R-matrix approach with proper boundary conditions for dissipative and nondissipative collision processes

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We develop an R-matrix approach to treating collision processes which explicitly takes into account, by means of a simple energy-dependent analytic function, the out-of-phase oscillations of the incident and scattered standing waves in the interior region. Thereby we avoid the use of the Bloch operator. In place of the Bloch operator the incident wave provides the source term in an inhomogeneous equation for the scattered wave. We take those subchannels not treated exactly into account *via* the optical potential, which is generally non-Hermitian due to dissipation at the boundary. The optical potential is constructed on a real analytic basis using a resolvent that satisfies outgoing-wave boundary conditions. The use of an analytic basis together with the direct determination of the K matrix, rather than the R matrix, at the boundary (this is done by matching the interior wave function to the nearly exact analytic solution beyond the boundary) makes the method particularly well suited to the treatment of ultracold collisions. We have tested our method by applying it to one-photon single-ionization of He($1s^2$) accompanied by excitation to $He^+(2s)$ or $He^+(2p)$ for photon energies above the complete breakup threshold, where the optical potential is non-Hermitian. Excellent agreement with experiment is obtained for the cross sections for photoionization to both He^+ ($n = 1$) and to He^+ ($n = 2$). The $2s$-to-$2p$ branching ratio is strongly influenced by both the optical potential and, at photon energies less than a few tens of eV above the breakup threshold, the nonadiabatic dipole mixing of the $2s$ and $2p$ states.

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I. INTRODUCTION

Among the many methods for treating collision processes, the R-matrix approach holds a special appeal, as attested to by the breadth of applications in atomic and nuclear physics [1,2]. Its primary merit is that the Schrödinger equation has only to be solved numerically within a finite region, or "box," whose boundary R is sharply defined. Beyond the boundary the solution can be found, in principle to arbitrary accuracy, by an asymptotic expansion of the wave function. This is especially valuable when interactions are of long-range, for example, those of Coulomb or dipole nature. A further advantage of the R-matrix approach is that real boundary conditions can be imposed, so the numerical solution within the box is real. By matching the interior solution to the exterior one the R-matrix can be expressed in terms of a real, symmetric K matrix. Thereby the scattering matrix, that is, the S matrix from which the scattered flux can be extracted, is automatically unitary.

However, the R-matrix approach as traditionally applied is not without drawbacks. Often a basis is employed on which the representation of the Hamiltonian is not Hermitian. Although the Hamiltonian can be modified by adding a term, the "Bloch operator" [3], which acts at the boundary of the box to compensate for a spurious surface term and thereby ensures the modified Hamiltonian is Hermitian, this operator is singular and cannot easily be accounted for by the basis; as a result convergence with respect to basis size is slow, and a correction, the "Buttle correction," is often made [4]. Another issue relates to the inclusion of pseudostates in the basis which are supposed to model those subchannels not treated exactly. Pseudostates do not satisfy physical boundary conditions, and this can lead to unphysical consequences. For example, spurious resonances can appear. More significantly, since the S matrix is constrained to be unitary, pseudostates do not allow for the loss of flux into *open* subchannels that are omitted or not treated accurately; this can lead to erratic convergence.

In this paper we develop an R-matrix approach to treating a two-electron system which is free of the two drawbacks mentioned above. To achieve this goal we begin by dividing state space, where the real system resides, into P and Q subspaces [5,6]. Subchannels that are treated exactly are included in P space; the remaining subchannels belong to Q space. The P and Q subspaces are coupled by the "optical potential." The real system is governed by a Hermitian Hamiltonian H. However, the component of its wave function in P space is identical to the wave function for a fictitious system which resides only in P space and which is governed by an effective Hamiltonian that is the sum of a sub-Hamiltonian PHP, which is Hermitian, and the optical potential, which may be non-Hermitian. It is sufficient to solve the Schrödinger equation for this fictitious system since the component of the real system's wave function in Q space can be obtained from the component in P space by means of the Q space resolvent, assuming this is known.

We construct PHP on an analytic hybrid basis that has two length scales, short and long. The short length scale is the linear dimension of the region where the two electrons interact strongly, while the long length scale is the box radius R; the latter characterizes the distance beyond which the unbound electron moves in a local, static potential that results from just the Coulomb and dipole fields of the residual one-electron ion or atom. The basis functions are real standing waves, all of which vanish at the boundary of the box. Therefore, PHP is represented by a matrix that is automatically Hermitian.

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However, the P-space wave function does not converge uniformly on this basis since, in general, it does not vanish at the boundary. Nevertheless, the P-space wave function can be decomposed into two parts, a "scattered" wave which does vanish at the boundary and which converges *uniformly* with respect to basis size when it is expanded on the basis, and an "incident" wave which is out of phase with the scattered wave and does not vanish at the boundary. The incident wave is not expanded on the basis; rather, it replaces the Bloch operator as a source term. Thus, we rewrite the Schrödinger equation for the P-space wave function as an inhomogeneous equation whose inhomogeneous term contains the incident wave.

The only constraint on the incident wave is that it satisfies the correct boundary conditions at the origin and at infinity. It is not necessary that the incident wave be an eigenfunction of PHP since the sum of the scattered and incident waves is matched to an (almost exact) eigenfunction of PHP at the boundary, so the difference satisfies standing-wave boundary conditions and therefore can be described by the basis. However, the more closely that the incident wave resembles an eigenfunction of PHP, with an eigenvalue equal to the energy of interest, E say, the less is the demand placed on the basis. We choose the incident wave to have a simple, specified, analytic, energy-dependent form which vanishes appropriately at the origin, satisfies the exact standing-wave boundary conditions at infinity, and has some of the characteristics of an eigenfunction of PHP with eigenvalue E. As indicated above, the boundary is sufficiently far that beyond it we need retain only the long-range Coulomb $(1/r)$ and static dipole $(1/r^2)$ fields. By following the seminal paper of Seaton [7] we match the interior wave function *and* its derivative at the boundary to the analytic solution of the Schrödinger equation for a particle moving in a combination of Coulomb and dipole fields. Thereby we determine the K matrix, rather than the R matrix, at the boundary. This boundary need not be adjusted with E, at least not over a wide range of energies.

The basis functions that we employ to span Q space are also real and analytic but they contain no reference to the boundary of the box. In order to construct the optical potential we must obtain the Q-space resolvent which satisfies outgoing-wave boundary conditions at infinity. This is accomplished by exploiting the analytic properties of the resolvent with respect to its underlying time scale, a technique that has been described in detail elsewhere and is only briefly mentioned in this paper [8]. If Q space contains open subchannels, probability flux is transferred from P to Q space. Therefore, while the real system is *non*dissipative, the fictitious system is generally dissipative (it is governed by an effective Hamiltonian that is non-Hermitian). Consequently, the K matrix for the fictitious system is not necessarily real, and the corresponding S matrix is not necessarily unitary. Only if all subchannels that belong to Q space are closed are the S matrices for the fictitious and real systems the same; otherwise, the S matrix for the fictitious system is a nonunitary submatrix of the S matrix for the real system. However, both the K and the S matrices for the fictitious system are symmetric.

We have tested the method by applying it to one-photon single-ionization of helium accompanied by excitation to the $2s$ and $2p$ states of the residual ion He^+ at photon energies above the complete breakup threshold. In this region infinitely many subchannels are open and there is a significant loss of flux from P space. Furthermore, since the $2s$ and $2p$ bound states of the hydrogenic ion are degenerate in energy, the ion has a permanent dipole moment. Although the photoelectron moves swiftly and is only barely deflected by the dipole field, its electric field influences the permanent dipole moment of the ion and therefore influences the $2s$-to-$2p$ branching ratio.

The computational demands are modest, and we find that convergence with respect to basis size is rapid provided that we include the variational correction to the K matrix which follows from the Kohn variational principle. The calculations can easily be performed on a modern desktop.

In a companion paper we report on a study of the behavior of the photoionization cross section at photon energies close to, and up to a few eV above, the $n = 2$ ionization-excitation threshold [9]. We employed the same method, and found that the cross section has a cusp at threshold; this cusp is associated with the adiabatic transfer of population between the $2s$ and $2p$ states at asymptotically large distances.

In the next section we present a formal development of our method. In Sec. II A we briefly set up the framework of the optical potential. In Sec. II B we introduce a nontraditional scalar product which is useful for describing both dissipative and nondissipative processes. In Sec. II C we discuss the Bloch operator, and we show in Sec. II D that this operator is not needed. In Sec. III we describe the basis that we use to cover the interior region, that is, the region inside the box. As mentioned above, our basis functions are simple, real, analytic functions. In Sec. IV we discuss some of the differences between the traditional R-matrix approach and the one taken here. In Sec. V we present the results of our test application to photoionization of He with simultaneous excitation of He^+ at energies above the breakup threshold, and we compare our results to those of others. In Appendix A we generalize Seaton's method for including a static dipole field by adding the Coulomb field. In Appendix B we verify that the K matrix is symmetric, even though it is complex, and we derive the variational correction which follows from the Kohn variational principle.

II. HAMILTONIAN AND OPTICAL POTENTIAL

A. Optical potential

Consider a two-electron ion or atom whose Hamiltonian operator is $\mathbf{H}$ and whose energy E lies in the continuous spectrum. (Henceforth we use boldface for operators.) A stationary state is represented by a solution of the time-independent Schrödinger equation:

$$(\mathbf{H} - E\mathbf{1})|\Psi\rangle = 0. \tag{1}$$

Among those subchannels that are open below the threshold for complete breakup, consider the N_c most energetic, and suppose that in the remote past the system is prepared in one of these. There might be other less energetic subchannels that are open, and the system can evolve into any one of these, but they are not permitted to be entrance subchannels. We denote by $|\Psi^{(i)}(E)\rangle$ the solution of Eq. (1) which represents the system when it is prepared in the ith entrance subchannel; there are N_c independent solutions, with $i = 1,2,\ldots,N_c$.

Let $\mathbf{P}$ be the operator which projects onto the subspace spanned by the N_c entrance subchannels $i = 1,2,\ldots,N_c$. The orthogonal projection operator is $\mathbf{Q} = \mathbf{1} - \mathbf{P}$. If the kth electron is the one that remains bound, and if $\mathbf{P}_k$ projects onto the N_c most strongly bound states of the residual one-electron ion, we have [6]

$$\mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2 - \mathbf{P}_1\mathbf{P}_2. \tag{2}$$

The resolvents which act on the P and Q spaces, respectively, are

$$\mathbf{G}_P(E) \equiv \mathbf{P}/(E\mathbf{1} - \mathbf{PHP}), \tag{3}$$

$$\mathbf{G}_Q(E) \equiv \mathbf{Q}/(E\mathbf{1} - \mathbf{QHQ}). \tag{4}$$

The projection $\mathbf{P}|\Psi^{(i)}(E)\rangle$ is a solution of the homogeneous equation [5,6],

$$[\mathbf{H}_{\rm eff}(E) - E\mathbf{1}]\mathbf{P}|\Psi\rangle = 0, \tag{5}$$

where $\mathbf{H}_{\rm eff}(E)$ is an energy-dependent effective Hamiltonian which completely governs the dynamics within P space:

$$\mathbf{H}_{\rm eff}(E) = \mathbf{P}[\mathbf{H} + \mathbf{HQG}_Q(E)\mathbf{QH}]\mathbf{P} \tag{6}$$

$$\equiv \mathbf{PHP} + \mathbf{V}_{\rm opt}(E). \tag{7}$$

We can view $\mathbf{H}_{\rm eff}(E)$ as the Hamiltonian that governs a fictitious system which resides entirely in P space. The projection $\mathbf{Q}|\Psi^{(i)}(E)\rangle$ can be expressed directly in terms of the solution of Eq. (5) as

$$\mathbf{Q}|\Psi^{(i)}(E)\rangle = \mathbf{G}_Q(E)\mathbf{QHP}|\Psi^{(i)}(E)\rangle. \tag{8}$$

Since all possible entrance subchannels of interest belong to P space, none to Q space, $\mathbf{Q}|\Psi^{(i)}(E)\rangle$ must satisfy *outgoing-wave* boundary conditions. Therefore, $\mathbf{G}_Q(E)$ must be chosen accordingly. The method by which we evaluate $\mathbf{G}_Q(E)$ entails the time average of a series that is derived from an expansion of the time-translation operator in Laguerre polynomials; this method has been described in detail elsewhere and need not be pursued here [8].

