Nonlocal potentials in Penning and associative ionization

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Bound-continuum processes of the type $A^* + B \rightarrow A + B^+ + e$ or $(AB)^+ + e$, known as Penning and associative ionization, respectively, are considered. The derivation of the partial-wave Schrödinger equation through the Feshbach projection-operator formalism is reviewed. The potential-energy operator for the general case is then examined carefully and found to be not only collision-energy dependent but also nonlocal. Strict locality is obtained only in the limit of infinite collision energy. Nonlocality due to bound-continuum interaction increases in importance as the collision energy is reduced, and in certain dynamical situations for associative ionization it is found to be predominant. Thus, the common procedure of reducing the bound-continuum interaction to an imaginary local potential becomes suspect and the general validity of the attendant Franck-Condon approximation of vertical electronic transitions is also called into question. Two limiting situations—the high-energy ($E \rightarrow \infty$) and the low-energy ($E \rightarrow 0$) limits—are examined. In the former case, the local potential is isolated and the nonlocal part given explicitly to lowest order; in the latter, the predominant nonlocal part is given explicitly for the case of associative ionization.

I. INTRODUCTION

The diatomic collision processes

$$A^* + B \rightarrow \begin{cases} A + B^+ + e^- \\ (AB)^+ + e^- \end{cases} \quad (1)$$
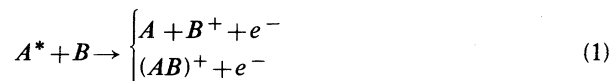
known as Penning and associative ionization,[1] respectively, are usually treated quantum mechanically by local, complex potentials, with the imaginary part of the local potential accounting for the bound-continuum interaction between the $A^* + B$ discrete electronic state and the $A + B^+ + e^-$ [or $(AB)^+ + e^-$] electronic continuum.[2-6] Though in many previous works on the subject[7-9] the necessarily nonlocal and energy-dependent nature of the potential has been explicitly derived in the formalism, the prevailing strategy was to achieve reduction to locality when the theory was being applied. A very interesting and instructive exception, however, is found in a numerical study of a related process: the associative detachment reaction $H + H^- (^2\Sigma_u^+) \rightarrow H_2(^1\Sigma_g^+) + e^-$ at incident energies such that only a few final states are energetically open.[10] This study concludes that the formulation of a local complex potential for inelastic scattering breaks down when the set of energetically open final states do not effectively produce closure. Subsequent to this work, we have also independently reached a similar conclusion,[11] that the Franck-Condon approximation, equivalent to the assumption of localized ionization events, is not always valid. This was demonstrated by a model study of the $He^*(^3S) + Ar$ Penning ionization system based on a semiclassical theory. In the present paper, we attempt to further substantiate the conclusions reached in Refs. 10 and 11 by a formal and analytical investigation of the origins of nonlocality and a judicious examination of the usual assumptions leading to locality.

The practical advantage of a local potential as opposed to a nonlocal one is, of course, that the former entails only coupled differential equations while the latter necessarily involves coupled integro-differential equations. The reduction-to-locality procedure rests on two main assumptions. The first one, which is usually made explicitly, is that the bound-continuum electronic coupling matrix element [Eq. (16)] is independent of the emitted-electron energy ϵ. The second one, usually made implicitly, is that the collision energy of the system is large. Besides these two assumptions, a strong supporting rationale for locality comes from the Franck-Condon principle of vertical (local) electronic transitions, which forms the basis of many semiclassical analyses.[4,12,13] In this work we will retain the first assumption and examine the consequences of relaxing the second.

Three results are demonstrated. First, a rigorously local potential is obtained only in the limit of infinite collision energy. Second, nonlocality increases in importance as the collision energy is reduced; and last, there are dynamical situations for associative ionization in which the nonlocal part of the imaginary part of the potential is predominant. In the last result it is seen that the nonlocality is largely due to the bound vibrational states supported by the associative complex $(AB)^+$ [Eq. (86)]. We examine, especially, two limiting situations, the high-energy ($E \rightarrow \infty$) and the low-energy ($E \rightarrow 0$) limits, where E is the total energy of the system defined with respect to the asymptotic energy of the $A + B^+$ electronic configuration. In the former case it is shown that the local part of the potential can be isolated, and the nonlocal part is given explicitly to lowest order. In the latter the predominant nonlocal part is given explicitly for the case of associative ionization. It is found that the low-energy situation entails the attractive feature that the nonlocal potential only involves a sum of separable kernels.

In Sec. II, to render the paper self-contained and for the purpose of establishing notation, we give a review of the

derivation of the relevant partial-wave Schrödinger equation through the Feshbach projection-operator formalism. In Sec. III we examine the origins of nonlocality and energy-dependence of the potential, track down the main assumptions leading to locality, and establish the three results mentioned above. Section IV is devoted to the derivation of the explicit results for the high- and low-energy limiting cases. Finally, in Sec. V, we discuss some important problems that are left unaddressed in the present work.

II. THE PARTIAL-WAVE SCHRÖDINGER EQUATION THROUGH THE FESHBACH PROJECTION-OPERATOR FORMALISM

The material contained in this section has been well presented in a number of previous works.[5,6] We will, nevertheless, furnish a review in the interest of completeness, stressing the points which are crucial for our later discussion. The reader familiar with the formalism may proceed directly to Sec. III, after taking note of the main results contained in Eqs. (48), (50), (56), and (61).

Throughout the paper we will assume a two-state model for the collision dynamics. A typical physical situation is depicted schematically in Fig. 1. The initial channel is specified by nuclear motion on the curve $W_d(R)$ and the final one by $W_+(R)$. $W_d(R)$ results from the electronic configuration of the A^*+B complex, while $W_+(R)$ results from that of the ion core complex $A+B^+$ or $(AB)^+$. The
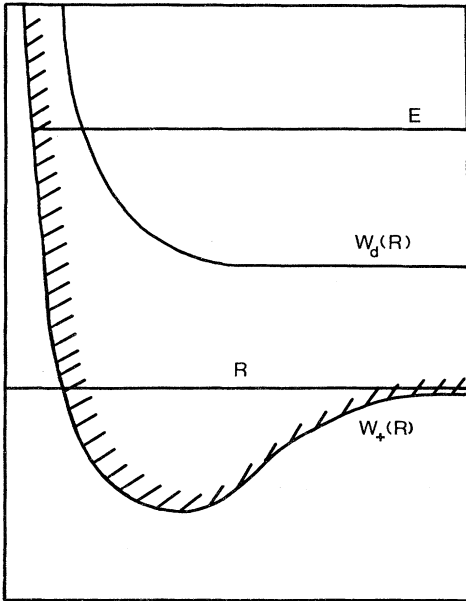

FIG. 1. Schematic representation of potential curves for two-state model of collisional ionization. $W_d(R)$ corresponds to the A^*+B electronic state, $W_+(R)$ to the $A+B^+$ $[(AB)^+]$ state. Hatched marks designate the electronic continuum of the emitted electron. E is the total energy of the system. Zero of energy is the asymptotic energy of the $W_+(R)$ curve.

