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Minimum principle for autoionizing states

Leonard Rosenberg
Department of Physics, New York University, New York, New York 10003

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An approximation procedure is introduced for the evaluation of the parameters that determine the positions, widths, and asymmetric shapes of resonance profiles associated with autoionizing states. The essential feature of the method is the availability of a minimum principle to aid in the optimization of trial functions. Such functions, suitably antisymmetrized, are used in the variational calculation of the nonresonant background contribution to the continuum wave function describing a resonant electron-ion scattering process. The rigor of the minimum principle can be maintained, even for atomic systems consisting of more than two electrons, if sufficiently accurate trial bound-state wave functions are employed in the description of ionic target states and those discrete states of the full system that are embedded in the continuum. The analysis of the general problem is preceded, for illustrative purposes, by a study of a solvable model of a resonant two-channel scattering system; the utility of the minimum principle is demonstrated by comparison of exact and variationally determined *s*-wave cross sections. The applicability of the formalism to the calculation of resonant photoionization and bound-state Compton scattering amplitudes is discussed briefly. [S1050-2947(96)00906-7]

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I. INTRODUCTION

The accurate determination of resonant continuum electron-atom and electron-ion wave functions poses a problem of long standing [1], with steady progress being made as computational techniques become increasingly more powerful. Results obtained are useful in the analysis of experimental multichannel scattering and photoionization cross sections. With resonances of the closed-channel type, the Feshbach projection-operator formalism [2] provides a well-defined procedure for decomposing of the wave function into resonant and nonresonant parts; it has been used effectively in numerical studies of autoionizing states of two-electron atoms [3–5]. In addition to providing a prescription for the calculation of resonance parameters, the Feshbach formalism allows for the use of a minimum principle for determining the nonresonant contribution to the wave function [6]. Construction of the Feshbach projection operators for systems of three or more electrons presents a difficult problem and a practical extension of this approach to the treatment of heavier atoms is (to my knowledge) presently unavailable [7]. To fill this gap an alternative procedure [8] has been described recently in which the modified Hamiltonian, that in the Feshbach method is formed by projecting out low-lying states of the target and that enters into the determination of the effective (or optical) potential, is obtained rather by subtraction of certain separable interactions from the physical Hamiltonian. These interactions can be generated from standard Rayleigh-Ritz calculations. Our purpose here is to demonstrate explicitly that in this alternative procedure a clear separation of resonant and nonresonant terms in the wave function of an autoionizing state is achieved and that the minimum principle is preserved if the Rayleigh-Ritz calculations are performed with sufficient accuracy.

In order to describe the essential features of the method in the simplest terms a solvable two-channel model is introduced in Sec. II, with parameters chosen such that a single closed-channel resonance exists. This allows us to illustrate the application of the minimum principle to a resonant scattering process and to compare the variationally determined *s*-wave cross section with that obtained from the exact numerical solution. The general case is taken up in Sec. III where the structure of an autoionizing state of an atomic system is analyzed and a calculational procedure for determining resonance profiles for electron-ion and photon-ion interactions, based on the use of a minimum principle, is outlined.

II. A SIMPLE MODEL

We consider here a particle in a center of force described by a two-channel short-range potential with diagonal elements V_1 and V_2 and off-diagonal elements $V_{12}=V_{21}=U$. The dynamics are defined by the coupled equations

$$\begin{aligned} H_1 f_1 + U f_2 &= E f_1, \\ H_2 f_2 + U f_1 &= E f_2, \end{aligned} \tag{2.1}$$

where $H_i = K + V_i + \epsilon_i$, $i=1,2$, K is the kinetic energy, and the ϵ_i represent the channel thresholds. We assume that channel 2 is closed, i.e., $E<\epsilon_2$, and that standing-wave boundary conditions are imposed in channel 1. Following a standard procedure we introduce the resolvent operators $G_i(E)=(E-H_i)^{-1}$ and express the formal solution to the second of Eqs. (2.1) as

$$f_2 = G_2 U f_1. \tag{2.2a}$$

This leads to the integral equation

$$f_1 = F_1 + G_1 \mathscr{V} f_1, \tag{2.2b}$$

with the effective potential defined as

$$\mathscr{V}(E) = U G_2(E) U. \tag{2.3}$$

The incident wave satisfies $(H_1-E)F_1=0$ and has the asymptotic form

$$F_1(r)\sim\left(\frac{2m}{\hbar^2\pi k}\right)^{1/2}\sin(kr+\delta^{\mathrm{bg}}); \tag{2.4}$$

we consider only s-wave scattering and define $\hbar^2k^2/2m=E-\epsilon_1$. A formal solution of Eq. (2.2b) may be written as

$$f_1=F_1+G_1\mathscr{T}F_1, \tag{2.5}$$

where the scattering operator satisfies

$$\mathscr{T}=\mathscr{V}+\mathscr{V}G_1\mathscr{T}. \tag{2.6}$$

We note that the s-wave phase shift is given by the relation $\delta=\delta^{\mathrm{bg}}+\delta'$ where the contribution δ', the correction to the background scattering phase shift, is obtained from an examination of the asymptotic form of the channel 1 wave function. From Eq. (2.2b), along with the relation $\mathscr{V}f_1=\mathscr{T}F_1$, we find that