The Hamiltonian **PHP** accounts only for transitions within P space, while the optical potential

$$\mathbf{V}_{\rm opt}(E) = \mathbf{PHQG}_Q(E)\mathbf{QHP} \tag{9}$$

accounts for both real and virtual transitions from P to Q space. If real transitions take place to Q space, as happens when more than N_c subchannels are open, $\mathbf{G}_Q(E)$ generates both damped and undamped outgoing waves, corresponding to closed and open subchannels, respectively. Writing $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}_{ee}$, where $\mathbf{V}_{ee}$ is the interaction between electrons, and noting that $\mathbf{P}$ and $\mathbf{Q}$ each commute with $\mathbf{H}_0$, we have $\mathbf{PHQ} = \mathbf{PV}_{ee}\mathbf{Q}$ and $\mathbf{QHP} = \mathbf{QV}_{ee}\mathbf{P}$.

While $\mathbf{Q}|\Psi^{(i)}(E)\rangle$ is required to satisfy outgoing-wave boundary conditions, we have the freedom to impose S-matrix or K-matrix boundary conditions, or variants of these, on the solutions of Eq. (1). If we impose S-matrix boundary conditions—expressed by Eqs. (A13) or (A17) below—and normalize the solutions on the energy scale, so that

$$\langle\Psi^{(i)}(E)|\Psi^{(j)}(E')\rangle = \delta_{ij}\delta(E - E'), \tag{10}$$

the incoming flux in each entrance subchannel i is independent of i. From these solutions we can construct the $N_c \times N_c$ submatrix of the S matrix for the real system; this submatrix is the S matrix for the fictitious system that resides in P space. Since the flux associated with the real system is conserved, the S matrix for the real system is unitary. However, the S matrix for the fictitious system need not be unitary; it is unitary if no more than N_c subchannels are open, that is, if the submatrix is in fact the whole S matrix for the real system.

The freedom that we exercised in choosing the boundary conditions that fix the solutions of Eq. (1) extends to Eq. (5). Here it is most advantageous to impose standing-wave, that is, K-matrix, boundary conditions—expressed by Eqs. (A1) or (A2) below—because the K matrices for both the real and the fictitious systems are symmetric. In general the K matrix for the fictitious system is complex, but if no more than N_c subchannels are open it is real and the corresponding S matrix is automatically unitary. The symmetry of the K matrix follows from the property that both $\mathbf{H}$ and $\mathbf{PHP}$ are Hermitian when they are sandwiched between standing waves that are in phase with each other.

This last remark deserves brief elaboration because while $\mathbf{H}$ is Hermitian on state space—the space of *all* physically realizable (normalizable) states—standing waves which extend to infinity are not physically realizable and exist only in an ideal limit. However, this is only a formal technicality. A standing wave carries no net energy across a surface, nor does a superposition of standing waves that are in phase, and therefore no physical effect can arise from slowly damping out these waves at asymptotically large distances.

In general $\mathbf{V}_{\rm opt}(E)$, and therefore the effective Hamiltonian $\mathbf{H}_{\rm eff}(E)$, are not Hermitian; only if the open subchannels number N_c are they Hermitian. Hence, in general the fictitious system is *dissipative*; that is, the probability for finding it in P space is not conserved in time. To deal with dissipative systems we introduce, in the next section, a dual space which has a *linear* correspondence with state space, in contrast to the customary dual space which has an *anti*linear correspondence with state space. A bra in the new dual space has a one-to-one linear correspondence with a space-time-reflected ket in state space.

B. Space-time reflections

Consider for the moment any system whose Hamiltonian operator $\mathbf{H}(t)$ is Hermitian on state space, where for generality we allow $\mathbf{H}(t)$ to depend on the time, so the system can be open or closed. Furthermore, suppose that $\mathbf{H}(t)$ is invariant under individual time-reversal and spatial reflections in the xy and yz planes. We denote the operator which simultaneously effects all three reflections by $\boldsymbol{\Upsilon}$. The projection of the total angular momentum of the system along the z axis is reversed under either a time reflection ($t \to -t$) or a space reflection ($x \to -x$) in the yz plane, but the product of these two reflections leaves the z component of the angular momentum unchanged, as does a space reflection ($z \to -z$) in the xy plane. Note that the product of the two space reflections is equivalent to a rotation through π about the y axis.

Suppose that the system of interest is composed of two subsystems which undergo a collision. Let the system enter the collision along the direction of the positive z axis in subchannel i, in the center-of-mass frame. After the collision has occurred the scattered wave is a superposition of outgoing waves; the fragments move outward in all directions in various subchannels. Now consider the mapping of this state under $\boldsymbol{\Upsilon}$. The transformed state describes a collision which begins with the system entering from all directions in various subchannels; when the collision is over the system exits along the direction of the positive z axis in subchannel i. Thus, the transformed state describes the time reverse of the radial motion in the original collision, but the angular motion in the original collision is preserved by the rotation through π about the y axis.

The operator $\boldsymbol{\Upsilon}$ is *anti*unitary, and, adopting the Wigner phase convention [10], it has the property

$$\boldsymbol{\Upsilon}^2 = \mathbf{1} \tag{11}$$

for both fermionic and bosonic systems. The invariance of the Hamiltonian is expressed by

$$\boldsymbol{\Upsilon}^\dagger \mathbf{H}(t)\boldsymbol{\Upsilon} = \mathbf{H}(-t). \tag{12}$$

The state ket $|\Psi(t)\rangle$ at time t can be expressed in terms of the state ket at the boundary time $t = 0$ through the *unitary* time-translation operator $\mathbf{U}(t)$; we have $|\Psi(t)\rangle = \mathbf{U}(t)|\Psi(0)\rangle$, where $\mathbf{U}(t)$ is a solution of

$$i\hbar\frac{d}{dt}\mathbf{U}(t) = \mathbf{H}(t)\mathbf{U}(t), \tag{13}$$

subject to the boundary condition

$$\mathbf{U}(0) = \mathbf{1}. \tag{14}$$

Pre- and postmultiplying both sides of Eq. (13) by $\boldsymbol{\Upsilon}$, using Eq. (12) to replace $\mathbf{H}(t)$ by $\boldsymbol{\Upsilon}^\dagger\mathbf{H}(-t)\boldsymbol{\Upsilon}$, and taking into account that $\boldsymbol{\Upsilon}$ complex conjugates c numbers, it follows from $\boldsymbol{\Upsilon}\boldsymbol{\Upsilon}^\dagger = \mathbf{1}$, after changing the sign of t, that

$$i\hbar\frac{d}{dt}\boldsymbol{\Upsilon}^\dagger\mathbf{U}(-t)\boldsymbol{\Upsilon} = \mathbf{H}(t)\boldsymbol{\Upsilon}^\dagger\mathbf{U}(-t)\boldsymbol{\Upsilon}. \tag{15}$$

Since $\boldsymbol{\Upsilon}^\dagger\mathbf{U}(-t)\boldsymbol{\Upsilon}$ satisfies the same boundary condition as $\mathbf{U}(t)$, that is, $\boldsymbol{\Upsilon}^\dagger\mathbf{U}(0)\boldsymbol{\Upsilon} = \mathbf{1}$, we have

$$\boldsymbol{\Upsilon}^\dagger\mathbf{U}(t)\boldsymbol{\Upsilon} = \mathbf{U}(-t). \tag{16}$$

Let $|\Phi(t)\rangle$ be another state ket, whose space-time reflection is

$$|\Phi^*(t)\rangle = \boldsymbol{\Upsilon}|\Phi(-t)\rangle. \tag{17}$$

Note the reciprocal relationship

$$|\Phi(t)\rangle = \boldsymbol{\Upsilon}|\Phi^*(-t)\rangle. \tag{18}$$

It follows from Eq. (16) that the scalar product of one state ket with the space-time reflection of another is conserved in time:

$$\begin{aligned}\langle\Phi^*(t)|\Psi(t)\rangle &= \{\langle\Psi(t)|[\boldsymbol{\Upsilon}|\Phi(-t)\rangle]\}^* \\ &= \{\langle\Psi(0)|\mathbf{U}^\dagger(t)[\boldsymbol{\Upsilon}\,\mathbf{U}(-t)|\Phi(0)\rangle]\}^* \\ &= \{\langle\Psi(0)|\mathbf{U}^\dagger(t)[\boldsymbol{\Upsilon}\boldsymbol{\Upsilon}^\dagger\mathbf{U}(t)\boldsymbol{\Upsilon}|\Phi(0)\rangle]\}^* \\ &= \langle\Phi^*(0)|\Psi(0)\rangle,\end{aligned} \tag{19}$$

where the large square brackets are necessary for antilinear operators, and where in arriving at the last step we used the unitarity of $\mathbf{U}(t)$ and the antiunitarity of $\boldsymbol{\Upsilon}$.

We conclude that when a system is nondissipative, conservation of probability can be expressed by the preservation of either the traditional norm $\langle\Psi(t)|\Psi(t)\rangle$, which is always positive definite, or the nontraditional "norm" $\langle\Psi^*(t)|\Psi(t)\rangle$. On the other hand, when a system is dissipative, $\langle\Psi(t)|\Psi(t)\rangle$ is not conserved, because probability flux escapes from the subspace of available states. However, $\langle\Psi^*(t)|\Psi(t)\rangle$ is conserved, because it is a measure of both the flux that leaves the subspace of available states and the equally intense space-time-reflected flux that enters this subspace [11]. In the remainder of this paper a bra appears almost always as the dual of a space-time-reflected ket, and this is indicated by an asterisk (as above).