continuum of the final configuration is furnished by the free, emitted electron (specified by energy ϵ and a direction of motion). Formally the corresponding states are represented by the kets $|\phi_d,\vec{R}\rangle\rangle$ and $|\phi_{\vec{\epsilon}},\vec{R}\rangle\rangle$. Double brackets are used because we need separate Hilbert spaces to describe the two different kinds of degrees of freedom, the collective electronic $\vec{r}$ and the internuclear $\vec{R}$. These kets satisfy the following orthonormality requirements:

$$\langle\langle\phi_d,\vec{R}\mid\phi_d,\vec{R}'\rangle\rangle=\delta^3(\vec{R}-\vec{R}') ,\tag{2}$$

$$\langle\langle\phi_{\vec{\epsilon}},\vec{R}\mid\phi_{\vec{\epsilon}'},\vec{R}'\rangle\rangle=\delta^3(\vec{R}-\vec{R}')\delta(\vec{\epsilon}-\vec{\epsilon}') ,\tag{3}$$

where

$$\delta(\vec{\epsilon}-\vec{\epsilon}')\equiv\delta(\hat{k}-\hat{k}')\delta(\epsilon-\epsilon') ,\tag{4}$$

$\vec{k}$ being the momentum of the electron with energy ϵ $(\epsilon=\hbar^2k^2/2m)$. We further impose the forms

$$\langle\langle\vec{r},\vec{R}'\mid\phi_d,\vec{R}\rangle\rangle=\delta^3(\vec{R}-\vec{R}')\phi_d(\vec{r},\vec{R}) ,\tag{5}$$

$$\langle\langle\vec{r},\vec{R}'\mid\phi_{\vec{\epsilon}},\vec{R}\rangle\rangle=\delta^3(\vec{R}-\vec{R}')\phi_{\vec{\epsilon}}(\vec{r},\vec{R})\tag{6}$$

for the coordinate representations of these kets. The wave functions ϕ_d and $\phi_{\vec{\epsilon}}$ are in practice obtained as variational, configuration-interaction (CI) electronic wave functions, appropriate to the initial and final electronic configurations of the system, respectively.[14] Conditions (5) and (6) imply

$$|\phi_d,\vec{R}\rangle\rangle=|\vec{R}\rangle|\phi_d(\vec{R})\rangle ,\tag{7}$$

$$|\phi_{\vec{\epsilon}},\vec{R}\rangle\rangle=|\vec{R}\rangle|\phi_{\vec{\epsilon}}(\vec{R})\rangle ,\tag{8}$$

where

$$|\phi_d(\vec{R})\rangle\equiv\int d^3r\,|\vec{r}\rangle\phi_d(\vec{r},\vec{R}) ,\tag{9}$$

$$|\phi_{\vec{\epsilon}}(\vec{R})\rangle\equiv\int d^3r\,|\vec{r}\rangle\phi_{\vec{\epsilon}}(\vec{r},\vec{R}) .\tag{10}$$

Also,

$$\langle\vec{r}\mid\phi_d(\vec{R})\rangle=\phi_d(\vec{r},\vec{R}) ,\tag{11}$$

$$\langle\vec{r}\mid\phi_{\vec{\epsilon}}(\vec{R})\rangle=\phi_{\vec{\epsilon}}(\vec{r},\vec{R}) .\tag{12}$$

Writing the total Hamiltonian as

$$H=-\frac{\hbar^2}{2\mu}\nabla_R^2+H_e(\vec{r},\vec{R}) ,\tag{13}$$

the potential surfaces $W_d(R)$ and $W_+(R)$ are then given by

$$\langle\phi_d(\vec{R})\mid H_e\mid\phi_d(\vec{R})\rangle=W_d(R) ,\tag{14}$$

$$\langle\phi_{\vec{\epsilon}}(\vec{R})\mid H_e\mid\phi_{\vec{\epsilon}'}(\vec{R})\rangle=\delta(\vec{\epsilon}-\vec{\epsilon}')[W_+(R)+\epsilon] .\tag{15}$$

One also introduces a crucial quantity, the bound-continuum electronic coupling matrix element $V(\vec{\epsilon},\vec{R})$, defined by

$$\langle\phi_{\vec{\epsilon}}(\vec{R})\mid H_e\mid\phi_d(\vec{R})\rangle=V(\vec{\epsilon},\vec{R}) .\tag{16}$$

This is the quantity responsible for the ionization process.

Calling the total energy of the system E, referred to the asymptotic energy of the $A + B^+$ electronic configuration, the Schrödinger equation is

$$(H - E) | \psi \rangle\rangle = 0 . \qquad (17)$$

Projection operators Q and P are now introduced to separate the entrance-channel subspace (Q subspace) from the exit-channel subspace (P subspace)[15]:

$$Q = | \phi_d \rangle \langle \phi_d | , \qquad (18)$$

$$P = \int d\vec{\epsilon} \, | \phi_{\vec{\epsilon}} \rangle \langle \phi_{\vec{\epsilon}} | , \qquad (19)$$

where

$$\int d\vec{\epsilon} \equiv \int_0^\infty d\epsilon \int d\hat{\epsilon} . \qquad (20)$$

P and Q satisfy the usual conditions

$$Q + P = 1 , \qquad (21)$$

(completeness)

$$P^2 = P , \qquad (22)$$

$$Q^2 = Q , \qquad (23)$$

and

$$PQ = QP = 0 . \qquad (24)$$

The Schrödinger equation (17) is then equivalent to the coupled equations

$$(H_{PP} - E) P | \psi \rangle\rangle = -H_{PQ} Q | \psi \rangle\rangle , \qquad (25)$$

$$(H_{QQ} - E) Q | \psi \rangle\rangle = -H_{QP} P | \psi \rangle\rangle , \qquad (26)$$

where

$$H_{PP} \equiv PHP, \qquad (27a)$$

$$H_{QQ} \equiv QHQ . \qquad (27b)$$

The homogeneous equations

$$(H_{PP} - E) P | \psi_P \rangle\rangle = 0 , \qquad (28)$$

$$(H_{QQ} - E) Q | \psi_Q \rangle\rangle = 0 \qquad (29)$$

lead to the following coordinate representations:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + W_+(R) + \epsilon - E \right] \psi_{P\vec{\epsilon}}(\vec{R})$$
$$= -\int d\vec{\epsilon}' T_{\vec{\epsilon}\vec{\epsilon}'} \psi_{P\vec{\epsilon}'}(\vec{R}) , \qquad (30)$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + T_{dd} + W_d(R) - E \right] \psi_d(\vec{R}) = 0 . \qquad (31)$$

The nuclear wave functions $\psi_d(\vec{R})$ and $\psi_{P\vec{\epsilon}}(\vec{R})$ are simply

$$\psi_d(\vec{R}) = \langle \vec{R} | \psi_d \rangle \equiv \langle \vec{R} | \langle \phi_d | \psi_Q \rangle\rangle , \qquad (32)$$

$$\psi_{P\vec{\epsilon}}(\vec{R}) = \langle \vec{R} | \psi_{P\vec{\epsilon}} \rangle \equiv \langle \vec{R} | \langle \phi_{\vec{\epsilon}} | \psi_P \rangle\rangle , \qquad (33)$$

whereas T_{dd} and $T_{\vec{\epsilon}\vec{\epsilon}'}$ are the nondiabatic (nuclear motion) coupling operators given by

$$T_{dd} = -\frac{\hbar^2}{2\mu} (\langle \phi_d | \nabla_R^2 | \phi_d \rangle + 2 \langle \phi_d | \vec{\nabla}_R | \phi_d \rangle \cdot \vec{\nabla}_R) , \qquad (34)$$

$$T_{\vec{\epsilon}\vec{\epsilon}'} = -\frac{\hbar^2}{2\mu} (\langle \phi_{\vec{\epsilon}} | \nabla_R^2 | \phi_{\vec{\epsilon}'} \rangle + 2 \langle \phi_{\vec{\epsilon}} | \vec{\nabla}_R | \phi_{\vec{\epsilon}'} \rangle \cdot \vec{\nabla}_R) . \qquad (35)$$