$$\tan\delta'=-\pi\langle F_1|\mathscr{T}|F_1\rangle. \tag{2.7}$$

Suppose now that the closed channel supports a single bound state, with $H_2|B\rangle=E_b|B\rangle$, $\epsilon_1<E_b<\epsilon_2$, and $\langle B|B\rangle=1$. Separating off the pole contribution to G_2 we have

$$G_2=|B\rangle(E-E_b)^{-1}\langle B|+G_2^Q. \tag{2.8}$$

The nonresonant remainder is represented as $G_2^Q=Q(E-H_2)^{-1}Q$, with $Q=1-|B\rangle\langle B|$; this resolvent is negative definite for energies below the channel 2 threshold. This would provide the basis for the use of a minimum principle if one could construct trial functions orthogonal to the bound-state wave function, as required by the presence of the projection operator Q. The bound-state wave function is known in the model studied here. Since it is imprecisely known in general, and since we wish to illustrate the general method, we adopt an alternative to the decomposition (2.8) that allows for the preservation of the minimum principle and, consequently, the avoidance of ‘‘variational collapse’’ in a Rayleigh-Ritz type of construction of the resolvent. Thus we write

$$G_2=|B\rangle[(E-E_b)^{-1}-E^{-1}]\langle B|+G_2^{\mathrm{nr}}, \tag{2.9}$$

with $G_2^{\mathrm{nr}}=(E-H_{2,\mathrm{mod}})^{-1}$ and

$$H_{2,\mathrm{mod}}=H_2-\frac{H_2|B\rangle\langle B|H_2}{\langle B|H_2|B\rangle}. \tag{2.10a}$$

The bound state has not been projected out of the spectrum of the modified Hamiltonian but rather its energy is displaced upward to zero, and this serves our purpose equally well—we require only that it be above E. The practical advantage of this alternative lies in the fact that with only an approximation B_t to the bound-state wave function available we may introduce the approximation

$$\hat{H}_2=H_2-\frac{H_2|B_t\rangle\langle B_t|H_2}{\langle B_t|H_2|B_t\rangle} \tag{2.10b}$$

in place of $H_{2,\mathrm{mod}}$ in the definition of G_2^{nr} and this preserves the minimum principle applicable to the calculation of G_2^{nr} provided that B_t is sufficiently accurate to give binding. More precisely, it has been shown [9] that with the trial-bound-state energy $E_{bt}=\langle B_t|H_2|B_t\rangle$ lying below ϵ_2, and with the energy $\overline{\epsilon_2}$ determined to satisfy

$$\overline{\epsilon_2}\leqslant\frac{E_b}{E_{bt}}\,\epsilon_2, \tag{2.11}$$

the operator $\hat{H}_2-\overline{\epsilon_2}$ is positive. Then the resolvent $(E-\hat{H}_2)^{-1}$, an approximation to $G_2^{\mathrm{nr}}(E)$ that can be improved systematically as B_t is improved, will be negative (and satisfy the minimum principle) for $E<\overline{\epsilon_2}$ [10]. For the sake of clarity the following discussion will be carried out in terms of the exact state B.

With the pole term separated off as shown in Eq. (2.9) the effective potential is decomposed as

$$\mathscr{V}=\mathscr{V}_{cc}+\mathscr{V}_{cb}(E-E_b)^{-1}\mathscr{V}_{bc}, \tag{2.12}$$

where we have defined $\mathscr{V}_{cc}=UG_2^{\mathrm{nr}}U$, $\mathscr{V}_{cb}=(E_b/E)^{1/2}U|B\rangle$, and $\mathscr{V}_{bc}=(E_b/E)^{1/2}\langle B|U$. The solution of Eq. (2.6) for the scattering operator is readily shown to have the form

$$\mathscr{T}=\mathscr{T}_{cc}+\mathscr{T}_{cb}(E-E_r)^{-1}\mathscr{T}_{bc}. \tag{2.13}$$

The quantities appearing on the right-hand side are conveniently expressed in terms of the Green's function satisfying the integral equation

$$G_1'=G_1+G_1\mathscr{V}_{cc}G_1'. \tag{2.14}$$

The resonance energy may then be written as $E_r=E_b+\mathscr{T}_{bb}$ with the level shift defined as

$$\mathscr{T}_{bb}=\mathscr{V}_{bc}G_1'\mathscr{V}_{cb}. \tag{2.15a}$$

The remaining quantities are given by the relations

$$\mathscr{T}_{cc}=\mathscr{V}_{cc}+\mathscr{V}_{cc}G_1'\mathscr{V}_{cc}, \tag{2.15b}$$

$$\mathscr{T}_{bc}=\mathscr{V}_{bc}+\mathscr{V}_{bc}G_1'\mathscr{V}_{cc}, \tag{2.15c}$$

$$\mathscr{T}_{cb}=\mathscr{V}_{cb}+\mathscr{V}_{cc}G_1'\mathscr{V}_{cb}. \tag{2.15d}$$