Now we return to the fictitious system governed by the energy-dependent but static Hamiltonian $\mathbf{H}_{\rm eff}(E)$, with E real. Since $\mathbf{H}$ is invariant under space-time reflections, so is the first term on the right side of Eq. (7); that is,

$$\boldsymbol{\Upsilon}^\dagger(\mathbf{PHP})\boldsymbol{\Upsilon} = \mathbf{PHP}. \tag{20}$$

On the other hand, adding an infinitesimal positive imaginary part $i0$ to E as a reminder that E lies on the upper edge of the unitarity cut, we have $\boldsymbol{\Upsilon}^\dagger\mathbf{G}(E+i0)\boldsymbol{\Upsilon} = \mathbf{G}(E-i0) = \mathbf{G}(E+i0)^\dagger$, so the second term on the right side of Eq. (7) has the property

$$\boldsymbol{\Upsilon}^\dagger\mathbf{V}_{\rm opt}(E)\boldsymbol{\Upsilon} = \mathbf{V}_{\rm opt}(E)^\dagger. \tag{21}$$

Premultiplying both sides of the time-dependent Schrödinger equation

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = [\mathbf{PHP} + \mathbf{V}_{\rm opt}(E)]|\Psi(t)\rangle \tag{22}$$

by $\boldsymbol{\Upsilon}$, changing the sign of t, and using Eqs. (17), (20), and (21) and the antiunitarity of $\boldsymbol{\Upsilon}$ yields

$$i\hbar\frac{d}{dt}|\Psi^*(t)\rangle = [\mathbf{PHP} + \mathbf{V}_{\rm opt}(E)^\dagger]|\Psi^*(t)\rangle. \tag{23}$$

Therefore, the time-rate of change of the norm appropriate to a dissipative system governed by the effective Hamiltonian $\mathbf{H}_{\rm eff}(E)$ is

$$i\hbar\frac{d}{dt}\langle\Psi^*(t)|\Psi(t)\rangle = \langle\Psi^*(t)|[\mathbf{PHP} - (\mathbf{PHP})^\dagger]|\Psi(t)\rangle. \tag{24}$$

Note that $\mathbf{V}_{\rm opt}(E)$ drops out; in other words, whereas the time-rate of change of $\langle\Psi(t)|\Psi(t)\rangle$ accounts for both dissipative and nondissipative losses, the time-rate of change of $\langle\Psi^*(t)|\Psi(t)\rangle$ expresses only nondissipative loss.

C. Bloch operator

Let us divide configuration space into two parts, the interior and exterior of a box which is a hypersphere of hyperradius R. Suppose that the Hamiltonians $\mathbf{H}$ and $\mathbf{H}_{\rm eff}(E)$ are rotationally invariant, so all planes are equal with respect to spatial reflections. In this section, and the next one, we focus on the region interior to the box. We use the subscript "int" to indicate that integration is confined to the interior. Evaluating

the right side of Eq. (24) on the boundary, we find the rate of nondissipative loss to be

$$\hbar\frac{d}{dt}\langle\Psi^*(t)|\Psi(t)\rangle_{\rm int} = \langle\Psi^*(t)|\left\{\frac{1}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}} + \left[\frac{1}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}}\right]^\dagger\right\}|\Psi(t)\rangle_{\rm int}, \quad (25)$$

where $\vec{\mathbf{j}}$ is the probability current operator and where $\vec{A}(R)$ is the vector potential for a fictitious magnetic field which in position space is normal to the boundary surface, where it is localized with amplitude c:

$$\vec{A}(R) = c\delta(r-R)\hat{R}. \quad (26)$$

According to Eq. (25) we can attribute any nondissipative loss of probability flux from within the box to a Hermitian interaction at the boundary of the box between the probability current and a magnetic field.

However, the *total* nondissipative loss of flux within the box, summed over all pathways, must be zero. This constraint can be automatically fulfilled by representing the wave function on a discrete "standing-wave basis" composed of functions that vanish at the boundary R. Unfortunately, as discussed in the Introduction, the wave function does not converge uniformly on this basis. Therefore, suppose that we choose a more suitable basis, albeit one which does not ensure that the preceding constraint is automatically fulfilled. In this case a spurious current appears at the boundary. One way around this difficulty is well known. To paraphrase Bloch, we can add to the Hamiltonian a non-Hermitian coupling to a magnetic field whose purpose is to absorb the spurious current [3]. The coupling to a (mathematically) real magnetic field, that is,

$$\frac{1}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}},$$

is not a suited for this purpose because it is not invariant under time reversal. On the other hand, the coupling to a purely imaginary magnetic field, that is,

$$\frac{i}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}},$$

is both non-Hermitian and invariant under space-time reflections. Thus, we can add the "Bloch operator" $\frac{i}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}}$ to $\mathbf{H}$ in **PHP**; the modified Hamiltonian operator

$$\mathbf{H}_{\rm mod} \equiv \mathbf{H} + \frac{i}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}} \quad (27)$$

is *both* Hermitian *and* invariant under space-time reflections. This modification to the true Hamiltonian must be offset by subtracting a similar source term from the optical potential, a prescription originally proposed by Bloch for nondissipative systems, but which is evidently also applicable to dissipative systems.

In summary, the equation for $\mathbf{P}|\Psi\rangle$ inside the box can be written in the form

$$(E\mathbf{1} - \mathbf{P}\mathbf{H}_{\rm mod}\mathbf{P})\mathbf{P}|\Psi\rangle = \mathbf{P}\left[\mathbf{V}_{\rm opt}(E) - \frac{i}{2c}\vec{A}(R)\cdot\vec{\mathbf{j}}\right]\mathbf{P}|\Psi\rangle. \quad (28)$$

If real boundary conditions are applied, $\mathbf{P}\mathbf{H}_{\rm mod}\mathbf{P}$ is Hermitian and its eigenvalue spectrum is real and discrete. The inverse of $(E\mathbf{1} - \mathbf{P}\mathbf{H}_{\rm mod}\mathbf{P})$ can be represented by its spectral decomposition. Let $|\tilde{\mathcal{E}}_n\rangle$ be an eigenket of $\mathbf{P}\mathbf{H}_{\rm mod}\mathbf{P}$ with eigenvalue $\tilde{\mathcal{E}}_n$. The solution of Eq. (5) within the box is

$$\mathbf{P}|\Psi\rangle = \sum_n \frac{|\tilde{\mathcal{E}}_n\rangle\langle\tilde{\mathcal{E}}_n|}{E-\tilde{\mathcal{E}}_n}\left[\mathbf{V}_{\rm opt}(E) - \frac{i}{2}\vec{A}(R)\cdot\vec{\mathbf{j}}\right]\mathbf{P}|\Psi\rangle. \quad (29)$$

This solution can be matched to the solution outside the box to yield the K matrix and hence the S matrix.

D. Separation of incident and scattered waves

The addition of a term to the Hamiltonian which couples the probability current to a fictitious magnetic field lacks physical justification. A more serious drawback of the Bloch operator is that its spatial representation is singular, so convergence with respect to basis size is expected to be slow. Thus, a correction, the Buttle correction, is often invoked [4].

In this section we describe an approach which does not require the Bloch operator. We decompose $\mathbf{P}|\Psi\rangle$ into an incident wave $\mathbf{P}|\Psi_{\rm inc}\rangle$ and a "scattered" wave $\mathbf{P}|\Psi_{\rm scat}\rangle$ where the quotes signify that $\mathbf{P}|\Psi_{\rm inc}\rangle$ and $\mathbf{P}|\Psi_{\rm scat}\rangle$ have merely the characteristics of incident and scattered waves. We expand $\mathbf{P}|\Psi_{\rm scat}\rangle$ within the box on a basis whose radial basis functions vanish at the boundary of the box (they also vanish at the origin in order to satisfy regular boundary conditions there). We specify $\mathbf{P}|\Psi_{\rm inc}\rangle$ within the box so that it mimics the incident wave; this term is not part of the basis. We can reexpress Eq. (5) as

$$(E\mathbf{1} - \mathbf{PHP})\mathbf{P}|\Psi_{\rm scat}\rangle = \mathbf{V}_{\rm opt}(E)\mathbf{P}|\Psi\rangle + (\mathbf{PHP} - E\mathbf{1})\mathbf{P}|\Psi_{\rm inc}\rangle. \quad (30)$$

Since the basis satisfies standing-wave boundary conditions **PHP** is Hermitian on this basis. The formal solution of Eq. (30) within the box is

$$\mathbf{P}|\Psi_{\rm scat}\rangle = \mathbf{G}_P(E)[\mathbf{V}_{\rm opt}(E)|\Psi_{\rm scat}\rangle + \mathbf{V}_{\rm opt}(E)|\Psi_{\rm inc}\rangle + (\mathbf{H} - E\mathbf{1})\mathbf{P}|\Psi_{\rm inc}\rangle], \quad (31)$$

and this solution automatically satisfies standing-wave boundary conditions when $\mathbf{G}_P(E)$ is replaced by its spectral decomposition.

Let $|\mathcal{E}_n\rangle$ be an eigenket of **PHP** with (real) eigenvalue $\mathcal{E}_n$; it is simultaneously an eigenket of both $\boldsymbol{\Upsilon}$ and $\mathbf{P}$ with unit eigenvalues. Using the completeness of the $|\mathcal{E}_n\rangle$ on the subspace to which $\mathbf{P}|\Psi_{\rm scat}\rangle$ belongs, Eq. (31) becomes

$$\mathbf{P}|\Psi_{\rm scat}\rangle = \sum_n \frac{|\mathcal{E}_n\rangle}{E-\mathcal{E}_n}\left[\sum_m \langle\mathcal{E}_n|\mathbf{V}_{\rm opt}(E)|\mathcal{E}_m\rangle_{\rm int}\langle\mathcal{E}_m|\Psi_{\rm scat}\rangle_{\rm int} + \langle\mathcal{E}_n|\mathbf{V}_{\rm opt}(E)|\Psi_{\rm inc}\rangle_{\rm int} + \langle\mathcal{E}_n|(\mathbf{H} - E\mathbf{1})\mathbf{P}|\Psi_{\rm inc}\rangle_{\rm int}\right]. \quad (32)$$

We have assumed that the spatially nonlocal optical potential is sufficiently weak at distances beyond R that it does not act outside the box. This is a reasonable assumption even when Q space contains open subchannels. The reason is as follows: The unbound electron has a smaller (asymptotic) linear momentum in an open subchannel in Q space than it does in an open subchannel in P space. Therefore, the integrand of a matrix

element of $\mathbf{PV}_{ee}\mathbf{Q}$ oscillates with respect to large values of the radial coordinate of the unbound electron. Consequently, the contribution from large distances to the integral washes out. Although the difference in the momenta of the unbound electron in P and Q spaces shrinks as the total energy of the system increases, this is offset by the energy denominator of the resolvent $\mathbf{G}_Q(E)$ which appears in the optical potential.

Premultiplying both sides of Eq. (32) by $\langle\mathcal{E}_n|$ yields the following system of inhomogeneous linear equations for the matrix elements $\langle\mathcal{E}_n|\Psi_{\rm scat}\rangle_{\rm int}$:

$$\sum_m[(E-\mathcal{E}_n)\delta_{nm}-\langle\mathcal{E}_n|\mathbf{V}_{\rm opt}(E)|\mathcal{E}_m\rangle_{\rm int}]\langle\mathcal{E}_m|\Psi_{\rm scat}\rangle_{\rm int} = \langle\mathcal{E}_n|\mathbf{V}_{\rm opt}(E)|\Psi_{\rm inc}\rangle_{\rm int}+\langle\mathcal{E}_n|(\mathbf{H}-E\mathbf{1})\mathbf{P}|\Psi_{\rm inc}\rangle_{\rm int}. \quad (33)$$

The functional form of $|\Psi_{\rm inc}\rangle$ is specified (in position space), but its amplitude is left unspecified and is determined by matching the interior and exterior solutions and their derivatives at the boundary of the box. Thus, the inhomogeneous term on the right side of Eq. (33) is fixed up to the normalization of $|\Psi_{\rm inc}\rangle$, as are the solutions of Eqs. (32) and (33).