We now assume (the adiabatic approximation) or, if possible, the CI wave functions ϕ_d and $\phi_{\vec{\epsilon}}$ are chosen such that

$$\langle \phi_d | \vec{\nabla}_R | \phi_d \rangle = \langle \phi_d | \nabla_R^2 | \phi_d \rangle = 0 , \qquad (36)$$

$$\langle \phi_{\vec{\epsilon}} | \vec{\nabla}_R | \phi_{\vec{\epsilon}'} \rangle = \langle \phi_{\vec{\epsilon}} | \nabla_R^2 | \phi_{\vec{\epsilon}'} \rangle = 0 . \qquad (37)$$

The homogeneous Schrödinger equations (30) and (31) then reduce to elastic potential scattering problems on the potential surfaces $W_+(R) + \epsilon$ and $W_d(R)$, respectively:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + W_+(R) + \epsilon - E \right] \psi_{P\vec{\epsilon}}(\vec{R}) = 0 , \qquad (38)$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + W_d(R) - E \right] \psi_d(\vec{R}) = 0 . \qquad (39)$$

The formal solution of Eq. (26) is

$$Q | \psi^+ \rangle\rangle = Q | \psi_Q^+ \rangle\rangle + G_Q^+ QHP | \psi^+ \rangle\rangle , \qquad (40)$$

with the Green's operator G_Q^+ given by

$$G_Q^+ = [Q(E + i\eta - H)Q]^{-1} . \qquad (41)$$

Meanwhile,

$$P | \psi^+ \rangle\rangle = G_P^+ PHQ | \psi^+ \rangle\rangle , \qquad (42)$$

where G_P^+ is defined similarly as G_Q^+, and there is no "homogeneous part" because of the initial condition that the system is initially entirely in the Q subspace. Thus, the formal solution to Eq. (26) can be expressed in terms of the homogeneous solution $| \psi_Q^+ \rangle\rangle$ as

$$Q | \psi^+ \rangle\rangle = (1 - G_Q^+ QHPG_P^+ PHQ)^{-1} Q | \psi_Q^+ \rangle\rangle . \qquad (43)$$

The coordinate representation of this equation then reads

$$\chi_d^+(\vec{R}) = \psi_d^+(\vec{R}) + \int d^3R' g_d^+(\vec{R}, \vec{R}')$$
$$\times \int d^3R'' \langle \vec{R}' | F^+ | \vec{R}'' \rangle \chi_d^+(\vec{R}'') , \qquad (44)$$

where

$$\chi_d^+(\vec{R}) \equiv \langle \vec{R} | \langle \phi_d | \psi^+ \rangle\rangle , \qquad (45)$$

$$F^+ \equiv \langle \phi_d | HPG_P^+ PH | \phi_d \rangle \qquad (46)$$

and

$$g_d^+(\vec{R}, \vec{R}') \equiv \langle \vec{R} | \langle \phi_d | G_Q^+ | \phi_d \rangle | \vec{R}' \rangle \qquad (47)$$

is the Green's function for Eq. (39). Hence the integro-differential equation for $\chi_d^+(R)$ equivalent to the integral equation (44) can be written as

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + W_d(R) - E \right]\chi_d^+(\vec{R})$$

$$= -\int d^3R' \langle \vec{R}\,|\,F^+\,|\,\vec{R}'\rangle\chi_d^+(\vec{R}') \; . \quad (48)$$

This is the Schrödinger equation we seek, with the energy-dependent and nonlocal potential specified by the kernel

$$\langle \vec{R}\,|\,F^+\,|\,\vec{R}'\rangle = \int d\vec{\epsilon}\,V^*(\vec{\epsilon},\vec{R})V(\vec{\epsilon},\vec{R}')G_P^+(E-\epsilon;\vec{R},\vec{R}') \; .$$

$$(49)$$

$G_P^+(E-\epsilon;\vec{R},\vec{R}')$ is the Green's function for the potential scattering problem specified by the potential $W_+(R)$, with total energy $E-\epsilon$. It can be expressed explicitly as

$$G_P^+(E-\epsilon;\vec{R},\vec{R}') = \int d\vec{E}' \frac{\psi_P^+(\vec{E}',\vec{R})\psi_P^{+*}(\vec{E}',\vec{R}')}{E+i\eta-\epsilon-E'}$$

$$+ \sum_n \frac{\psi_{Pn}(\vec{R})\psi_{Pn}^*(\vec{R}')}{E-\epsilon-E_n} \; , \quad (50)$$

where the positive-energy (continuum) outgoing states $\psi_P^+(\vec{E}',\vec{R})$ and the bound states $\psi_{Pn}(\vec{R})$ form a complete set, with the summation index n denoting the sum over rotational (JM) and vibrational (v) states. As in Eq. (20),

$$\int d\vec{E}' = \int_0^\infty dE' \int d\hat{E}' \; . \quad (51)$$

The energy dependence of the Green's function is crucial: It expresses the fact that part of the total energy of the system is carried away by the electron. As we shall demonstrate (Sec. III), it is largely this situation which leads to the energy dependence and the nonlocality of the potential in Eq. (48).

We now simplify this equation by partial-wave expansions:

$$\chi_d^+(\vec{E},\vec{R}) = \sum_{J,M} Y_{JM}^*(\hat{E})Y_{JM}(\hat{R})i^J \frac{\chi_J^+(E,R)}{R} \; , \quad (52)$$

$$\psi_P^+(\vec{E},\vec{R}) = \sum_{J,M} Y_{JM}^*(\hat{E})Y_{JM}(\hat{R})i^J \frac{F_J^+(E,R)}{R} \; , \quad (53)$$

$$\psi_{Pn}(\vec{R}) = Y_{JM}(\hat{R})\frac{F_J(E_J^v,R)}{R} \; . \quad (54)$$

The Green's function G_P^+ can also be expanded:

$$G_P(E-\epsilon;\vec{R},\vec{R}')$$

$$= \sum_{J,M} Y_{JM}(\hat{R})Y_{JM}^*(\hat{R}')\frac{1}{RR'}\mathscr{G}_{PJ}(E-\epsilon;R,R') \; , \quad (55)$$

where the Jth partial-wave Green's function $\mathscr{G}_{PJ}$ is given by

$$\mathscr{G}_{PJ}(E-\epsilon;R,R') = \int_0^\infty dE' \frac{F_J^+(E',R)F_J^{+*}(E',R')}{E-\epsilon-E'}$$

$$+ \sum_v \frac{F_J(E_J^v,R)F_J(E_J^v,R')}{E-\epsilon-E_J^v} \; . \quad (56)$$

The partial-wave expansion of the coupling term $V(\vec{\epsilon},\vec{R})$ has to be treated with care, since the electronic wave function $\phi_{\vec{\epsilon}}(\vec{r},\vec{R})$ is usually computed with the body-fixed symmetry axis $\hat{R}$ as the quantization axis for electronic angular momentum. One can partial-wave expand in terms of the angular momentum of the free electron:

$$\phi_{\vec{\epsilon}}^{\pm}(\vec{r},\vec{R}) = \sum_{l,m} [Y_{lm}^*(\hat{\epsilon})]_{\hat{R}}[Y_{lm}(\hat{r})]_{\hat{R}}i^l\mathscr{F}_l^{\pm}(\epsilon,r,\{\vec{r}\};\vec{R}) \; .$$

$$(57)$$

The superscripts $+$ $(-)$ denote the possibility of outgoing (incoming) free electrons; $\vec{r}$ is the coordinate of the free electron and $\{\vec{r}\}$ the collective coordinates of the bound ones. The subscript $\hat{R}$ denotes the circumstance that the arguments of the spherical harmonics are with respect to $\hat{R}$ as the Z axis. $\mathscr{F}_l^{\pm}$ stands for the product of the lth partial wave radial wave function of the free electron and the wave function of the rest of the (bound) electrons. From Eq. (16) one then obtains

$$V(\vec{\epsilon}^{\pm},\vec{R}) = \sum_{l,m} Y_{lm}(\hat{\epsilon})_{\hat{R}}(-i)^l$$

$$\times \int d^3r\,d\{\vec{r}\}[Y_{lm}^*(\hat{r})]_{\hat{R}}\mathscr{F}_l^{\pm*}H_e\phi_d \; . \quad (58)$$

Since $\hat{R}$ is a symmetry axis for the collision $A+B$ complex, the integral only depends on the magnitude R. Further, electronic angular momentum along $\hat{R}$ must be conserved for the ionization process, implying that there must be a selection rule for m such that the integral can be written

$$(-i)^l \int d^3r\,d\{\vec{r}\}[Y_{lm}^*(\hat{r})]_{\hat{R}}\mathscr{F}_l^{\pm*}H_e\phi_d$$

$$= \mathscr{V}_{lm}^{\pm}(\epsilon,R)\delta_{mm_0} \; , \quad (59)$$

where m_0 is the difference between the projection of the electronic angular momentum for ϕ_d and $\phi_{\vec{\epsilon}}$ along $\vec{R}$. We then have, on transforming to the space-fixed $A+B$ (c.m.) frame

$$V(\vec{\epsilon}^{\pm},\vec{R}) = \sum_{l,k} Y_{lk}(\hat{\epsilon})D_{km_0}^{(l)}(\hat{R})\mathscr{V}_{lm_0}^{\pm}(\epsilon,R) \; . \quad (60)$$

$\hat{R}$ denotes the set of Euler angles $(\phi_R,\theta_R,0)$ when the axis $\hat{R}$ is specified by the angles ϕ_R and θ_R with respect to the c.m. frame, and $D_{km_0}^{(l)}(\hat{R})$ is the appropriate rotation matrix element.

Equations (52)–(56) and (49) are next used in the right-hand side (rhs) of Eq. (48) and the result compared with the partial-wave expansion of the left-hand side (lhs) to finally obtain the partial-wave Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + W_d(R) + \frac{\hbar^2}{2\mu}\frac{J(J+1)}{R^2} - E \right]\chi_J^+(E,R)$$

$$= -\int_0^\infty dR' \left[\sum_{l,J'}(2J'+1)\begin{bmatrix} l & J' & J \\ 0 & 0 & 0 \end{bmatrix}^2 \left[\int_0^\infty d\epsilon\, \mathcal{V}_{l0}^{+*}(\epsilon,R)\mathcal{V}_{l0}^+(\epsilon,R')\mathcal{G}_{PJ'}^+(E-\epsilon;R,R') \right] \right]\chi_J^+(E,R') , \tag{61}$$

where we have specialized Eq. (60) to the case $m_0 = 0$ for simplicity.[5] A few points are to be noted about this equation. First, if the rhs were set equal to zero, it reduces to the Jth partial-wave equation for the potential scattering problem specified by the potential $W_d(R)$. Hence the rhs represents the entire effect of the bound-continuum coupling leading to ionization. Second, it is a coupled integro-differential equation with the Jth partial wave of the entrance channel coupled to many J' partial waves of the exit channel. The allowed J' values are related to J and l, the total angular momentum of the free, emitted electron, by the triangle inequality, as expressed through the presence of the 3-j symbol. Third, the interaction potential is, in general, nonlocal and energy dependent.

III. ORIGIN OF NONLOCALITY AND THE ASSUMPTIONS LEADING TO LOCALITY

The assumption that is usually made explicitly at this point is that the quantities $\mathcal{V}_{l0}(\epsilon,R)$ are ϵ independent.[5,6] We will retain this assumption in order to focus on the more fundamental and irremovable source of nonlocality, namely, the characteristic energy dependence of the Green's function $\mathcal{G}_{PJ'}^+$ in Eq. (61). As noted earlier, this dependence simply reflects the physical situation that the emitted electron carries away from the $A+B$ system an amount of energy equal to ϵ. Because of the presence of the integral over ϵ, this electron is actually capable of escaping with any positive energy, even with $\epsilon > E$. An investigation of the nonlocal nature of the potential must therefore begin with a consideration of the quantity

$$I_J(E,R,R') \equiv \int_0^\infty d\epsilon\, \mathcal{G}_{PJ}^+(E-\epsilon;R,R') . \tag{62}$$

The limits and especially the contour of integration require some care. The variable of integration is first changed from ϵ to $E' \equiv E - \epsilon$. The limits of integration are then between E and $-\infty$. If one naively takes the contour of integration along the real E' axis, one would immediately run into ambiguities because of the analytic properties of $\mathcal{G}_{PJ}(E';R,R')$: For fixed R and R' $\mathcal{G}_{PJ}(E';R,R')$ has a branch cut along the positive real E' axis with a branch point at $E'=0$ and simple poles corresponding to bound states at $E'=E_J^v$ on the negative real E' axis on the first (physical) sheet [see Eq. (56)]. The question is as follows: How should the integration contour be taken on the cut (along the positive real axis) physical sheet with respect to the positive real axis and the poles? We reason as follows. The $+$ superscript attached to $\mathcal{G}_{PJ}$ in Eq. (62) means that E is to approach the real axis from above [see Eqs. (41) and (50)], i.e., the fixed quantity E is situated on the upper rim of the cut. On the

other hand, in the integral over ϵ, since we are considering outgoing-wave emitted-electron wave functions, the variable ϵ is also to approach the real axis from above. This then means that the variable $E' \equiv E - \epsilon$ is always to approach the real axis from below. The implied contour of integration $C'(E, -\infty)$ for

$$I_J(E,R,R') = \int_{C'} dE'\, \mathcal{G}_{PJ}(E';R,R')$$
$$= \int_C dE'\, \mathcal{G}_{PJ}(E';R,R') \tag{63}$$

is thus that depicted in Fig. 2. C' can then always be deformed to the contour C, since there are no singularities besides the branch point $E'=0$ and the bound-state poles on the physical sheet. From now on we will consider the contour C and also assume that $E'=0$ does not correspond to a bound state.