(The relation $\mathscr{T}_{cc}G_1=\mathscr{V}_{cc}G_1'$ is useful in confirming these results.) A similar analysis, in which Eq. (2.2b) for the channel 1 wave function is combined with the decomposition (2.12) of the effective potential, leads to the separation $f_1=f_1^{\mathrm{nr}}+f_1^{\mathrm{r}}$ into nonresonant and resonant components with

$$f_1^{\mathrm{nr}}=F_1+G_1'\mathscr{V}_{cc}F_1, \tag{2.16a}$$

$$f_1^{\mathrm{r}}=G_1'\mathscr{V}_{cb}(E-E_r)^{-1}\mathscr{V}_{bc}f_1^{\mathrm{nr}}. \tag{2.16b}$$

An analogous decomposition $f_2=f_2^{\mathrm{nr}}+f_2^{\mathrm{r}}$ of the channel 2 wave function is obtained by combining Eq. (2.2a) and (2.9); we find that

$$f_2^{\mathrm{nr}}=G_2^{\mathrm{nr}}Uf_1^{\mathrm{nr}}, \tag{2.17a}$$

$$f_2^{\mathrm{r}}=(1+G_2^{\mathrm{nr}}UG_1'U)|B\rangle\left(\frac{E_b}{E}\right)^{1/2}(E-E_r)^{-1}\mathscr{V}_{bc}f_1^{\mathrm{nr}}. \tag{2.17b}$$

A significant step in the calculational procedure is the construction of the resolvent G_2^{nr} appearing in the expression $\mathscr{V}_{cc}=UG_2^{\mathrm{nr}}U$. We remark that this operator, which describes the nonresonant scattering in the closed channel (including the effects of distant resonances) is neglected in some simplified treatments [11]. Such an approximation will be adequate in many cases but it is not generally valid. (A case in which it is grossly inappropriate is described below.) Since G_2^{nr} is negative, a variational approximation introducing a negative error may be taken to be of the separable form [8]

$$G_{2t}^{\mathrm{nr}}(E)=|\xi\rangle\frac{1}{\langle\xi|(E-H_{2,\mathrm{mod}})|\xi\rangle}\langle\xi|, \tag{2.18}$$

where the modified Hamiltonian is that defined in Eq. (2.10a), and where the trial function ξ is optimized by the minimization of a diagonal expectation value of G_{2t}^{nr}. In the numerical application of this simple model described below, in which square-well potentials are assumed, the bound-state function is known precisely. More generally, the modified Hamiltonian shown in Eq. (2.10b) would be employed.

The variational approximation for the nonresonant component of the effective potential is given by the separable form $\mathscr{V}_{cc}\approx UG_{2t}^{\mathrm{nr}}U$, and in this approximation the integral Eq. (2.14) has the solution

$$G_1'=G_1+G_1U|\xi\rangle D^{-1}\langle\xi|UG_1, \tag{2.19a}$$

with

$$D=\langle\xi|(E-H_{2,\mathrm{mod}}-UG_1U)|\xi\rangle. \tag{2.19b}$$

Then, with the definition

$$|B'\rangle=|B\rangle+|\xi\rangle D^{-1}\langle\xi|UG_1U|B\rangle, \tag{2.20}$$

and use of Eqs. (2.13), (2.15), and (2.7), we have

$$-\frac{1}{\pi}\tan\delta'=|\langle F_1|U|\xi\rangle|^2D^{-1}+|\langle F_1|U|B'\rangle|^2\left(\frac{E_b}{E}\right)(E-E_r)^{-1}. \tag{2.21}$$

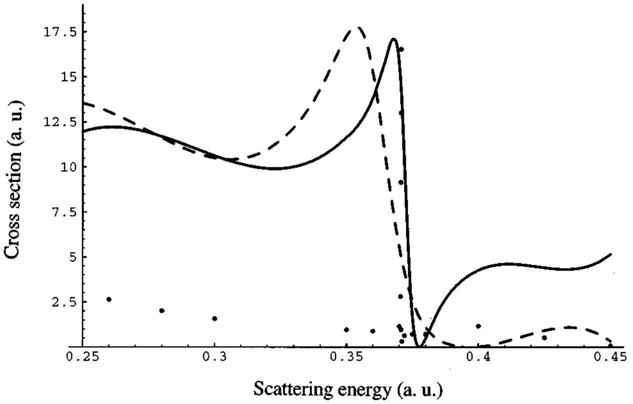

FIG. 1. Cross section for s-wave resonance scattering in a solvable two-channel model. The solid curve is the exact cross section and the dashed curve was obtained variationally. Results obtained with closed-channel, nonresonant scattering ignored appear as isolated points; the resonance width so calculated is too small to be resolved graphically.