Note that while the matrix elements $\langle\mathcal{E}_m|\mathbf{V}_{\rm opt}(E)|\mathcal{E}_n\rangle_{\rm int}$ are, in general, complex, they are symmetric, that is, since $|\mathcal{E}_n\rangle$ is an eigenket of $\boldsymbol{\Upsilon}$ with unit eigenvalue,

$$\begin{aligned}\langle\mathcal{E}_m|\mathbf{V}_{\rm opt}(E)|\mathcal{E}_n\rangle_{\rm int} &= (\langle\mathcal{E}_m|\boldsymbol{\Upsilon}^\dagger)[\mathbf{V}_{\rm opt}(E)\boldsymbol{\Upsilon}|\mathcal{E}_n\rangle_{\rm int}]\\ &= \{\langle\mathcal{E}_m|[\boldsymbol{\Upsilon}^\dagger\mathbf{V}_{\rm opt}(E)\boldsymbol{\Upsilon}|\mathcal{E}_n\rangle_{\rm int}]\}^*\\ &= [\langle\mathcal{E}_m|\mathbf{V}_{\rm opt}(E)^\dagger|\mathcal{E}_n\rangle_{\rm int}]^*\\ &= \langle\mathcal{E}_n|\mathbf{V}_{\rm opt}(E)|\mathcal{E}_m\rangle_{\rm int}, \end{aligned} \quad (34)$$

where in the last step but one we used Eq. (21).

III. INTERIOR REGION

In the preceding subsection we framed the solution of Eq. (5) in terms of the eigenkets of the operator **PHP** without distinguishing the bound electron from the unbound one. In practice, $\mathbf{H}$ is represented by a matrix $\underline{H}(r)$, where r is the radial coordinate of the unbound electron and where we have integrated over the remaining coordinates, that is, over the angular coordinates and the radial coordinate of the bound electron. (Here and elsewhere we distinguish matrices by underscoring the appropriate symbol.) Thus, while Eq. (33) displays the formal structure of the linear equations we want to solve, the actual equations we solve are those that result from expanding $\mathbf{P}|\Psi_{\rm scat}\rangle$ on the "channel basis," as we discuss in the present section. We express Eq. (5) on this basis in matrix form:

$$[\underline{H}_{\rm eff}(r)-E\underline{1}]\underline{F}(r)=0, \quad (35)$$

where $\underline{H}_{\rm eff}(r)$ is the matrix representation of $\mathbf{H}_{\rm eff}$ on the channel basis and where $\underline{F}(r)$ is the "channel matrix" whose columns are independent solutions of Eq. (5) in the channel representation.

A. Channel basis

The total angular momentum of the system is conserved, and we assume the system is in an eigenstate of the total angular momentum operator and its projection along the z axis. Let $\vec{r}_1$ and $\vec{r}_2$ locate bound and unbound electrons, respectively, relative to the nucleus. The expressions given in this section, and the next one, *must be symmetrized with respect to the electrons*. If i is the entrance subchannel the solution of Eq. (5), that is, the projection of the wave function in P space, has the form

$$\frac{1}{r_1r_2}\sum_j F_j^{(i)}(r_2)\phi_j(r_1,\hat{r}_1,\hat{r}_2)=\frac{1}{r_1r_2}[\vec{F}^{(i)}(r_2)]^{\rm t}\cdot\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2) \quad (36)$$

everywhere in position space. The "channel function" $F_j^{(i)}(r_2)$ is the radial wave function of the unbound electron, 2, and t denotes transpose. The wave function of the bound electron, 1, in state j is $\phi_j(r_1,\hat{r}_1,\hat{r}_2)$; we have incorporated the coupling of the angular momentum of the two electrons in $\phi_j(r_1,\hat{r}_1,\hat{r}_2)$. The ϕ_j form the channel basis, which is orthonormal, that is,

$$\int dr_1d^2\hat{r}_1d^2\hat{r}_2\;\vec{\phi}^*(r_1,\hat{r}_1,\hat{r}_2)\otimes\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2)=\underline{1}, \quad (37)$$

where without compromise we choose the length R of the box to be sufficiently large that the ϕ_j vanish outside the box, so the region of integration can be confined to the box. Thus, the superscript i and the subscript j, respectively, on $F_j^{(i)}(r_2)$ denote the solution (the entrance subchannel) and the component of this solution on the channel basis; the sum on the right side of Eq. (36) is over $N_{\rm c}$ open subchannels. We choose ϕ_j to be an eigenfunction of $\boldsymbol{\Upsilon}$. The general solutions of Eq. (5), everywhere in position space, are the elements of a column vector $\vec{\Psi}(\vec{r}_1,\vec{r}_2)/(r_1r_2)$ of dimension $N_{\rm c}$; each element is a solution of the form $[\vec{F}^{(i)}(r_2)]^{\rm t}\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2)/r_1r_2$, corresponding to a particular entrance channel i. Thus, we have

$$\vec{\Psi}(\vec{r}_1,\vec{r}_2)=\underline{F}^{\rm t}(r_2)\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2), \quad (38)$$

with $\underline{F}(r_2)$ the channel matrix, whose columns are the vectors $\vec{F}^{(i)}(r_2)$.

Let $\underline{V}_{\rm opt}(r,r')$ represent $\mathbf{V}_{\rm opt}$ on the channel basis. The incident- and scattered-wave components of a particular solution, that is, $\langle\vec{r}_1,\vec{r}_2|\mathbf{P}|\Psi_{\rm inc}\rangle$ and $\langle\vec{r}_1,\vec{r}_2|\mathbf{P}|\Psi_{\rm scat}\rangle$, are elements of the vectors $\underline{F}^{\rm t}_{\rm inc}(r_2)\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2)$ and $\underline{F}^{\rm t}_{\rm scat}(r_2)\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2)$, respectively. Taking the outer product of Eq. (35) with $\vec{\phi}^*(r_1,\hat{r}_1,\hat{r}_2)$ and integrating over $r_1,\hat{r}_1$, and $\hat{r}_2$ using Eq. (37) yields the following inhomogeneous integral equation for $\underline{F}_{\rm scat}(r)$:

$$\underline{F}^{\rm t}_{\rm scat}(r)=\int_0^R dr'\big[\underline{F}^{\rm t}_{\rm scat}(r')\underline{D}(r,r')+\underline{F}^{\rm t}_{\rm inc}(r')\underline{B}(r,r')+\underline{F}^{\rm t}_{\rm inc}(r')\underline{C}(r,r')\big], \quad (39)$$

where, introducing a column vector $\vec{\psi}_m(R)$ of dimension $N_{\rm c}$ defined by

$$\vec{\psi}_m(r_2)=\int dr_1d^4\hat{r}_1,\hat{r}_2\;\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2)\langle\mathcal{E}_m|\vec{r}_1,\vec{r}_2\rangle, \quad (40)$$

we have

$$\underline{B}(r,r')=\sum_n\frac{\vec{\psi}_n(r)\otimes\vec{\psi}_n^*(r')}{E-\mathcal{E}_n}[\underline{H}(r')-E\underline{1}], \quad (41)$$

$$\underline{C}(r,r') = \sum_n \frac{\vec{\psi}_n(r) \otimes \int_0^R dr'' \vec{\psi}_n^*(r'')}{E - \mathcal{E}_n} \underline{V}_{\rm opt}(r'',r'), \quad (42)$$

$$\underline{D}(r,r') = \sum_n \sum_m \langle \mathcal{E}_n | \mathbf{V}_{\rm opt}(E) | \mathcal{E}_m \rangle \frac{\vec{\psi}_m(r) \otimes \vec{\psi}_n^*(r')}{E - \mathcal{E}_n}. \quad (43)$$

The complete channel matrix is $\underline{F}(r) = \underline{F}_{\rm scat}(r) + \underline{F}_{\rm inc}(r)$. We reduce the integral equation (39) to a system of linear equations by expanding $\underline{F}_{\rm scat}(r)$ on a basis; this basis is described in Sec. III C below.

B. Incident wave

A judicious choice for the functional form of $\underline{F}_{\rm inc}(r)$ is critical to account for the correct behavior of the incident wave at small and large distances. Writing

$$\underline{F}^{\rm t}_{\rm inc}(r) = \underline{N}^{\rm t}\, \underline{\mathcal{F}}^{\rm t}_{\rm inc}(r), \quad (44)$$

where $\underline{N}$ is the normalization matrix, we choose $\underline{\mathcal{F}}_{\rm inc}(r)$ to be a diagonal matrix whose diagonal elements are

$$\mathcal{F}_{i,{\rm inc}}(r) = \hat{j}_{l_i}\left[k_i r + \gamma_i \ln\left(1 + \frac{2k_i r}{c_i}\right) + \frac{\delta_i(k_i) r}{b_i + r}\right]. \quad (45)$$

Here $\hbar k_i$ and l_i are the asymptotic momentum and the angular momentum quantum number of the unbound particle, respectively, $\gamma_i = (Z-1)/(a_0 k_i)$ with $Z = 2$, the atomic number of the nucleus, $\hat{j}_l(x)$ is a Riccati-Bessel function, that is,

$$\hat{j}_l(x) = \sqrt{\frac{\pi x}{2}} J_{l+\frac{1}{2}}(x), \quad (46)$$

with $J_\nu(x)$ a regular Bessel function, b_i and c_i are fixed positive parameters, and $\delta_i(k_i)$ is a variational parameter. The functions $\mathcal{F}_{i,{\rm inc}}(r)$ are regular at the origin and have the asymptotic forms

$$\mathcal{F}_{i,{\rm inc}}(r) \to \sin\left[k_i r - \frac{1}{2} l_i \pi + \gamma_i \ln\left(1 + \frac{2k_i r}{c_i}\right) + \delta_i(k_i)\right]. \quad (47)$$

The parameter b_i characterizes the radius of the core in subchannel i; in our calculations we fixed its value to be 4 a.u. in all subchannels. The logarithmic term $\ln[1 + (2k_i r/c_i)]$ accounts for Coulomb distortion at large distances, that is, distances where $k_i^2 r a_0 \gtrsim 1$. Since $r < R$ in the interior region this logarithmic term is warranted only if $k_i^2 R a_0 \gtrsim 1$; thus, c_i serves as an appropriate cutoff parameter, whose value we fixed to be

$$c_i = 1 + \frac{1}{k_i^2 R a_0}. \quad (48)$$

Evidently, $\delta_i(k_i)$ is a phase shift which supplements the phase shift $-\frac{1}{2} l_i \pi$ due to free-particle scattering from the angular momentum barrier. The "optimal" values of the $\delta_i(k_i)$ can be determined from the Kohn variational principle. However, we find that satisfactory accuracy can be achieved without optimization by fixing $\delta_i(k_i)$ to have the smallest absolute value for which

$$\mathcal{F}_{i,{\rm inc}}(R) \approx 1; \quad (49)$$

this ensures that $\mathcal{F}_{i,{\rm inc}}(r)$ is out of phase with the basis functions that we introduce in the next section. Thus, using the asymptotic form of $\hat{j}_l(x)$ we take

$$\delta_i(k_i) \approx -k_i R + l_i \frac{\pi}{2} - \gamma_i \ln\left(1 + \frac{2k_i R}{c_i}\right) + (2n+1)\frac{\pi}{2}, \quad (50)$$

where the integer n is chosen so that

$$-\pi/2 < \delta_i(k_i) \leqslant \pi/2. \quad (51)$$

The scattered wave $\underline{F}_{\rm scat}(r)$ within the box is the solution of Eq. (39), unique up to the normalization matrix $\underline{N}$. We solve Eq. (39) by first expanding $\underline{F}_{\rm scat}(r)$ on a suitable basis.