To evaluate I_J we first separate the real and imaginary parts of $\mathcal{G}_{PJ}(E;R,R')$ for real values of E. We have, for E complex,

$$\mathcal{G}_{PJ}(E;R,R') = \int_0^\infty dE' \frac{F_J^+(E',R)F_J^{+*}(E',R')}{E-E'}$$
$$+ \sum_v \frac{F_J(E_J^v,R)F_J(E_J^v,R')}{E-E_J^v} . \tag{64}$$

For real E, then, with P the principal value,

$$\mathcal{G}_{PJ}(E\pm i\eta;R,R') = \left[P \int_0^\infty dE' \frac{F_J^+(E',R)F_J^{+*}(E',R')}{E-E'} \right.$$
$$\left. + \sum_v \frac{F_J(E_J^v,R)F_J(E_J^v,R')}{E-E_J^v} \right]$$
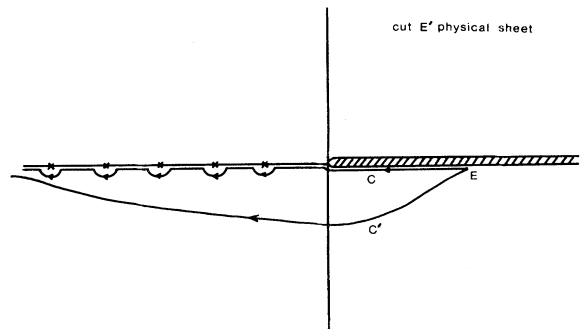$$\mp i\pi F_J^+(E,R)F_J^{+*}(E,R'), \quad E > 0 \tag{65}$$

FIG. 2. Contours of integration for $I_J(E,R,R')$. $E'=0$ is assumed not to correspond to a bound state. Cut is along the positive real E' axis. Crosses represent the bound-state poles.

$$\mathcal{G}_{PJ}(E;R,R') = - \int_0^\infty dE' \frac{F_J^+(E',R)F_J^{+*}(E',R')}{|E|+E'}$$

$$+ \sum_v \frac{F_J(E_J^v,R)F_J(E_J^v,R')}{E-E_J^v}, \quad E \le 0 . \quad (66)$$

Since $F_J^+(E',R)F_J^{+*}(E',R')$ (for real E') and the bound-state radial wave functions are always real (see Appendix I), we have achieved our purpose. We also note that the quantity $F_J^+(E,R)F_J^{+*}(E,R')$ is single valued in E. With the use of the contour C, I_J can then be written as

$$I_J(E,R,R') = -R_E - i\pi\gamma_E - P' - i\pi\Sigma_{\text{res}} , \quad (67)$$

where

$$R_E = \mathrm{P} \int_0^E dE' \int_0^\infty dE'' \frac{F_J^+(E'',R)F_J^{+*}(E'',R')}{E'-E''}$$

$$+ \sum_v F_J(E_J^v,R)F_J(E_J^v,R')\ln\left[\frac{E+|E_J^v|}{|E_J^v|}\right] , \quad (68)$$

$$\gamma_E = \int_0^E dE' F_J^+(E',R)F_J^{+*}(E',R') , \quad (69)$$

$$P' = - \int_0^\infty dE \int_0^\infty dE' \frac{F_J^+(E',R)F_J^{+*}(E',R')}{E+E'}$$

$$- \sum_v F_J(E_J^v,R)F_J(E_J^v,R')\mathrm{P}\int_0^\infty \frac{dE}{E-|E_J^v|} , \quad (70)$$

and Σ_{res} denotes the sum of the residues of $\mathcal{G}_{PJ}$ at the bound-state poles:

$$\Sigma_{\text{res}} = \sum_v F_J(E_J^v,R)F_J(E_J^v,R') . \quad (71)$$

The quantities R_E, γ_E, P', and Σ_{res} are all real.

It is immediately noted that the principal-value integral in Eq. (70) is logarithmically divergent. The problem of infinities, however, are basic to many bound-continuum theories, and we will not presume to treat it here. We will just make the observation that all infinities in I_J necessarily come from the real part and assume that either all these infinities are renormalizable, or when the energy (ϵ) dependence of $\mathcal{V}_{10}(\epsilon,R)$ is taken into account in the ϵ integral in Eq. (61), the latter becomes convergent. In either case, the real contribution of I_J to the rhs of Eq. (61)—an energy shift term with respect to the dominant real potential $W_d(R)$—is assumed to be small and set equal to zero. We are thus focusing on the nonlocal width terms in Eq. (61). The "renormalized" I_J and I_f^R can then be written as

$$I_J^R = -i\pi\Sigma_{\text{res}} - i\pi\gamma_E . \quad (72)$$

In view of Eqs. (69) and (71), and bearing in mind the completeness property of the set $\{F_J^+(E,R),F_J(E_J^v,R)\}$, i.e.,

$$\int_0^\infty dE\, F_J^+(E,R)F_J^{+*}(E,R')$$

$$+ \sum_v F_J(E_J^v,R)F_J(E_J^v,R') = \delta(R-R') , \quad (73)$$

we see that as E is decreased $I_f^R(E,R,R,')$ departs progressively from $-i\pi\delta(R-R')$ and nonlocality consequently increases in importance. This is readily seen from the R'

integral in the rhs of Eq. (61).

What happens when E becomes so small, or even negative, such that $-i\pi\delta(R-R')$ is a hopelessly poor representation for I_f^R? In the situation depicted in Fig. 1, it does not make much sense to consider $E < W_d(\infty)$, because there would not be much probability for collision happening in the first place. In this case, assuming $W_d(\infty) - W_+(\infty) \gg 0$, one may use the high-energy $(E \to \infty)$ approximation (to be given explicitly in Sec. IV) in which the local contribution to I_f^R is dominant. In various other situations, however, E can be small or negative, and yet collision can happen very readily. One such situation is depicted in Fig. 3, where ionization would necessarily entail a final bound $(AB)^+$ complex. This is a typical situation for associative ionization. Obviously, the local potential is a poor approximation here. Indeed, the energy E can be made so negative that only a very small number or even a single bound state need be included in I_f^R. The imaginary part of the potential is then manifestly and completely nonlocal.

We now proceed to demonstrate that, in the vigorous limit of $E \to \infty$, I_J leads to an entirely local potential. The method of proof is based on the function-analytic proof of the completeness of the set of eigenfunctions of the radial Schrödinger equation [Eq. (73)], as presented by Newton.[16]

It follows from Eq. (67) that, for $E \to \infty$,

$$I_J(\infty,R,R') = -R_\infty - i\pi\gamma_\infty - P' - i\pi\Sigma_{\text{res}} . \quad (74)$$

We consider the quantity

$$K_J(R,R') = \int_{C''} dE\, \mathcal{G}_{PJ}(E;R,R') , \quad (75)$$
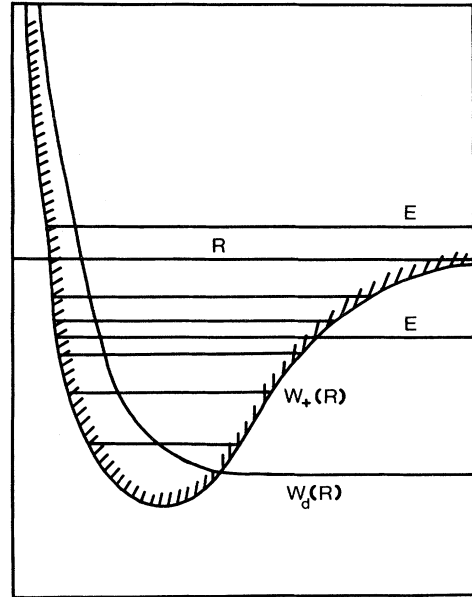