With the potential matrix $\mathbf{V}(r)$ taken to be of the square-well form the model is exactly solvable [12] and this allows us to judge the accuracy of the approximation. The parameters were chosen as

$$\frac{2m}{\hbar^2}\mathbf{V}(r)=-\frac{1}{a_0^2}\begin{pmatrix}0.06 & 0.3\\ 0.3 & 0.55\end{pmatrix},\quad r<6a_0 \tag{2.22}$$

where a_0 is the Bohr radius, and $\mathbf{V}(r)=\mathbf{0}, r\geqslant 6a_0$. The separation between channel thresholds was taken to be $\epsilon_2-\epsilon_1=0.5$ a.u. With these parameters one finds a closed-channel bound state at $E_b=0.314$ a.u. and an associated ''Feshbach'' resonance in the s-wave cross section; the exact cross section is shown as the solid curve in Fig. 1. (The energy scale was fixed by setting $\epsilon_1=0$.) Note that the strong interchannel coupling built into the model has led to rather large values for the level shift and width. The trial function was taken to be of the simple form

$$\xi(r)=\exp(-c_1r)-\exp(-c_2r)-c_3r\,\exp(-c_4r). \tag{2.23}$$

A search, by no means exhaustive, for the parameters giving the minimum value of $\langle F_1|UG_{2t}^{\mathrm{nr}}U|F_1\rangle$ led to the set $c_1/a_0=2.8$, $c_2/a_0=3.2$, $c_4/a_0=4.5$, and $c_3=0.17$. Use of the minimum principle in this search is essential since the parameters appear nonlinearly. The dashed curve in Fig. 1 gives the result of the variational calculation of the cross section. One sees that a more elaborate trial function would be required to do more than reproduce the general shape of the exact cross section. On the other hand, the improvement over the approximation in which the potential $\mathscr{V}_{cc}$ is ignored—values of the cross section so obtained are shown as isolated points in Fig. 1—is dramatic. The extent of this discrepancy is undoubtedly atypical but the example suggests that the effects of the nonresonant interaction can be substantial and should be carefully examined in general.

III. APPLICATION TO ATOMIC SYSTEMS

A. Summary of the scattering formalism

To keep the discussion reasonably self-contained we begin by reviewing the essential features of the effective-potential formalism derived earlier [8]. We consider the scattering of an electron by an N-electron ion of nuclear charge $Z|e|$. The eigenvalue equation for the target bound states is written as

$$h(n)|\chi_\gamma(\overline{n})\rangle=\epsilon_\gamma|\chi_\gamma(\overline{n})\rangle, \tag{3.1}$$

with negative eigenvalues $\epsilon_1\leqslant\epsilon_2\leqslant\ldots\leqslant\epsilon_p$ and with $h(n)$ representing the Hamiltonian of the N-electron system remaining after the nth electron has been removed. We use the abbreviated notation [13]

$$\chi_\gamma(\overline{n})=\chi_\gamma(1,2,\ldots,n-1,n+1,\ldots,N+1) \qquad (3.2)$$

for the antisymmetric target state, with the space and spin coordinates of the jth particle represented by the symbol j. The full Hamiltonian is $H=h(n)+K(n)+V(n)$, where $K(n)$ is the kinetic energy of the nth electron to which is added its monopole Coulomb interaction with the residual system. $V(n)$ is the interaction of the nth electron with the residual system, with the monopole Coulomb potential subtracted off. [Effects of long-range Coulomb distortion appear in the eigenstates of $K(n)$.] We introduce the modified Hamiltonian

$$\hat{H}=H-\sum_{n=1}^{N+1}\sum_{\gamma=1}^{p}\frac{h(n)|\chi_{\gamma t}(\overline{n})\rangle\langle\chi_{\gamma t}(\overline{n})|h(n)}{\langle\chi_{\gamma t}(\overline{n})|h(n)|\chi_{\gamma t}(\overline{n})\rangle}, \qquad (3.3)$$

where the $\chi_{\gamma t}(\overline{n})$ are trial target states to be obtained from a standard (multilevel) Rayleigh-Ritz calculation [14,15]. In the following, for notational simplicity, we assume that these states are exact eigenstates, in which case $\hat{H}$ will have ϵ_{p+1} as its lowest continuum threshold energy. If, as is usually the case, the target states are imprecisely known an upper bound $\overline{\epsilon^{p+1}}$ on this lowest threshold can be obtained provided the trial target states are sufficiently accurate to give binding. Then for $E<\overline{\epsilon_{p+1}}$ the construction of the resolvent $(E-\hat{H})^{-1}$ can be approached using a minimum principle, as shown below. (The similarity between this procedure and the treatment of resonant states described in Sec. II should be clear. Additional details can be found in Ref. [9].)

We look for the continuum wave function of the full system, corresponding to an incident channel with index ν, in the form

$$\Psi_\nu(1,2,\ldots,N+1)=\mathscr{A}\sum_\gamma\chi_\gamma(\overline{1})f_{\gamma\nu}(1)+M_\nu(1,2,\ldots,N+1), \qquad (3.4)$$

where $\mathscr{A}$ is the antisymmetrizer defined by the relation

$$\mathscr{A}\chi(\overline{1})f(1)=\sum_{n=1}^{N+1}(-1)^{n+1}\chi(\overline{n})f(n). \qquad (3.5)$$