C. Scattered wave

The integral equation (39) for the scattered wave $\underline{F}_{\rm scat}(r)$ reduces to a system of linear equations once we expand $\underline{F}_{\rm scat}(r)$ on a basis. We employed a basis whose radial part is composed of simple, real, analytic basis functions of two types, Riccati-Bessel and Sturmian functions, each of which is regular, and therefore vanishes, at the origin. We denote these basis functions by $u_{nl}(r)$ and $v_{nl}(r)$, where

$$u_{nl}(r) = \frac{1}{\sqrt{R}} \hat{j}_l(k_n r), \quad (52)$$

$$v_{nl}(r) = \sqrt{\frac{\kappa}{n(n-l)_{2l+1}}} (2\kappa r)^{l+1} L^{2l+1}_{n-l-1}(2\kappa r) e^{-\kappa r}, \quad (53)$$

with $L^\mu_\nu(x)$ an associated Laguerre polynomial.

The parameters κ and k_n are real, positive wave numbers. We fix the value of κ in each subchannel, but we choose this value to be sufficiently large that the $v_{nl}(r)$ vanish at the boundary $r = R$; thus, the $v_{nl}(r)$ satisfy standing-wave boundary conditions:

$$v_{nl}(0) = v_{nl}(R) = 0. \quad (54)$$

Consequently, the ordinal numbers of the $v_{nl}(r)$ are limited to the range

$$n - l \ll \kappa R. \quad (55)$$

The $v_{nl}(r)$ are mutually orthogonal over the interval $0 \leqslant r < \infty$ with respect to the weight function $1/r$, whereas the $u_{nl}(r)$ are mutually orthogonal over the interval $0 \leqslant r \leqslant R$ with respect to a weight function of unity provided that the wave numbers k_n are chosen to be

$$k_n = \alpha_n / R, \;\; n = 1,2,3,\ldots, \quad (56)$$

where, with β a fixed but open parameter, the α_n are roots of the equation

$$(1 - 2\beta) J_{l+\frac{1}{2}}(x) + 2x J'_{l+\frac{1}{2}}(x) = 0, \quad (57)$$

where the prime indicates the derivative with respect to x. Thus, the $u_{nl}(r)$ have a fixed logarithmic derivative at $r = R$:

$$\left.\frac{du_{nl}(r)}{dr}\right|_R = \beta u_{nl}(R). \quad (58)$$

As noted in the Introduction, we choose the $u_{nl}(r)$ so that they too satisfy standing-wave boundary conditions:

$$u_{nl}(0) = u_{nl}(R) = 0. \quad (59)$$

Hence, we let β become infinite; accordingly, the α_n are the roots of

$$J_{l+\frac{1}{2}}(x) = 0. \quad (60)$$

The basis functions $u_{nl}(r)$ and $v_{nl}(r)$, respectively, have long and short length scales, R and $1/\kappa$. The $u_{nl}(r)$ are eigenfunctions of the radial kinetic energy operator, and if a sufficiently large number of them are selected they span the region $0 \leqslant r \leqslant R$ more or less uniformly, and they build in the regular oscillations of the unbound particle's wave function at distances $l/k \ll r \leqslant R$ where the particle is almost free. In the region where the interaction is strong, that is, $l/k \lesssim r \ll R$, the wave function may vary rapidly; the more compact $v_{nl}(r)$ are needed to describe this short-range behavior. In particular, because $v_{nl}(r)/r^l$ behaves *linearly* with r when $r \sim 0$, it can account (at least partially) for the cusp in the wave function which arises from the Coulomb singularity of the potential at the origin. In contrast, $u_{nl}(r)/r^l$ is an even function of r; its derivative vanishes when $r \sim 0$, and therefore it cannot mimic a cusp at the origin. [An infinite number of the $u_{nl}(r)$ are required to mimic the cusp.] We choose the wave numbers k_n of the $u_{nl}(r)$ to cover two (generally nonoverlapping) ranges, namely, the long-wavelength range where n runs from 1 up to a number of order 10, and the shorter-wavelength range which depends on the subchannel and is defined so that the energies $\hbar^2 k_n^2/(2\mu)$ surround the energy of the unbound electron (of mass μ) in each subchannel.

The expansion of the scattered wave $\underline{F}_{\rm scat}(r)$ on this hybrid basis ensures that it vanishes at both $r = 0$ and $r = R$. Since $\underline{F}_{\rm inc}(r)$ also vanishes at $r = 0$, so does the full channel matrix $\underline{F}(r)$, which is the sum $\underline{F}_{\rm inc}(r) + \underline{F}_{\rm scat}(r)$. Since $\underline{F}(r)$ is matched at $r = R$ to the "exact" solution outside the box, and since the exact solution inside the box vanishes at $r = 0$, the error in $\underline{F}(r)$ inside the box vanishes at both $r = 0$ and $r = R$ and therefore is incorporated in the solution $\underline{F}_{\rm scat}(r)$ of Eq. (39).

Neglecting exponentially small contributions of order $e^{-\kappa R}$ in Eqs. (62) and (63) below, we have

$$\int_0^R dr\ u_{ml}(r)u_{nl}(r) = \frac{1}{2}[\hat{j}_l'(\alpha_n)]^2\delta_{mn}, \tag{61}$$

$$\int_0^R dr\ v_{ml}(r)\frac{1}{r}v_{nl}(r) = \frac{\kappa}{n}\delta_{mn}, \tag{62}$$

$$\int_0^R dr\ v_{ml}(r)v_{nl}(r) = \delta_{mn} - \frac{1}{2}\sqrt{\frac{(n \mp l)(n \pm l \pm 1)}{n(n \pm 1)}}\delta_{m,n\pm1}, \tag{63}$$

where $\hat{j}_l'(x)$ is the derivative with respect to x of $\hat{j}_l(x)$. Note that the $u_{ml}(r)$ are not orthogonal to the $v_{nl}(r)$. Indeed, the entire set of eigenfunctions $u_{nl}(r), n = 1,2,3,\ldots$ is complete, so in principle the $v_{nl}(r)$ are redundant. This raises the question as to whether numerical linear dependence intrudes when a finite number of both the $u_{ml}(r)$ and the $v_{ml}(r)$ are included; the answer is no, as long as the inequality (55) is obeyed. Note that matrix elements constructed on the u and v subspaces, respectively, scale with R and $1/\kappa$.

IV. COMPARISON WITH TRADITIONAL *R*-MATRIX APPROACH

The formalism described in the preceding two sections can be applied to a stationary collision or half-collision process. In a collision process a system enters and leaves a "box" whose linear dimension is R. In a half-collision process (which is intrinsically dissipative) an unstable system initially resides within the box. The boundary at $r = R$ is fictitious and in reality not impenetrable, so in both processes probability flux, and therefore energy, cross the boundary. The flow of energy across a surface cannot be described by a finite superposition of standing waves that are in phase with one another; at least one wave must be out of phase with the others. On the other hand, a Hamiltonian that is represented on a basis of standing waves that are out of phase is not Hermitian.

In the traditional R-matrix approach a basis is employed on which the matrix representation of the Hamiltonian is non-Hermitian. The singular Bloch operator must be added to the Hamiltonian as a source term to compensate for a spurious current at the boundary.

In the present approach, where state space is divided into P and Q subspaces, the problem reduces to that of a fictitious system residing in P space. The sub-Hamiltonian PHP is represented by a Hermitian matrix. However, the P-space wave function does not converge uniformly on the basis formed by the eigenfunctions of this matrix. Only the scattered-wave part of the P-space wave function converges uniformly. The incident-wave is out of phase with the scattered wave and is not expanded on the basis; it is fully specified up to its normalization, and it provides a source term in analogy with the Bloch operator.

In the traditional approach, that part of the basis which simulates the continuum is often composed at least partially from numerical solutions to a simple but suitable differential equation. The basis need cover only the relatively small volume where electron exchange and correlation are important. The R matrix is determined at the boundary. It satisfies the Kohn variational principle. However, the derivative of the wave function at the R-matrix boundary is, in general, not continuous. In the outer region, where the interaction of the unbound electron with the residual target can be replaced by its multipole expansion, the Schrödinger equation is integrated numerically out to a distance that is sufficiently large for the wave function to be matched to the free-particle wave function, distorted by the Coulomb potential if there is a nonvanishing monopole. The K matrix is determined by this matching.

In the present approach a basis composed entirely of analytic functions is employed. This basis is required to cover a region well beyond where electron exchange and correlation are important. We choose the boundary to be sufficiently far so that beyond the boundary it is reasonable to retain only the monopole and the static dipole terms in the multipole expansion of the interaction of the unbound electron with the residual target. The derivative of the wave function at the boundary *is* continuous. Both the inner solution and its derivative are matched at the boundary to the closed-form solution of the Schrödinger equation for a particle moving in a local potential that results from a combination of Coulomb and dipole fields. Therefore, we derive the K matrix, rather than the R matrix, at the boundary. The details are given in Appendix A. The resulting K matrix has a first-order error. However, the first-order correction can be readily obtained from the Kohn variational principle, as shown in Appendix B.

The incident wave depends on the energy of the system, so matrix elements involving the incident wave must be

recalculated at each energy. Furthermore, the basis on which the scattered wave is expanded is energy dependent since the wave numbers k_n of the Riccati-Bessel basis functions $u_{nl}(r)$ are chosen so that at least a few of the energies $\hbar^2 k_n^2/(2\mu)$ surround the energy of the unbound electron in each subchannel. By contrast, the R matrix is traditionally diagonalized on an energy-independent basis and the same matrix is applicable at all energies. This is possible because the R matrix can be determined at a boundary which is much closer to the origin than the boundary at which the K matrix can be determined.

In the traditional approach the loss of probability from a subchannel due to excitation or ionization to subchannels that are not described exactly is taken into account through the inclusion in the basis of pseudostates (which do not, however, satisfy physical boundary conditions). In the present approach those subchannels that are not described exactly are relegated to Q space, a space that is spanned by a basis that, in principle, is complete. The Q-space wave function accounts for the loss of flux from P space and is coupled to the P-space wave function by the optical potential. The Q-space wave function is expressed through a Q-space resolvent that satisfies outgoing-wave boundary conditions.

V. PHOTOIONIZATION OF He WITH SIMULTANEOUS EXCITATION TO $He^+(2s)$ OR $He^+(2p)$

We have applied our method to one-photon single-ionization of He accompanied by excitation to the $2s$ and $2p$ states of He^+. We chose the light to be linearly polarized, and the photon energy to be in the range 80 eV (just above the complete breakup threshold) to 250 eV.