FIG. 3. Example of dynamical situation where nonlocal effects due to bound vibrational states of the $(AB)^+$ complex are important. Total energy E is assumed to be small or negative.

where C'' is the contour on the physical sheet shown in Fig. 4 with an infinite semicircle. By Cauchy's residue theorem, it is immediately seen that

$$K_J(R,R') = 2\pi i \, \Sigma_{\text{res}} \; . \tag{76}$$

On the other hand, we can write out the explicit contributions from the various segments of the contour:

$$K_J(R,R') = R_\infty - i\pi\gamma_\infty + l + P' + i\pi\Sigma_{\text{res}} \; , \tag{77}$$

where l is the contribution from the infinite semicircle. From the previous two equations it then follows that

$$R_\infty - i\pi\gamma_\infty + l + P' = i\pi\Sigma_{\text{res}} \; . \tag{78}$$

We now consider another quantity

$$L_J(R,R') = \int_{C'''} dE \; \mathscr{G}_{PJ}(E;R,R') \; , \tag{79}$$

where C''' is the contour on the physical sheet shown in Fig. 5, with an infinite circle. It can be shown that (see Appendix B) the contribution from the infinite circle is equal to $2l$, if K_J and L_J are considered in the context of the quantities

$$\int_0^\infty dR' h(R') K_J(R,R')$$

and

$$\int_0^\infty dR' h(R') L_J(R,R') \; ,$$

where $h(R')$ is an arbitrary well-behaved function of R' (square integrability will suffice). These are precisely the type of quantities of interest on the rhs of Eq. (61). Again, by comparing the residue theorem result with the explicit contributions of the segments of C''' to L_J, we obtain

$$-i\pi\gamma_\infty + l = i\pi\Sigma_{\text{res}} \; . \tag{80}$$

Equation (78) then implies that

$$R_\infty + P' = 0 \; . \tag{81}$$

We finally have, from Eqs. (74) and (80),

$$I_J(\infty, R, R') = -l \; . \tag{82}$$
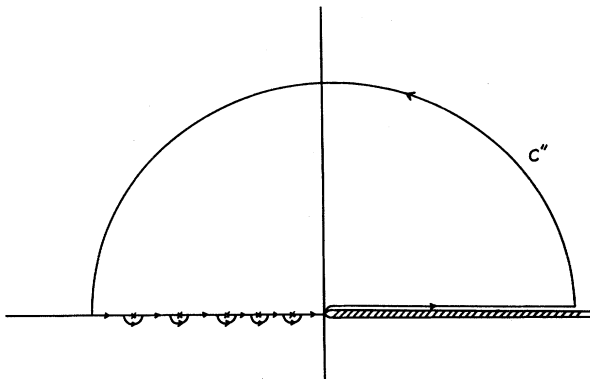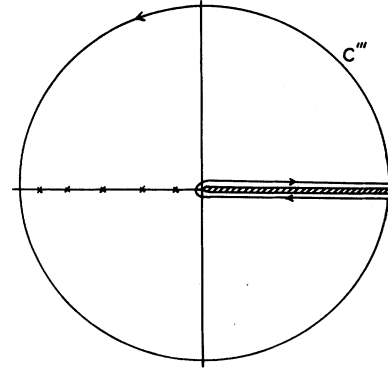
FIG. 5. Contour of integration for $L_J(R,R')$. Circle has infinite radius. Crosses represent bound-state poles.

The quantity

$$M(R) = \int_0^\infty dR' h(R') l(R,R') \tag{83}$$

is easily evaluated, as one can make use of the asymptotic form ($|E| \to \infty$) of the Green's function on the infinite semicircle, which is just the free-particle Green's function. In fact, the result is simply (details in Appendix B)

$$M(R) = i\pi h(R) \; , \tag{84}$$

which means that, in the exact limit $E \to \infty$, the potential is entirely local, as claimed. One might have argued that this result follows directly from Eqs. (72) and (73). This is, indeed, legitimate, provided we make the renormalization argument and neglect the shift term. Our demonstration, however, is more rigorous since it shows that the "infinities" R_∞ and P' cancel each other out exactly [Eq. (81)].

IV. THE LOW-ENERGY $(E \to 0)$ AND HIGH-ENERGY $(E \to \infty)$ LIMITS

The dynamical configuration represented in Fig. 3 with $E \to 0$ is a situation for associative ionization for which the low-energy-limit expression given below [Eq. (86)] is useful. For this case, from Eqs. (72), (69), and (71),

$$I_J^R(0,R,R') = -i\pi \sum_{\text{res}}$$
$$= -i\pi \sum_v F_J(E_J^v,R) F_J(E_J^v,R') \; . \tag{85}$$

This results in the following $E \to 0$ form for the rhs of Eq. (61):

$$i\pi \sum_{l,J',v} (2J'+1) \begin{bmatrix} l & J' & J \\ 0 & 0 & 0 \end{bmatrix}^2 \mathscr{V}_{l0}^{+*}(R) F_{J'}(E_{J'}^v,R)$$
$$\times \int_0^\infty dR' \mathscr{V}_{l0}^+(R') F_{J'}(E_{J'}^v,R') \chi_J^+(E,R') \; . \tag{86}$$

Here the bound-continuum part of the potential is completely nonlocal, coming entirely from the effects of the bound vibrational $(AB)^+$ states. Even though the coupling

FIG. 4. Contour of integration for $K_J(R,R')$. Semicircle has infinite radius. Crosses represent bound-state poles.

scheme is, in general, still quite involved, at least the lower J states can be treated with relative ease. This is owing to the fortunate situation that the kernel of the integro-differential equation (61) has been reduced to a sum of separable kernels.

Next, we consider the high-energy $(E \to \infty)$ limit. We can again make use of the function-analytic method as demonstrated in Sec. III (details in Appendix B). The procedure is to calculate

$$I_J^R(E \to \infty, R, R') = -i\pi\Sigma_{\text{res}} - i\pi\gamma_{E \to \infty} \tag{87}$$

for asymptotically large E but not in the *exact* limit as $E \to \infty$. For simplicity we will assume that

$$|E_J| < E \tag{88}$$

for all bound states in the P channel. $I_J^R(E \to \infty)$ can be evaluated by considering the integral

$$L_J'(R, R') = \int_{C^{iv}} dE \, \mathcal{G}_{PJ}(E; R, R') , \tag{89}$$

where C^{iv} is the same contour as C''' (Fig. 5), with the only difference that the circle has only an asymptotically large but not infinite radius, such that C^{iv} still contains all the bound-state poles. The same reasoning that led to Eq. (80) allows us to conclude that

$$\int_0^\infty dR' h(R') I_J^R(E \to \infty, R, R')$$
$$= -\frac{1}{2} \int_0^\infty dR' h(R') \int_{C(iv)} dE \, \mathcal{G}_{PJ}(E; R, R') , \tag{90}$$

where C(iv) denotes the circular part in C^{iv}.

