 11–14 show that individual-state excitation cross sections are very sensitive to the detailed choice for switching functions, and also the detailed properties of f_k's appropriate to adiabatic bound states can be derived from several independent considerations [cf. J. Rankin and W. R. Thorson, Phys. Rev. A **18**, 1990 (1978); W. R. Thorson, M. Kimura, J. H. Choi, and S. K. Knudson, *ibid.* **24**, 1768 (1981)]. In the present context, a key consideration is the dramatic effect of state-specific switching functions on couplings between bound and continuum levels.

[17]See, for example, A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962), Vol. II, Chap. XVII, Secs. 10–13.

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[19]Electron detachment in collisions of H^- ions with inert neutrals such as He is a simple problem which might be modeled in this way. Delos *et al.* have presented a simplified model of such processes in which it is assumed that (1) a suitable zeroth-order Hamiltonian can be defined

having a continuum and a quasibound level transiently embedded in it during collision, such that the quasibound level is diabatically coupled to the continuum and (2) the continuum in question is "simple" in the same sense as we use the term in this paper—for example, the continuum states map versus internuclear separation R by the same prescription as we use in Eq. (2.3b). However, they did not include continuum-continuum couplings in their treatment. [Cf. R. D. Taylor and J. B. Delos, Proc. R. Soc. London, Ser. A **379**, 179 (1982); **379**, 209 (1982); T. S. Wang and J. B. Delos, J. Chem. Phys. **79**, 4306 (1983); Phys. Rev. A **29**, 542 (1984); **29**, 552 (1984); **33**, 3832 (1986).] Our formulation would permit inclusion of the continuum couplings in a numerical close-coupling approach to the same problem. It is not difficult to construct models of the H^--He system which would satisfy the requirements of the approach described.

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