We took the box radius to be $R = 50$ a.u. in our calculations and we included independent-electron orbtial angular momentum quantum numbers ranging from 0 to 3. Four subchannels, that is, $1s\epsilon p$, $2s\epsilon p$, $2p\epsilon s$, and $2p\epsilon d$, were included in P space. We solved the system of linear equations that emerge from the integral equation (39) for the P-space scattered wave $\underline{F}_{\rm scat}(r)$ after representing $\underline{F}_{\rm scat}(r)$ on the hybrid basis described in Sec. III C. The radial functions were mostly Riccati-Bessel functions, typically 52 for the $1s$ subchannel and 45 for the other subchannels; only a few Sturmian functions, restricted by the inequality (55), were included, namely, 10 for the $1s$ subchannel and 4 for the other subchannels. Hence, the linear equations for the P-space scattered wave numbered no more than about 250. The phase shifts $\delta_i(k_i)$ belonging to the incident wave were not optimized and were fixed as stated by Eqs. (50) and (51). The radial component of the Q-space wave function was represented on a basis composed entirely of Sturmian functions, unrestricted by the inequality (55); either 15 or 30 radial Sturmian functions per electron per angular momentum quantum number were included. The ground-state wave function was represented on a similar basis, employing 30 Sturmian functions per electron per angular momentum quantum number; we obtained the estimate $-2.903\,30$ a.u. for the ground-state energy, with an error of 0.015% compared to Pekeris' estimate. [12]

The construction of the ground-state wave function entailed a matrix of dimension 1860×1860. The largest matrix involved in the construction of the Q-space wave function was of dimension 2700×2700. These matrices were calculated rapidly using Gauss-Laguerre quadrature and were constructed only once since they were built entirely from Sturmian functions—the matrix elements scaled with the basis wave number (i.e., with the characteristic distance covered by the basis). The most time-consuming part of the calculation was the construction of the matrix PHQ representing the coupling of P and Q spaces (a matrix whose dimension was no more than about 250×2700). Most of this matrix was constructed only once, using Gauss-Legendre quadrature, but part of the matrix, the part containing the 4×2700 elements that couple the (four components of the) "incident" wave to the Q-space basis, was recalculated at each energy. In addition, the wave numbers of the Riccati-Bessel functions in the P-space basis were adjusted at three different intervals within the full range of energies considered; this required a larger part of the matrix to be recalculated (but only three times). Nevertheless, the calculation was manageable on a modern desktop.

We changed the sizes of the P- and Q-space bases (e.g., from 15 to 30 radial Sturmian functions per electron per angular momentum quantum number in Q space) to verify that our results are converged; the departure from convergence would be not be visible on the figures. The symmetry of the K matrix provides a useful but not foolproof indication of numerical accuracy. A more reliable measure of numerical accuracy is the relative size of the variational correction. Generally, our estimates of the K matrix were symmetric to at least three significant figures before adding the variational correction and to seven or more significant figures after adding this correction. We found the variational correction to be substantially less than 1% on average. Results obtained in the length gauge differed from those obtained in the velocity gauge by less than 1%; such differences would be not be visible on the figures.

At high photon energies the photon is absorbed by one of the electrons as it passes close to the nucleus, which is possible if this electron has no orbital angular momentum. Since the total orbital angular momentum of $He(1s^2)$ is zero the spectator electron must also have no orbital angular momentum. As the photoelectron escapes, carrying away unit angular momentum, the spectator electron can relax into the $2s$ state of He^+ with a probability given by the sudden approximation, that is,

$$|\langle 2s, Z|1s, Z_{\rm eff}\rangle|^2 = \frac{2^{11}(ZZ_{\rm eff})^3(Z - Z_{\rm eff})^2}{(Z + 2Z_{\rm eff})^8}, \qquad (64)$$

where $Z_{\rm eff}$ is the effective nuclear charge seen by the spectator electron prior to photoabsorption by the active electron. If the spectator electron does relax into the $2s$ state, its state subsequently evolves into a mixture of degenerate $2s$ and $2p$ states since the photoelectron continues to interact, if only weakly, with the bound spectator; but the sum of the $2s$ and $2p$ populations remains almost constant. The probability that the spectator electron relaxes into the $1s$, rather than the $2s$, state of He^+ is approximately

$$|\langle 1s, Z|1s, Z_{\rm eff}\rangle|^2 = \frac{2^6(ZZ_{\rm eff})^3}{(Z + Z_{\rm eff})^6}. \qquad (65)$$

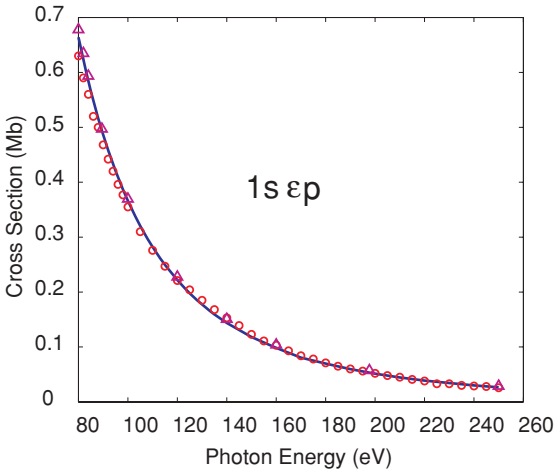

FIG. 1. (Color online) Cross section for photoionization to the $1s$ state of He^+. Thick solid line, present results, including optical potential; triangles, Decleva *et al.* [13]; circles, experimental data from Bizau and Wuilleumier [15].

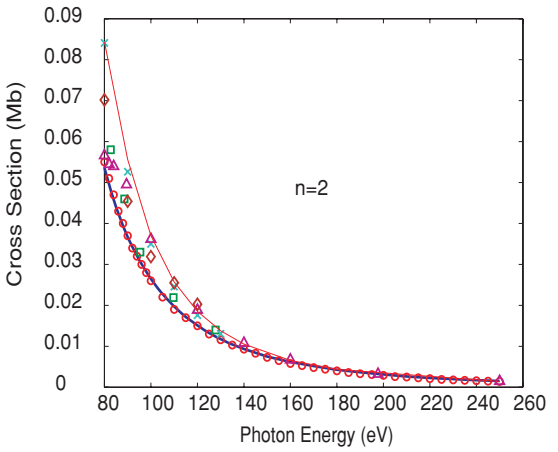

FIG. 2. (Color online) Cross section for photoionization accompanied by excitation, summed over the $n = 2$ states of He^+. Thick solid line, present results, including optical potential; thin solid line, present results, excluding optical potential; crosses, Sánchez and Martín [16]; triangles, Decleva *et al.* [13]; diamonds, Berrington *et al.* [17]; circles, experimental data from Bizau and Wuilleumier [15]; squares, experimental data from Woodruff and Samson [18].

Hence, *within the sudden approximation* the ratio of the cross sections for excitation to the $n = 2$ and $n = 1$ levels approaches a constant at asymptotically high photon energies:

$$\frac{\sigma_{2p+2s}}{\sigma_{1s}} \approx \frac{2^5\left(Z^2 - Z_{\rm eff}^2\right)^2 (Z + Z_{\rm eff})^4}{(Z + 2Z_{\rm eff})^8}. \tag{66}$$

To the extent that the sudden approximation is valid the optical potential can be neglected. If we do omit the optical potential and compare our resulting estimate 0.048 for the ratio $\sigma_{2p+2s}/\sigma_{1s}$ at 250 eV with the constant on the right side of Eq. (66), we obtain $Z_{\rm eff} \approx 1.45$. This value of $Z_{\rm eff}$ is somewhat smaller than the value $27/16 \approx 1.69$ which minimizes the ground-state energy of He in a crude independent-particle model; the smaller value is plausible because when the active electron is close to the nucleus the spectator electron is more fully screened from the nucleus. With the optical potential included, we estimate the ratio $\sigma_{2p+2s}/\sigma_{1s}$ to be 0.578 at 250 eV compared to the values 0.509 and 0.566, respectively, predicted by Decleva *et al.* [13] and measured by Wehlitz *et al.* [14]

Cross sections for photoionization to the $1s$ and to the $n = 2$ states of He^+ are shown in Figs. 1 and 2 for photon energies from 80 to 250 eV. The case where He^+ is left in the ground state is not an especially rigorous test of our method; inclusion of the optical potential makes little difference and would be barely visible were we to show this difference on Fig. 1. Nevertheless, it is reassuring that our results compare favorably with both the experimental data of Bizau and Wuilleumier [15] and the theoretical results of Decleva *et al.* [13]. The latter authors also employed a variant of the R-matrix method; they used a B-spline basis in the inner region, and joined the wave function in this region to the asymptotic wave function in the outer region by a least-squares fit at the boundary. (However, they did not include the dipole contribution to the asymptotic wave function.) The case where He^+ is left in an excited state is a more demanding test; in this case inclusion of the optical potential does affect the cross section, as is evident from Fig. 2. Again our results compare favorably with the experimental data of Bizau and Wuilleumier [15] and, a bit less favorably, with the experimental data of Woodruff and Samson [18]. We show various theoretical results in Fig. 2, those of Decleva *et al.* [13], Sánchez and Martín [16], who used a Slater-type basis to represent both discrete and (properly normalized) continuum states, and Berrington *et al.* [17], who used the traditional R-matrix method. At photon energies below 140 eV there are significant differences between our results and those of the other theoretical groups. These differences are, overall, of the same magnitude as the differences that we find by including or excluding the optical potential, and we suspect that the source of the discrepancies is the imperfect treatment in the other theories of the loss of flux to the continuum. Since our results are converged with respect to the basis in Q space it appears that the loss of flux from P space is well accounted for by our complex optical potential. As the photon energy increases beyond about 120 eV the differences that result from including or excluding the optical potential rapidly diminish, and accordingly the theoretical results of Sánchez and Martín [16] and Decleva *et al.* [13] converge rapidly toward our results. (Results of Berrington *et al.* [17] are not available beyond 120 eV.)

Finally, we consider the $2p/2s$ branching ratio. Suppose that at time $t = 0$, shortly after photoejection has occurred, the bound electron is in the $2s$ state of He^+. At asymptotically high energies the photoelectron moves in a straight line, and the first-order probability amplitude that the ion undergoes a transition to the $2p$ state is, with $a \sim a_0$,

$$-\frac{i}{\hbar}\int_0^\infty \frac{\langle 2p|z|2s\rangle}{a^2 + v^2t^2} = -i\left(\frac{3\pi e^2 a_0}{2Z\hbar a v}\right). \tag{67}$$

Therefore, at very high photon energies the $2p$-to-$2s$ branching ratio is

$$\frac{\sigma_{2p}}{\sigma_{2s}} \approx \left(\frac{3\pi\hbar}{2Zmav}\right)^2, \tag{68}$$

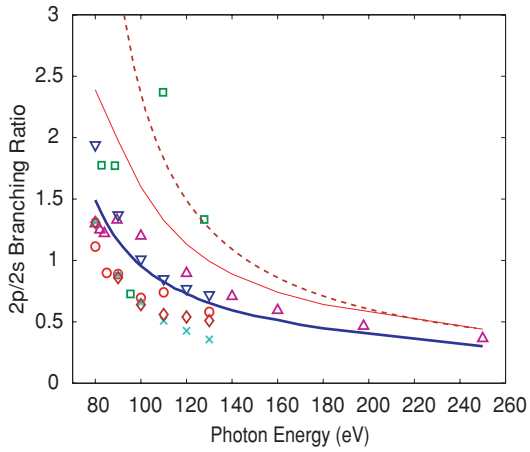

FIG. 3. (Color online) Branching ratio for populations of the $2p$ and $2s$ states of He^+. Thick solid line, present results, including optical potential; thin solid line, present results, excluding optical potential; dashed line, crude formula, Eq. (68) of text; crosses, Sánchez and Martín [16]; triangles, Decleva *et al.* [13]; diamonds, Berrington *et al.* [17] (length gauge); inverted triangles, Berrington *et al.* [17] (velocity gauge); circles, experimental data from Bizau *et al.* [19]; squares, experimental data from Woodruff and Samson [18].

which is inversely proportional to the photon energy when this is very high. Results for the branching ratio are shown in Fig. 3. We have chosen the value of the parameter a in Eq. (68) so as to give perfect agreement at 250 keV between this crude formula and our results obtained from omitting the optical potential. (We find $a = 0.4a_0$, considerably smaller than the characteristic radius $2a_0$ of the $2s$ or $2p$ ion.) However, the optical potential makes a significant contribution to the branching ratio even at 250 eV. The results of Decleva *et al.* approach ours as the photon energy increases, but there is little agreement between the various theoretical results in the range 80–120 eV, and we suspect that is due to the imperfect treatment in the other theories of both the loss of flux to the continuum and the dipole coupling of the photoelectron to the ion.