We now evaluate

$$N'(R) \equiv \int_0^\infty dR' h(R') \int_{C(iv)} dE \, \mathcal{G}_{PJ}(E; R, R') \tag{91}$$

by using the technique detailed in Appendix B for $M(R)$, where the integral is done in the k plane instead $(E = \hbar^2 k^2/2\mu)$. First, compare Eq. (91) with Eq. (B1). $N'(R)$ is thus also given by Eq. (B6), with the understanding that in the integral for $f(R)$ [Eq. (B7)], the semicircu-

lar contour (in the k plane) only has an asymptotically large radius instead of an infinite one. Now, consider the following contour in the k plane for $f(R)$: starting from $-K$ on the real axis, running along the real axis to $-\delta$, encircling the origin with an infinitesimal circle of radius δ, continuing along the real axis to $+K$, and finally returning to $-K$ on a semicircle in the upper half-plane of radius K, with $E = \hbar^2 K^2/2\mu$. We have

$$f(R) = -\lim_{\delta \to 0} \left[\int_{-K}^{\delta} \frac{dk}{k} e^{ikR} + \int_{\delta}^{K} \frac{dk}{k} e^{ikR} \right.$$
$$\left. + \int_{\pi}^{0} i \, d\phi \, e^{i\delta e^{i\phi} R} \right]$$
$$= i\pi - 2i \int_0^{KR} dx \frac{\sin x}{x} = i\pi - 2i \, \text{Si}(KR) , \tag{92}$$

where $\text{Si}(z)$ denotes the sine-integral function. Referring to Eq. (61) we see that $h(R')$ is of the form

$$h(R') = \mathcal{V}_{l0}^+(R')\chi_J^+(E, R') . \tag{93}$$

The radial wave function $\chi_J^+(E, R')$ has the property that [see Eq. (52)]

$$\chi_J^+(E, R') \to 0 \quad \text{as} \quad R' \to 0 \tag{94}$$

while we can assume that the bound-continuum coupling vanishes asymptotically, i.e.,

$$\mathcal{V}_{l0}^+(R') \to 0 \quad \text{as} \quad R' \to \infty . \tag{95}$$

Thus, it follows from Eq. (B6) that

$$N'(R) = 2i\pi h(R) - (-1)^J \int_0^\infty dR' h'(R') f(R + R')$$
$$- \int_0^R dR' h'(R') f(R - R')$$
$$+ \int_R^\infty dR' h'(R') f(R' - R) . \tag{96}$$

Combining this result with Eqs. (90) and (92), and substituting into the rhs of Eq. (61), we finally arrive at the $E \to \infty$ limit for the rhs of Eq. (61):

$$i\pi \left[\sum_l |\mathcal{V}_{l0}^+(R)|^2 \right] \chi_J^+(E, R) - i \sum_{l,J'} (2J' + 1) \begin{bmatrix} l & J' & J \\ 0 & 0 & 0 \end{bmatrix}^2 \mathcal{V}_{l0}^{+*}(R)$$

$$\times \left[\int_0^R dR' \frac{d}{dR'} [\mathcal{V}_{l0}^+(R')\chi_J^+(E, R')] \left[\frac{\pi}{2} - \text{Si}[K(R - R')] \right] \right.$$

$$- \int_R^\infty dR' \frac{d}{dR'} [\mathcal{V}_{l0}^+(R')\chi_J^+(E, R')] \left[\frac{\pi}{2} - \text{Si}[K(R' - R)] \right]$$

$$\left. + (-1)^J \int_0^\infty dR' \frac{d}{dR'} [\mathcal{V}_{l0}^+(R')\chi_J^+(E, R')] \left[\frac{\pi}{2} - \text{Si}[K(R + R')] \right] \right] , \tag{97}$$

where, for the first term, we have made use of the relationship

$$\sum_{j_3, m_3} (2j_3+1) \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{bmatrix} \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{bmatrix} = \delta_{m_1 m_1'} \delta_{m_2 m_2'} . \quad (98)$$

This term represents the entirely local portion. It contains the imaginary part of the complex potential

$$W_J(R) = W_d(R) - i\pi \Gamma_J(R) \quad (99)$$

that is usually used in local theories, where

$$\Gamma_J(R) = \sum_l |\mathscr{V}_{l0}^+(R)|^2 . \quad (100)$$

It is important to note that $W_J(R)$ is also energy independent. The other terms depend critically on energy. In fact, since $\mathrm{Si}(x) \to \pi/2$ as $x \to \infty$, these terms must be perturbation terms for $K \to \infty$, i.e., for large energy.

V. SUMMARY AND CONCLUDING REMARKS

In this work we have traced the main assumption leading to the local approximation [Eqs. (99) and (100)], namely, the infinite collision-energy assumption. Besides rendering the potential local, this assumption also makes the partial-wave equations [Eq. (61)] uncoupled, thus simplifying the problem enormously. However, we have also seen that, even if we retain the other assumption leading to locality, namely, the assumption of the ϵ independence of the coupling $V(\vec{\epsilon}, \vec{R})$, nonlocality cannot be avoided if we go to the low-energy regime, especially if the dynamical situation allows associative ionization. Furthermore, the partial-wave equations are coupled, and except for very low J states, one may have to resort to decoupling approximation schemes. We have produced explicit forms for the nonlocal potential for the low- and high-energy limiting cases. For the former, the nonlocal term is separable, whereas for the latter, it is only a perturbation. Thus these cases offer significant simplifications; and in our view, further work investigating the effects of the nonlocal potential may profitably start from these two extreme situations. The case of intermediate collision energy is far more difficult, since the nonlocal term is neither small nor separable.

One could consider various ramifications of the problem. Despite the fact that there exists computational evidence that the ϵ dependence of the bound-continuum coupling matrix elements can be small,[17,18] the most obvious improvement to the theory is perhaps the incorporation of this dependence. Once this is done, the theory becomes nonlocal even if the $E \to \infty$ limit is taken; and localization procedures would necessarily be approximate, depending on the nature of the ϵ dependence. In the absence of an exact knowledge of this dependence (which is usually the case), it may be very difficult to draw general conclusions. One possible direction of attack, however, is to consider empirical functional forms for $\mathscr{V}_{l0}(\epsilon, R)$ for real $\epsilon > 0$, and then analytically continue them to complex ϵ. The ϵ integral in Eq. (61) may then be considered in the light of the analytic properties of $\mathscr{V}_{l0}(\epsilon, R)$, just as in the present work, the integral is done by consideration of the analytic properties of $\mathscr{G}_{PJ}(E - \epsilon; R, R')$. It is thus conceivable that the singularities of $\mathscr{V}_{l0}(\epsilon, R)$ may play the same role as the bound-state poles of $\mathscr{G}_{PJ}$.

There is one concrete situation where the ϵ dependence of $V(\vec{\epsilon}, \vec{R})$ may be important: the case of laser-induced Penning or associative ionization. Unlike the field-free case, $V(\vec{\epsilon}, \vec{R})$ now originates from the radiative coupling between bound and free electrons, and should be strongly dependent on the energy of the free electron. This complication, however, is compensated for to a certain extent by the maneuverability of the laser frequency. This effectively allows one to tune E instead, possibly to regions where either the high- or low-energy limits become applicable. Thus, the field-induced processes offer abundant and convenient dynamical situations for the study of nonlocal effects.