Incoming-wave boundary conditions are assumed since we later apply the theory to a photoionization process. [The conventional superscript $(-)$ indicating such boundary conditions is omitted to simplify notation. The details of the vector coupling that gives the product $\chi_\gamma f_{\gamma\nu}$ well-defined total orbital angular momentum and spin quantum numbers is likewise omitted here.] The completely antisymmetric function M_ν, which contains the effects of virtual excitations, is given in terms of the resolvent $\hat{G}(E)=(E-\hat{H})^{-1}$ as

$$M_\nu=\hat{G}(E)\sum_\gamma\mathscr{A}\hat{V}(1)\chi_\gamma(\overline{1})f_{\gamma\nu}(1), \qquad (3.6)$$

and is asymptotically decaying for E lying below the continuum threshold of $\hat{H}$. The modified potential appearing in Eq. (3.6) is defined by

$$\hat{V}(n)=V(n)-\sum_{n'\neq n}\sum_\gamma\epsilon_\gamma|\chi_\gamma(\overline{n'})\rangle\langle\chi_\gamma(\overline{n'})|, \qquad (3.7)$$

and arises as a consequence of the subtraction procedure based on Eq. (3.3). This procedure leads to a prescription for determining the functions $f_{\gamma\nu}$ that can be summarized as follows. Let F_ν be the regular solution, normalized on the energy scale, of the wave equation $(K-E_\nu)|F_\nu\rangle=0$ for an electron interacting with the monopole Coulomb field of the target. The associated propagator is

$$\mathscr{G}_\nu(E)=(E-\epsilon_\nu-K-i\eta)^{-1}-(E-K)^{-1}, \qquad (3.8)$$

where η is a positive infinitesimal. [Recall that incoming-wave boundary conditions are assumed. The second term on the right in Eq. (3.8) is nonsingular for E lying below the continuum threshold of K, so that this term does not contribute to the asymptotic particle flux. Its presence is required by the particular subtraction procedure used here. Compare with the first term on the right in Eq. (2.9).] The effective potential is given by the expression [8]

$$\mathscr{V}_{\alpha\gamma}(E)=\langle\chi_\alpha(\overline{1})|\{[E-K(1)](\mathscr{A}-1)+\mathscr{A}\hat{V}(1)+\hat{V}(1)\hat{G}(E)\mathscr{A}\hat{V}(1)\}|\chi_\gamma(\overline{1})\rangle. \qquad (3.9)$$

The scattering operator is obtained by solving a one-body integral equation of the form

$$\mathscr{T}_{\alpha\nu}=\mathscr{V}_{\alpha\nu}+\sum_\gamma\mathscr{V}_{\alpha\gamma}\mathscr{G}_\gamma\mathscr{T}_{\gamma\nu}, \qquad (3.10)$$

and once this is accomplished the one-electron wave functions appearing in Eqs. (3.4) and (3.6) can be found by evaluation of the expression

$$f_{\alpha\nu}=F_\nu\delta_{\alpha\nu}+\mathscr{G}_\alpha\mathscr{T}_{\alpha\nu}F_\nu. \qquad (3.11)$$

B. Resonance decomposition of wave functions and Green's functions

The equivalent one-body integral Eq. (3.10) for the scattering operator can be solved by routine numerical methods and this leaves as the chief dynamical problem the construction of the resolvent $\hat{G}$ appearing in Eq. (3.9) for the effective potential. For a range of energies below the continuum threshold of the modified Hamiltonian $\hat{H}$ a minimum principle is available as an aid in this calculation. Any discrete states lying below threshold must be effectively ''subtracted out'' for the minimum principle to be applicable. Such a procedure, applied in Sec. II to a simple model, will now be described in the context of the more general effective potential formalism. One is led in this way to a variational determination of the continuum wave functions and Green's functions, explicitly decomposed into resonant and nonresonant components. Results obtained this way can be useful in studies of photon-atom interactions as well as in electron-ion scattering.

Assuming for simplicity that a single isolated bound state of $\hat{H}$ exists, satisfying $(\hat{H}-E_b)|B\rangle=0$ and normalized to unity, we introduce the nonresonant resolvent

$$\hat{G}^{\mathrm{nr}}(E)=\left(E-\hat{H}+\frac{\hat{H}|B\rangle\langle B|\hat{H}}{\langle B|\hat{H}|B\rangle}\right)^{-1}, \qquad (3.12)$$

in which the bound-state pole singularity has been displaced upward to zero energy. It will be convenient in the following to assume $|B\rangle$ to be precisely known, with the understanding that the minimum principle will be preserved when a sufficiently accurate trial function is inserted into Eq. (3.12). We now have the decomposition [analogous to that shown in Eq. (2.9)]

$$\hat{G}(E)=|B\rangle\,\frac{E_b}{E}\,\frac{1}{E-E_b}\,\langle B|+\hat{G}^{\rm nr}, \tag{3.13}$$

which, when inserted into Eq. (3.9), leads to the resonance decomposition

$$\mathscr{V}_{\alpha\nu}=\mathscr{V}^{\rm nr}_{\alpha\nu}+\mathscr{V}_{\alpha b}\,\frac{1}{E-E_b}\,\mathscr{V}_{b\nu} \tag{3.14}$$

with $\mathscr{V}^{\rm nr}_{\alpha\nu}$ obtained from Eq. (3.9) by the replacement of $\hat{G}$ with $\hat{G}^{\rm nr}$. A corresponding decomposition of the scattering operator [compare with Eqs. (2.13)–(2.15)] is obtained by combining Eqs. (3.14) and (3.10), yielding

$$\mathscr{T}_{\alpha\nu}=\mathscr{T}^{\rm nr}_{\alpha\nu}+\mathscr{T}_{\alpha b}\,\frac{1}{E-E_r}\,\mathscr{T}_{b\nu}. \tag{3.15}$$