VI. CONCLUSION

We have described a method for treating collision processes which shares most of the advantages of the standard R-matrix approach, but which accommodates the proper boundary conditions by supplementing the basis for the interior region with an incident wave that takes into account the out-of-phase oscillations of incident and scattered waves. The incident and scattered waves are both standing waves; but whereas the scattered wave vanishes at the boundary of the interior region, the incident wave does not vanish at this boundary—rather, it satisfies the correct asymptotic boundary condition at large distances. The probability flux that is lost to subchannels not treated exactly is accounted for by the optical potential, which is constructed using a resolvent that satisfies outgoing-wave (rather than standing-wave) boundary conditions. We have demonstrated the efficacy of the method by employing an analytic basis to calculate cross sections for photoionization of He accompanied by excitation to the $2s$ and $2p$ states of He^+ at photon energies above the complete breakup threshold. The use of an analytic basis together with the direct determination of the K matrix at the boundary (by matching to the nearly exact analytic solution beyond the boundary) makes the method particularly well suited to the treatment of ultracold collisions.

APPENDIX A: EXTERIOR REGION

In the region exterior to the box we attach a subscript to $\underline{F}(r)$ and its elements to indicate the type of asymptotic boundary condition that the solutions satisfy. The customary K-matrix asymptotic boundary conditions satisfied by the ith column of the channel matrix are, for $r \gg R$,

$$F^{(i)}_{Kj}(r) \to \frac{1}{\sqrt{2\pi k_j}}\left[\sin\left(k_j r - \frac{1}{2}l_j\pi + \gamma_j \ln 2k_j r + \sigma_{l_j}\right)\delta_{ji} + \cos\left(k_j r - \frac{1}{2}l_j\pi + \gamma_j \ln 2k_j r + \sigma_{l_j}\right)K_{ji}\right]. \tag{A1}$$

The index j refers to the subchannel in which the unbound particle leaves the collision, $\hbar k_j$ and l_j are the asymptotic momentum and the angular momentum quantum number, respectively, of this particle, $\sigma_{l_j}(k_j)$ (which we abbreviate as σ_{l_j}) is the Coulomb phase shift, and $\gamma_j = Z'/(a_0 k_j)$ with $Z' = Z - 1$ and Z the atomic number of the nucleus. The prefactor $1/\sqrt{2\pi k_j}$ ensures that the solutions which satisfy S-matrix boundary conditions (see below) are normalized on the energy scale.

However, since orbital angular momentum is exchanged over very large distances due to static dipole coupling, more suitable asymptotic boundary conditions with no dependence on angular momentum are ($r \gg R$)

$$F^{(i)}_{\tilde{K}j}(r) \to \frac{1}{\sqrt{2\pi k_j}}[\sin(k_j r + \gamma_j \ln 2k_j r + \sigma_0)\delta_{ji} + \cos(k_j r + \gamma_j \ln 2k_j r + \sigma_0)\tilde{K}_{ji}]. \tag{A2}$$

We include the s-wave Coulomb phase shift σ_0 in all subchannels since this accounts for most of the Coulomb scattering at large distances, particularly near threshold, and its presence ensures smooth threshold behavior.

Following Seaton [7] we write

$$\underline{F}_{\tilde{K}}(r \geqslant R) = \underline{F}_{\sin}(r) + \underline{F}_{\cos}(r)\underline{\tilde{K}}, \tag{A3}$$

where the matrices $\underline{F}_{\sin}(r)$ and $\underline{F}_{\cos}(r)$ are, for all $r \geqslant R$,

$$\underline{F}_{\sin}(r) = \underline{X}\,\underline{G}_{\sin}(r)\underline{X}^{\dagger}, \tag{A4}$$

$$\underline{F}_{\cos}(r) = \underline{X}\,\underline{G}_{\cos}(r)\underline{X}^{\dagger}. \tag{A5}$$

Here $\underline{X}$ is the constant, energy-independent, unitary matrix that diagonalizes the Hermitian matrix which represents the long-range static interaction of the unbound electron with the residual one-electron ion, that is, the interaction $-Z'e^2\underline{1}/r + (\hbar^2/2)\underline{A}/r^2$, where $\underline{A}$ includes both the angular momentum $\hbar^2 l(l+1)$ of the unbound electron and the static dipole of the residual ion that results from the coupling of degenerate eigenstates. We denote a generic eigenvalue of $\underline{A}$ by $\mu(\mu+1)$; thus, μ is a generalized orbital angular momentum quantum

number. The matrices $\underline{G}_{\sin}(r)$ and $\underline{G}_{\cos}(r)$ are diagonal; their diagonal elements are, respectively,

$$G_{\mu,\sin}(r) = (2\pi k_i)^{-1/2}\left[\sin\left(\mu\frac{\pi}{2} - \tilde{\sigma}_\mu\right) I_\mu(r) + \cos\left(\mu\frac{\pi}{2} - \tilde{\sigma}_\mu\right) R_\mu(r)\right], \tag{A6}$$

$$G_{\mu,\cos}(r) = (2\pi k_i)^{-1/2}\left[\cos\left(\mu\frac{\pi}{2} - \tilde{\sigma}_\mu\right) I_\mu(r) - \sin\left(\mu\frac{\pi}{2} - \tilde{\sigma}_\mu\right) R_\mu(r)\right], \tag{A7}$$

where $\tilde{\sigma}_\mu = \sigma_\mu - \sigma_0$, where σ_μ is the generalized Coulomb phase shift, defined for real and complex μ as

$$\sigma_\mu = -\frac{i}{2}\ln\left(\frac{\Gamma(\mu+1-i\gamma_i)}{\Gamma(\mu+1+i\gamma_i)}\right), \tag{A8}$$

and where, with μ replacing the conventional orbital angular momentum quantum number, $R_\mu(r)$ and $I_\mu(r)$ are, respectively, the regular and irregular Coulomb wave functions, normalized asymptotically to a (possibly complex) sine and cosine with unit amplitude. Since $G_{\mu,\sin}(r)$ and $G_{\mu,\cos}(r)$, respectively, have the form of a real sine and cosine with amplitude $1/\sqrt{2\pi k_i}$ at asymptotically large distances, and since they are solutions to real differential equations—the generalized centrifugal barrier is real—they are real functions for all r. Therefore, $\underline{G}_{\sin}(r)$ and $\underline{G}_{\cos}(r)$ are real, diagonal matrices which, up to overall real factors of $1/\sqrt{2\pi k_i}$ and sine or cosine, are equal to the identity matrix at asymptotically large r. An arbitrary component of Eq. (A4) is

$$F^{(i)}_{j,\sin}(r) = \sum_\mu X_{j\mu} G_{\mu,\sin}(r) X^*_{i\mu}. \tag{A9}$$

It follows that $\underline{F}_{\sin}(r)$ and $\underline{F}_{\cos}(r)$ are Hermitian matrices which become diagonal when $r \gg R$, with diagonal elements $F_{j,\sin}(r)$ and $F_{j,\cos}(r)$, respectively, that have the asymptotic forms

$$F_{j,\sin}(r) \to (2\pi k_j)^{-1/2}\sin(k_j r + \gamma_j \ln 2k_j r + \sigma_0), \tag{A10}$$

$$F_{j,\cos}(r) \to (2\pi k_j)^{-1/2}\cos(k_j r + \gamma_j \ln 2k_j r + \sigma_0), \tag{A11}$$

in accord with Eq. (A2).

The eigenvalues of $\underline{A}$ are real. If a is any such eigenvalue we have $\mu = -\frac{1}{2} \pm \sqrt{a+\frac{1}{4}}$. Hence, μ is complex if $a < -\frac{1}{4}$, in which case its real part is $-\frac{1}{2}$. When $a < -\frac{1}{4}$ the repulsive semiclassical angular momentum barrier $\hbar^2(l+\frac{1}{2})^2/(2r^2)$ is overwhelmed by an attractive inverse-square potential, and as discussed by Landau and Lifshitz the unbound particle would spiral into the nucleus if the attractive potential were to extend to the origin [20]. We choose the plus sign in $\mu = -\frac{1}{2} \pm \sqrt{a+\frac{1}{4}}$ in order that μ is real and positive when $a > 0$, in which case the regular solution $R_\mu(r)$ vanishes at the origin as required. Choosing the minus sign would amount to interchanging the roles of the regular and irregular solutions.

We have omitted from the Hamiltonian, in the exterior region, the optical potential and all but the static monopole and dipole interactions. The (approximate) general solutions of Eq. (5) in the exterior region which satisfy $\tilde{K}$-matrix conditions are elements of the vector

$$\vec{\Psi}_{\tilde{K}}(\vec{r}_1,\vec{r}_2) = \underline{F}^{\mathrm{t}}_{\tilde{K}}(r_2 \geqslant R)\vec{\phi}(r_1,\hat{r}_1,\hat{r}_2). \tag{A12}$$

The matrices $\underline{N}$ and $\tilde{K}$ are determined as usual by matching the interior and exterior solutions, $\underline{F}(r<R)$ and $\underline{F}_{\tilde{K}}(r>R)$, respectively, and their derivatives, at the boundary of the box. This matching is numerically unstable at, and close to, those discrete *real* energies at which one of the eigenvalues of the $\tilde{K}$ matrix has a pole. However, such poles are of no physical consequence (the corresponding poles of the S matrix have residues that vanish). Furthermore, all other eigenvalues of $\tilde{K}$ matrix usually vary slowly over the neighborhood of a pole on the real energy axis, so the $\tilde{K}$ matrix can be interpolated accurately over this neighborhood.

Rather than relate $\underline{\tilde{K}}$ to $\underline{K}$, it is simpler to proceed directly to the S-matrix. We start with the $\tilde{S}$-matrix boundary condition,

$$F^{(i)}_{\tilde{S}j}(r) \to (2\pi k_j)^{-1/2}(e^{-i(k_j r+\gamma_j \ln 2k_j r+\sigma_0)}\delta_{ji} - e^{i(k_j r+\gamma_j \ln 2_j kr+\sigma_0)}\tilde{S}_{ji}), \tag{A13}$$

where

$$\underline{\tilde{S}} = (\underline{1} + i\underline{\tilde{K}})/(\underline{1} - i\underline{\tilde{K}}). \tag{A14}$$

The solution $\vec{F}^{(i)}_{\tilde{S}}(r)$ is a linear combination of solutions $\vec{F}^{(j)}_{\tilde{K}}(r)$. The matrix whose columns are $\vec{F}^{(i)}_{\tilde{S}}(r)$ is

$$\underline{F}_{\tilde{S}} = -i\underline{F}_{\tilde{K}}(\underline{1} + \underline{\tilde{S}}). \tag{A15}$$

Hence, the general solution which satisfies $\tilde{S}$-matrix boundary conditions is

$$\vec{\Psi}_{\tilde{S}} = -i(\underline{1} + \underline{\tilde{S}})^{\mathrm{t}}\vec{\Psi}_{\tilde{K}}. \tag{A16}$$

The S matrix is defined by

$$F^{(i)}_{Sj}(r) \to (2\pi k_j)^{-1/2}\left(e^{-i(k_j r-\frac{1}{2}l_j\pi+\gamma_j \ln 2k_j r+\sigma_{l_j})}\delta_{ji} - e^{i(k_j r-\frac{1}{2}l_j\pi+\gamma_j \ln 2k_j r+\sigma_{l_j})}S_{ji}\right). \tag{A17}$$

It follows that

$$S_{ji} = e^{i(\frac{1}{2}l_j\pi-\tilde{\sigma}_{l_j})}\tilde{S}_{ji}e^{i(\frac{1}{2}l_i\pi-\tilde{\sigma}_{l_i})}, \tag{A18}$$

that is,

$$\underline{S} = \underline{D}\,\underline{\tilde{S}}\,\underline{D}, \tag{A19}$$

where $\underline{D}$ is a diagonal matrix whose diagonal elements are $e^{i(\frac{1}{2}l_j\pi-\tilde{\sigma_{l_j}})}$. We have $\underline{F}_S = \underline{F}_{\tilde{S}}\underline{D}$, and hence the general solution which satisfies S-matrix boundary conditions is

$$\vec{\Psi}_S = \underline{D}\vec{\Psi}_{\tilde{S}}. \tag{A20}$$

The K matrix is defined by

$$\underline{K} = i(\underline{1} - \underline{S})/(\underline{1} + \underline{S}). \tag{A21}$$

As shown above, $\underline{K}$, and therefore $\underline{S}$, are symmetric.