ACKNOWLEDGMENTS

APPENDIX A: THE RADIAL WAVE FUNCTIONS $F_J(E,R)$ AND $F_J(E_J^v, R)$

Here we collect a few useful facts concerning these wave functions. Throughout this paper we have used the normalization condition

$$\int d^3R \, \psi_P^*(\vec{E}, \vec{R}) \psi_P(\vec{E}', \vec{R}) = \delta(E - E') , \quad (A1)$$

where

$$\delta(\vec{E} - \vec{E}') = \delta(E - E') \delta(\hat{k} - \hat{k}') \quad (A2)$$

with

$$E = \hbar^2 k^2 / 2\mu . \quad (A3)$$

Equation (53) then implies the following normalization constant for $F_J(E,R)$:

$$F_J(E,R) = \left[\frac{2\mu k}{\pi \hbar^2} \right]^{1/2} \frac{\psi_J(k,R)}{k} , \quad (A4)$$

where

$$\psi_J(k,R) = \frac{k^{J+1}}{f_J(-k)} \phi_J(k,R) . \quad (A5)$$

$\phi_J(k,R)$ is the regular solution for the potential $W_+(R)$ satisfying the $R = 0$ boundary condition,

$$\lim_{R \to 0} \frac{(2J+1)!!}{R^{J+1}} \phi_J(k,R) = 1 , \quad (A6)$$

and is an entire function of k^2. It also has the property that it is real for real k and for the purely imaginary k's which correspond to bound states.[19] $f_J(k)$ is the Jost

function for $W_+(R)$. For real k, it satisfies[19]

$$f_J^*(-k)=f_J(k) \ . \tag{A7}$$

Hence,

$$F_J(E,R)F_J^*(E,R')=\frac{2\mu}{\pi\hbar^2}k^{2J+1}\frac{\phi_J(k,R)\phi_J(k,R')}{|f_J(k)|^2} \tag{A8}$$

is always real for real E. The bound-state wave functions are given in terms of the regular solution by

$$F_J(E_J^v,R)=\frac{\phi_J(i\kappa_J^v,R)}{N_J^v}\equiv\frac{\phi_J^v(R)}{N_J^v} \ , \tag{A9}$$

where $k=i\kappa_J^v$ corresponds to the vth vibrational bound state, and the normalization constant N_J is given by

$$(N_J^v)^2=\int_0^\infty dR[\phi_J^v(R)]^2 \ . \tag{A10}$$

APPENDIX B: EVALUATION OF $M(R)$ [EQ. (83)]

The method given below follows closely that presented by Newton,[16] with minor modifications to suit our purposes. We include it here for two reasons: first, for ease of reference and completeness; and second, some of the intermediate results are crucial for the $E\to\infty$ result [Eq. (97)] derived in Sec. IV. We begin by calculating

$$N(R)\equiv\int_0^\infty dR'h(R')\int_{C_1}dE\,\mathscr{G}_{PE}(E;R,R') \ , \tag{B1}$$

where C_1 is the large-circle part in the contour of Fig. 5. To do the integral, it is best to work in the k plane $(E=\hbar^2k^2/2\mu)$ because of the following asymptotic form of $\mathscr{G}_{PJ}(E;R,R')$:[16] as $|E|\to\infty$ on the physical sheet,

$$\mathscr{G}_{PJ}(E;R,R')\to\left[\frac{2\mu}{\hbar^2}\right]\left[\frac{1}{2ik}[e^{ik(R_>-R_<)}-(-1)^Je^{ik(R_>+R_<)}]+0\left[\frac{1}{|k|}e^{-v|R-R'|}\right]\right] \ , \tag{B2}$$

where $v=\text{Im}k$, and $R_>$ $(R_<)$ denote the smaller (larger) of R and R'. We note that the dominant term is just the free-particle Green's function, and the order term means that

$$0(g(k))=f(k)g(k) \ , \tag{B3}$$

such that $f(k)\to0$ as $|k|\to\infty$ in the upper half-plane. We then have

$$N(R)=\int_0^\infty dR'h(R')\int_{sc}\frac{k\,dk}{ik}[e^{ik(R_>-R_<)}-(-1)^Je^{ik(R_>+R_<)}] \ , \tag{B4}$$

where sc denotes an infinite semicircle in the upper half-plane in the positive direction. Breaking up the R' integral into two parts, we obtain

$$N(R)=\frac{1}{i}\int_0^R dR'h(R')\int_{sc}dk[e^{ik(R-R')}-(-1)^Je^{ik(R+R')}]$$

$$+\lim_{\zeta\to\infty}\frac{1}{i}\int_R^{R+\zeta}dR'h(R')\int_{sc}dk[e^{ik(R'-R)}-(-1)^Je^{ik(R+R')}]$$

$$=\frac{1}{i}\int_{sc}dk\left[\int_0^R dR'h(R')e^{ik(R-R')}-(-1)^J\int_0^R dR'h(R')e^{ik(R+R')}\right]$$

$$+\lim_{\zeta\to\infty}\frac{1}{i}\int_{sc}dk\left[\int_R^{R+\zeta}dR'h(R')e^{ik(R'-R)}-(-1)^J\int_R^{R+\zeta}dR'h(R')e^{ik(R+R')}\right] \ . \tag{B5}$$

Performing the R' integration by parts, we have

$$N(R)=2h(R)\int_{sc}\frac{dk}{k}-h(0)f(R)-\int_0^R dR'h'(R')f(R-R')$$

$$-(-1)^J\left[h(0)f(R)+\int_0^R dR'h'(R')f(R+R')\right]$$

$$-\lim_{\zeta\to\infty}\left[h(R+\zeta)f(R)-\int_R^{R+\zeta}dR'h'(R')f(R'-R)\right]$$

$$-(-1)^J\lim_{\zeta\to\infty}\left[\int_R^{R+\zeta}dR'h'(R')f(R+R')-h(R+\zeta)f(2R+\zeta)\right] \ , \tag{B6}$$

where

$$f(R)=\int_{sc}\frac{dk}{k}e^{ikR} \ , \tag{B7}$$

and $h'(R')$ denotes the derivative of $h(R')$. It is evident that for any fixed R, by Jordan's lemma, $f(R)\to0$ as the

radius of the semicircle approaches ∞. We thus have

$$N(R)=2h(R)\int_{sc}\frac{dk}{k}=2i\pi h(R) \ . \tag{B8}$$

If we now consider the semicircle in the E plane in C'' (Fig. 4), the equivalent k-plane contour would be a

quarter-circle (qc) in the positive direction in the first quadrant. The result is again given by Eq. (B6), but with all the sc contours replaced by qc contours. Since again, by Jordan's lemma,

$$f'(R) = \int_{qc} dk \frac{e^{ikR}}{k} \rightarrow 0 \tag{B9}$$

as the radius of qc approaches infinity,

$$M(R) = 2h(R) \int_{qc} \frac{dk}{k} = i\pi h(R) . \tag{B10}$$

Thus the E-plane infinite-semicircle contribution is exactly $\frac{1}{2}$ the infinite-full-circle contribution, confirming the assertion made directly after Eq. (79). Equation (B10) is also the result asserted by Eq. (84).

[1]For a review of both theoretical and experimental aspects of the problem, the reader may consult A. Niehans, in *Advances in Chemical Physics,* edited by J. Wm. McGowan (Wiley, New York, 1981), Vol. XLV, p. 399ff.

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