The various quantities appearing here are defined in terms of the solution of the integral equation

$$\mathscr{G}'_{\alpha\nu}=\mathscr{G}_{\alpha}\delta_{\alpha\nu}+\sum_{\gamma}\;\mathscr{G}_{\alpha}\mathscr{V}^{\rm nr}_{\alpha\gamma}\mathscr{G}'_{\gamma\nu}. \tag{3.16}$$

Thus the resonance energy is $E_r=E_b+\mathscr{T}_{bb}$, with

$$\mathscr{T}_{bb}=\sum_{\alpha,\gamma}\;\mathscr{V}_{b\alpha}\mathscr{G}'_{\alpha\gamma}\mathscr{V}_{\gamma b}. \tag{3.17a}$$

We also have

$$\mathscr{T}^{\rm nr}_{\alpha\nu}=\mathscr{V}^{\rm nr}_{\alpha\nu}+\sum_{\gamma,\sigma}\;\mathscr{V}^{\rm nr}_{\alpha\gamma}\mathscr{G}'_{\gamma\sigma}\mathscr{V}^{\rm nr}_{\sigma\nu}, \tag{3.17b}$$

$$\mathscr{T}_{\alpha b}=\mathscr{V}_{\alpha b}+\sum_{\gamma,\sigma}\;\mathscr{V}^{\rm nr}_{\alpha\gamma}\mathscr{G}'_{\gamma\sigma}\mathscr{V}_{\sigma b}, \tag{3.17c}$$

$$\mathscr{T}_{b\nu}=\mathscr{V}_{b\nu}+\sum_{\gamma,\sigma}\;\mathscr{V}_{b\gamma}\mathscr{G}'_{\gamma\sigma}\mathscr{V}^{\rm nr}_{\sigma\nu}. \tag{3.17d}$$

One may identify the real part of the level shift, defined in Eq. (3.17a), as $(\mathscr{T}^{(-)}_{bb}+\mathscr{T}^{(+)}_{bb})/2$ with the imaginary part determined from the remainder $(\mathscr{T}^{(-)}_{bb}-\mathscr{T}^{(+)}_{bb})/2$, where the superscript indicates the sign of the imaginary part of the energy variable in the Green's function $\mathscr{G}'_{\alpha\gamma}$ [16]. Recalling that the effective potential is Hermitian we see from Eq. (3.17a) that the imaginary part is obtained from an evaluation of the antihermitian part of $\mathscr{G}'_{\alpha\gamma}$. This is easily accomplished using Eq. (3.16) and the property $(\mathscr{G}^{(-)}_{\alpha}-\mathscr{G}^{(+)}_{\alpha})/2=i\pi\delta(E-\epsilon_{\alpha}-K)$ which follows from Eq. (3.8). The result may be conveniently expressed in terms of the open-channel propagator

$$g(E)=\sum_{\alpha,\sigma}\;|\chi_{\alpha}\rangle\mathscr{G}'_{\alpha\sigma}\langle\chi_{\sigma}|, \tag{3.18a}$$

which may be decomposed as

$$\begin{aligned} g(n,\overline{n};n',\overline{n'};E)&=g_P(n,\overline{n};n',\overline{n'};E)\\ &\quad+i\pi\sum_{\nu}\;|\psi_{\nu}(n,\overline{n})\rangle\langle\psi_{\nu}(n',\overline{n'})|, \end{aligned} \tag{3.18b}$$

where $g_P(E)\equiv[g(E-i\eta)+g(E+i\eta)]/2$ and

$$|\psi_{\nu}(n,\overline{n})\rangle=\sum_{\gamma}\;|\chi_{\gamma}(\overline{n})\rangle|f^{\rm nr}_{\gamma\nu}(n)\rangle. \tag{3.18c}$$

In accordance with notation established earlier the pair of arguments $(n,\overline{n})$ appearing in these equations serve to specify the partition of the system into two subsystems, one containing the nth electron and the other containing the residual N-electron system. (The interacting propagator is specified by both initial and final partitions, accounting for virtual rearrangement scattering.) The resonance energy may be expressed in terms of these functions as $E_r=E_b+\Delta+i\Gamma/2$ with

$$\Delta(E)=\left(\frac{E_b}{E}\right)\langle B|\mathscr{A}\hat{V}(1)g_P(1,\overline{1};1',\overline{1'};E)\hat{V}(1')|B\rangle, \tag{3.19a}$$

$$\begin{aligned} \Gamma(E)=2\pi\left(\frac{E_b}{E}\right)\sum_{\nu}\;&\langle B|\mathscr{A}\hat{V}(1)|\psi_{\nu}(1,\overline{1})\rangle\\ &\times\langle\psi_{\nu}(1',\overline{1'})|\hat{V}(1')|B\rangle. \end{aligned} \tag{3.19b}$$