APPENDIX B: *K* MATRIX

A. Symmetry

We denote the exact solutions of Eq. (5) which satisfy K-matrix boundary conditions by $\mathbf{P}|\Psi^{(i)}\rangle$ and $\mathbf{P}|\Psi^{(j)}\rangle$, where the superscripts (i) and (j) denote entrance subchannels i and j, respectively. By using Green's theorem, integrating over angular coordinates and the radial coordinate of the bound electron, recalling that the $\phi_j(r_1,\hat{r}_1,\hat{r}_2)$ are orthonormal, and neglecting oscillating surface terms which average to zero over large distances, we find that (with m the electron mass)

$$K_{ji} - K_{ij} = \frac{8\pi m}{\hbar^2}\langle\Psi^{(i)*}|[(\mathbf{PHP})^\dagger - \mathbf{PHP}]|\Psi^{(j)}\rangle, \quad \text{(B1)}$$

where $|\Psi^{(i)*}\rangle$ is the space-time-reflected solution. Since the only contribution to the integral comes from terms that are bilinear in standing waves that are in phase with each other at the surface, we can treat **PHP** as Hermitian, and hence the integral vanishes. To see this another way, without using Green's theorem, let us first multiply Eq. (5) by $\boldsymbol{\Upsilon}$, and use Eq. (21) together with the antiunitarity of $\boldsymbol{\Upsilon}$ to write

$$[\mathbf{PHP} + \mathbf{V}_{\rm opt}(E)^\dagger - E\mathbf{1}]\mathbf{P}|\Psi^{(i)*}\rangle = 0. \quad \text{(B2)}$$

From this last result, and Eq. (5), it follows by adding and subtracting $\mathbf{V}_{\rm opt}(E) - E\mathbf{1}$ to $(\mathbf{PHP})^\dagger - \mathbf{PHP}$ that the right side of Eq. (B1) does indeed vanish. Hence, the K matrix is symmetric. However, if real transitions out of P space occur, the K matrix is complex, and therefore not Hermitian; hence, the S matrix is not, in general, unitary, in accord with the loss of probability from P space.

B. Variational principle

Since Eq. (5) is homogeneous, the normalization of any solution is arbitrary. Hence, the normalization matrix $\underline{N}$ can be treated as an open variational "parameter" whose "optimal value" can be determined from the Kohn variational principle for the K-matrix $\underline{K}$. The zeroth-order estimates of $\underline{N}$ and $\underline{K}$ are those obtained by matching the interior and exterior solutions, $\underline{F}(r < R)$ and $\underline{F}_{\tilde{K}}(r > R)$, respectively, and their derivatives, at the boundary of the box. The Kohn variational principle yields the first-order variational correction $\delta\mathbf{K}$ to $\underline{K}$. Inclusion of this correction gives a K matrix whose error is of second order. After improving $\underline{K}$ we can improve $\underline{N}$ by rematching the interior and exterior solutions.

The K-matrix satisfies the Kohn variational principle

$$\delta\left\{K_{ij} + \frac{4\pi m}{\hbar^2}\langle\Psi^{(i)*}|\mathbf{P}[E\mathbf{1} - \mathbf{H}_{\rm eff}(E)]\mathbf{P}|\Psi^{(j)}\rangle_{\rm int}\right\} = 0 \quad \text{(B3)}$$

even for dissipative systems. This follows from consideration of

$$M_{ij} \equiv \langle\Psi^{(i)*}|\mathbf{P}[E\mathbf{1} - \mathbf{H}_{\rm eff}(E)]\mathbf{P}|\Psi^{(j)}\rangle_{\rm int}, \quad \text{(B4)}$$

which vanishes if $\mathbf{P}|\Psi^{(j)}\rangle$ is an exact solution of Eq. (5). For small variations about the exact solutions the change in M_{ij} is

$$\delta M_{ij} = \langle\Psi^{(i)*}|\mathbf{P}\big(\mathbf{H}^\dagger - \mathbf{H}\big)\mathbf{P}|\delta\Psi^{(j)}\rangle_{\rm int}. \quad \text{(B5)}$$

Applying Green's theorem, the only contribution to the integral on the right side of Eq. (B5), after integrating over angular coordinates and the radial coordinate of the bound electron, is the surface term at the boundary $r = R$. Using an overdot to indicate the derivative with respect to the radial coordinate of the free electron and introducing the matrix $\underline{M}$ whose elements are M_{ij}, we have

$$\begin{aligned}(2m/\hbar^2)\delta\underline{M} = {}& \underline{F}^{\rm t}(R^-)\delta\dot{\underline{F}}(R^-) - \dot{\underline{F}}^{\rm t}(R^-)\delta\underline{F}(R^-) \\ & + \dot{\underline{F}}^{\rm t}_{\tilde{K}}(R^+)\delta\underline{F}_{\tilde{K}}(R^+) - \underline{F}^{\rm t}_{\tilde{K}}(R^+)\delta\dot{\underline{F}}_{\tilde{K}}(R^+),\end{aligned} \quad \text{(B6)}$$

where R^- and R^+, respectively, are infinitesimally smaller and larger than R. The variations $\delta\underline{F}(R^-)$ and $\delta\dot{\underline{F}}(R^-)$ arise from the variation $\delta\underline{N}$ in the normalization matrix. Hence, taking note that $\underline{F}(R^-) = \underline{F}_{\tilde{K}}(R^+)$ and $\dot{\underline{F}}(R^-) = \dot{\underline{F}}_{\tilde{K}}(R^+)$, we have

$$\delta\underline{F}(R^-) = \underline{F}_{\tilde{K}}(R^+)\underline{N}^{-1}\delta\underline{N}, \quad \text{(B7)}$$

$$\delta\dot{\underline{F}}(R^-) = \dot{\underline{F}}_{\tilde{K}}(R^+)\underline{N}^{-1}\delta\underline{N}. \quad \text{(B8)}$$

The variations $\delta\underline{F}_{\tilde{K}}(R^+)$ and $\delta\dot{\underline{F}}_{\tilde{K}}(R^+)$ arise from the variation $\delta\underline{\tilde{K}}$ in the $\tilde{K}$ matrix. From Eq. (A3) we have

$$\delta\underline{F}_{\tilde{K}}(R^+) = \underline{F}_{\cos}(R^+)\delta\underline{\tilde{K}}, \quad \text{(B9)}$$

$$\delta\dot{\underline{F}}_{\tilde{K}}(R^+) = \dot{\underline{F}}_{\cos}(R^+)\delta\underline{\tilde{K}}. \quad \text{(B10)}$$

Introducing the Wronskian $\underline{\mathcal{W}}(\underline{A},\underline{B}) \equiv \underline{A}^{\rm t}\dot{\underline{B}} - \dot{\underline{A}}^{\rm t}\underline{B}$, it follows that

$$\begin{aligned}(2m/\hbar^2)\delta\underline{M} = {}& \{\underline{\mathcal{W}}[\underline{F}_{\sin}(R^+),\underline{F}_{\sin}(R^+)] \\ & + \underline{\mathcal{W}}[\underline{F}_{\sin}(R^+),\underline{F}_{\cos}(R^+)]\underline{K} \\ & + \underline{K}^{\rm t}\underline{\mathcal{W}}[\underline{F}_{\cos}(R^+),\underline{F}_{\sin}(R^+)] \\ & + \underline{K}^{\rm t}\underline{\mathcal{W}}[\underline{F}_{\cos}(R^+),\underline{F}_{\cos}(R^+)]\underline{K}\}\underline{N}^{-1}\delta\underline{N} \\ & - \underline{\mathcal{W}}[\underline{F}_{\cos}(R^+),\underline{F}_{\sin}(R^+)]\delta\underline{K} \\ & - \underline{K}^{\rm t}\underline{\mathcal{W}}[\underline{F}_{\cos}(R^+),\underline{F}_{\cos}(R^+)]\delta\underline{K}.\end{aligned} \quad \text{(B11)}$$

Since $\underline{F}_{\sin}(r)$ and $\underline{F}_{\cos}(r)$ are solutions of the Schrödinger equation (a second-order differential equation with no first-order derivative), and since the interaction is symmetric, the Wronskian of these solutions can be evaluated at any value of $r > R$. Letting r become infinite, $\underline{F}_{\sin}(r)$ and $\underline{F}_{\cos}(r)$ become diagonal matrices—recall Eqs. (A10) and (A11). When $\underline{A}$ is diagonal, $\underline{\mathcal{W}}(\underline{A},\underline{A})$ vanishes, and therefore the first, fourth, and sixth Wronskians on the right side of Eqs. (B11) vanish. Furthermore, the second and third Wronskians cancel because $\underline{\mathcal{W}}[\underline{F}_{\sin}(R^+),\underline{F}_{\cos}(R^+)] = -\frac{1}{2\pi}\underline{1} = -\underline{\mathcal{W}}[\underline{F}_{\cos}(R^+),\underline{F}_{\sin}(R^+)]$ and because $\underline{K}$ is symmetric. Only the fifth Wronskian survives, and we arrive at $(2m/\hbar^2)\delta\underline{M} = -\frac{1}{2\pi}\delta\underline{K}$; the Kohn variational principle follows.

We can simplify the variational correction after observing that

$$\left\langle\Psi^{(i)*}_{\rm scat}\right|\mathbf{P}[E\mathbf{1} - \mathbf{H}_{\rm eff}(E)]\mathbf{P}|\Psi^{(j)}\rangle_{\rm int} = 0, \quad \text{(B12)}$$

as follows by projecting Eq. (30) onto the subspace spanned by the "box basis," to which $|\Psi^{(j)}_{\rm scat}\rangle$ belongs. Therefore, we

arrive at

$$\delta K_{ij} = 4\pi(m/\hbar^2)\left\langle \Psi_{\rm inc}^{(i)*}\right|\mathbf{P}[E\mathbf{1} - \mathbf{H}_{\rm eff}(E)]\mathbf{P}|\Psi^{(j)}\rangle_{\rm int}. \tag{B13}$$

Inclusion of the variational correction δK_{ij} yields a substantial improvement in accuracy. After this correction has been incorporated the normalization matrix should be recalculated by matching the interior and exterior solutions (not their derivatives) using the corrected value of the K matrix.

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