Having separated the scattering operator into resonant and nonresonant parts we can now do the same for the wave function. Thus we write $f_{\alpha\nu}=f^{\rm nr}_{\alpha\nu}+f^{\rm r}_{\alpha\nu}$, with the nonresonant and resonant components determined by expanding the scattering operator appearing in Eq. (3.11) into its nonresonant and resonant components. We find, with the aid of Eqs. (3.16) and (3.17b),

$$f^{\rm nr}_{\alpha\nu}=F_{\alpha}\delta_{\alpha\nu}+\sum_{\gamma}\;\mathscr{G}'_{\alpha\gamma}\mathscr{V}^{\rm nr}_{\gamma\nu}F_{\nu}, \tag{3.20}$$

and

$$f^{\rm r}_{\alpha\nu}=\sum_{\gamma,\sigma}\;\mathscr{G}'_{\alpha\gamma}\mathscr{V}_{\gamma b}(E-E_r)^{-1}\mathscr{V}_{b\sigma}f^{\rm nr}_{\sigma\nu}. \tag{3.21}$$

In a similar way we write $M_{\nu}=M^{\rm nr}_{\nu}+M^{\rm r}_{\nu}$. Retaining only the nonresonant contributions in Eq. (3.6) we have

$$|M^{\rm nr}_{\nu}\rangle=\hat{G}^{\rm nr}\mathscr{A}\hat{V}(1)|\psi_{\nu}(1,\overline{1})\rangle. \tag{3.22}$$

This leaves the resonant part which, after some algebra, and with the omission of partition labels to simplify the writing, can be put in the form

$$|M^{\mathrm{nr}}_{\nu}\rangle=[1+\hat{G}^{\mathrm{nr}}\mathscr{A}\hat{V}g(E)\hat{V}]|B\rangle\,\frac{E_b}{E}\,\frac{1}{E-E_r}\,\langle B|\mathscr{A}\hat{V}|\psi_{\nu}\rangle. \tag{3.23}$$

Using these results we can decompose the full wave function as $\Psi_{\nu}=\Psi^{\mathrm{nr}}_{\nu}+\Psi^{\mathrm{r}}_{\nu}$ with

$$|\Psi^{\mathrm{nr}}_{\nu}\rangle=\mathscr{A}|\psi_{\nu}\rangle+\hat{G}^{\mathrm{nr}}\mathscr{A}\hat{V}|\Psi_{\nu}\rangle, \tag{3.24a}$$

$$|\Psi^{\mathrm{r}}_{\nu}\rangle=|B'(E)\rangle\,\frac{E_b}{E}\,\frac{1}{E-E_r}\,\langle B|\mathscr{A}\hat{V}|\psi_{\nu}\rangle, \tag{3.24b}$$

where

$$|B'(E)\rangle=[1+\mathscr{A}g(E)\hat{V}+\hat{G}^{\mathrm{nr}}(E)\mathscr{A}\hat{V}g(E)\hat{V}]|B\rangle. \tag{3.24c}$$

It has been shown previously how the structure of the resonant continuum wave function, analyzed in terms of the Feshbach projection operators, determines resonance profiles for scattering and photoionization cross sections [3–5]. To establish the correspondence between the present approach, which does not involve projection operators, and that earlier work we record the form taken by the matrix element for photoionization when the continuum wave function is decomposed as in Eqs. (3.24). The cross section is proportional to the absolute square of the matrix element $\langle\Psi_g|H'|\Psi_{\nu}\rangle$ where $|\Psi_g\rangle$ is the ground state of the atom and H' is the photon-atom interaction in the dipole approximation. To express the result in a form that parallels earlier work [5,17] as closely as possible we introduce some notation. We define the quantities

$$\epsilon=2\,\frac{(E-E_b-\Delta)}{\Gamma}, \tag{3.25}$$

$$\alpha_{\nu}=\frac{2\pi}{\Gamma}\,\frac{1}{\langle\Psi_g|H'|\Psi^{\mathrm{nr}}_{\nu}\rangle}\,\langle B|\mathscr{A}\hat{V}|\psi_{\nu}\rangle\sum_{\mu}\,\langle\Psi_g|H'|\Psi^{\mathrm{nr}}_{\mu}\rangle \times\langle\psi_{\mu}|\hat{V}|B\rangle\left(\frac{E_b}{E}\right), \tag{3.26}$$

and

$$q=\frac{\langle\Psi_g|H'|B'_P\rangle}{\pi\Sigma_{\mu}\langle\Psi_g|H'|\Psi^{\mathrm{nr}}_{\mu}\rangle\langle\psi_{\mu}|\hat{V}|B\rangle}, \tag{3.27a}$$

with

$$|B'_P(E)\rangle=[1+\mathscr{A}g_P(E)\hat{V}+\hat{G}^{\mathrm{nr}}(E)\mathscr{A}\hat{V}g_P(E)\hat{V}]|B\rangle. \tag{3.27b}$$

The matrix element may then be written as

$$\langle\Psi_g|H'|\Psi_{\nu}\rangle=\langle\Psi_g|H'|\Psi^{\mathrm{nr}}_{\nu}\rangle\left[1+\frac{\alpha_{\nu}(q+i)}{\epsilon-i}\right]. \tag{3.28}$$

This reproduces a standard representation [17], and provides a variational prescription for determining the weakly energy-dependent matrix elements that enter into the expression for the photoionization amplitude. The very close formal correspondence between the present results and those obtained in Ref. [5] using the Feshbach method should be noted.

The analysis of the resonance structure of the scattering amplitude and wave function can be extended to the full Green's function $G(E)=(E-H)^{-1}$, allowing for applications to higher-order processes. For example, in the bound-state Compton scattering process, atom + $\gamma\rightarrow$ion + $e^-+\gamma'$, the electron can be ejected into a resonant state and the effect of the interference between resonant and nonresonant components of the final-state wave function can be studied as described above for photoionization. One may also wish to examine the effect of an intermediate-state resonance, as determined by the structure of the Green's function, in which resonant and nonresonant contributions are isolated. We now indicate very briefly how that structure can be derived using the techniques introduced above.

The resolvent identity

$$G=\hat{G}+\hat{G}(H-\hat{H})G \tag{3.29}$$

provides an appropriate starting point since, by virtue of Eq. (3.3), the kernel is separable. (The target wave functions are taken to be exact here.) Then, by straightforward algebra [9], one arrives at the representation

$$G=\hat{G}+\sum_{i,j}\,\sum_{\alpha,\beta}\,[1+\hat{G}\hat{V}(i)]|\chi_{\alpha}(\overline{i)\rangle}(\mathscr{G}_{\alpha}(i)\,\delta_{i,j}\delta_{\alpha\beta} +\mathscr{G}_{\alpha}(i)\widetilde{\mathscr{T}}_{\alpha\beta}(i,j)\,\mathscr{G}_{\beta}(j))\langle\chi_{\beta}(\overline{j)|}[1+\hat{V}(j)\hat{G}]. \tag{3.30}$$

Here $\widetilde{\mathscr{T}}_{\alpha\beta}(i,j)$ is the scattering operator for distinguishable particles (particle j incident in channel β and particle i emergent in channel α), generated by the effective potential

$$\widetilde{\mathscr{V}}_{\alpha\beta}(i,j)=\langle\chi_{\alpha}(\overline{i)|}([E-K(i)](1-\delta_{ij})+\hat{V}(j) +\hat{V}(i)\hat{G}\hat{V}(j))|\chi_{\beta}(\widetilde{j})\rangle. \tag{3.31}$$

The antisymmetrized form given earlier in Eq. (3.9) is the version into which $\widetilde{\mathscr{V}}_{\alpha\beta}$ is transformed when operating in the space of antisymmetric states. As a consistency check one verifies that the wave function in the form (3.4) is generated from the Green's function (3.30) by application of the ''residue rule''

$$\Psi_{\nu}=\lim_{\eta\rightarrow 0}(-i\eta)G(E-i\eta)\mathscr{A}\chi_{\nu}(\overline{1})F_{\nu}(1). \tag{3.32}$$

Proceeding now in analogy with the earlier treatment of the wave function, we define the nonresonant component G^{nr} of the Green's function G by replacing $\widetilde{\mathscr{T}}_{\alpha\beta}$ and $\hat{G}$ appearing in Eqs. (3.30) and (3.31) by their nonresonant components $\widetilde{\mathscr{T}}^{\mathrm{nr}}_{\alpha\beta}$ and $\hat{G}^{\mathrm{nr}}$, respectively. Taking into account the fact that the bound-state wave function B is antisymmetric, the remainder can be expressed, after some rearrangement, in the notation established in connection with Eq. (3.24) for the wave function. The full Green's function then takes on the form

$$G(E)=G^{\mathrm{nr}}(E)+|B'(E)\rangle\left(\frac{E_b}{E}\right)\,\frac{1}{E-E_r}\,\langle B'(E)|, \tag{3.33}$$

with $|B'(E)\rangle$ given by Eq. (3.24c). This representation can be useful in the analysis of resonance profiles for a variety of higher-order processes, in addition to the photon-atom scattering example mentioned earlier.

IV. SUMMARY

A formulation of multichannel electron-ion scattering theory, applicable for scattering energies lying below the two-electron continuum threshold, has been presented. It allows for a clear separation of nonresonant and resonant components of the scattering amplitude and provides a calculational prescription that combines the use of minimum principles and one-body integral equations. Antisymmetrization requirements are explicitly accounted for, as are the effects of long-range Coulomb forces between projectile and target ion. The validity of the minimum principle is maintained provided that target wave functions are determined with sufficient accuracy—the essential requirement is that they should be accurate enough to give binding. Application of the method to systems consisting of more than two electrons is then feasible, this in contrast to resonance theories based on the use of Feshbach projection operators which are difficult to construct. As an illustration of the method, and in particular of the use of the minimum principle, a solvable two-channel scattering model was treated variationally with results compared to the exact cross section. The resonance analysis of the scattering amplitude has been extended here to the continuum wave function and to the full Green's function of the system, thereby allowing for applications to scattering processes that take place in the presence of a radiation field. In addition to the first-order and second-order reactions discussed briefly above, the theory can be extended to the treatment of multiphoton processes. This extension is fairly straightforward if one adopts the approximation that two-electron continuum states are excluded. A more elaborate revision would be required to overcome this limitation.

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