General form of the quantum-defect theory

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(Received 16 November 1978)

The quantum-defect-theory (QDT) treatment of an electron in the Coulomb field surrounding an ionic core is recast in a form largely independent of field characteristics and thus applicable, e.g., to square wells or to the Morse fields of diatomic molecules. The reformulation parallels Seaton's classification of alternative Coulomb-field wave functions, and makes it applicable to other fields. Wronskians of alternative pairs of base functions have an important role in the theory. For electron energies $\epsilon < 0$ in a Coulomb field these Wronskians reduce to trigonometric functions of $\nu = (-2\epsilon)^{-1/2}$, familiar in the QDT; other fields lead to trigonometric functions of different arguments. Quantum defects are generalized to eigenvalues of a reaction matrix, as in Seaton's work, but this matrix can now be calculated even below threshold energies with the introduction of a "smooth" Green's function appropriate to QDT applications.

I. INTRODUCTION

The quantum-defect theory (QDT) originates from the interpretation of Rydberg's formula for the levels of a regular series, $E_n = -R/(n-\mu)^2$; the quantum defect (or "Rydberg correction") μ embodies the influence of a nonhydrogenic ionic core upon the levels of an excited electron.[1] The possibility of parametrizing the effect of a complicated electron-core interaction compactly constitutes the main attraction of the QDT in its various forms. It rests on the fact that an excited electron moves in a simple field, typically Coulomb, when outside the core.

The main analytical development, by Seaton,[2] introduces alternative channels of electron excitation, distinguished by different core levels, different orbital momenta, etc., and is thus called multichannel QDT. This treatment starts from a close-coupling formulation of electron-ion scattering theory and extrapolates it to the discrete spectrum of Rydberg levels, thus interpreting perturbed series of levels in terms of scattering parameters. The interplay of Rydberg spectra and electron-core scattering has permitted extensive use of the MQDT formalism for semiempirical analysis of diverse phenomena,[3] whereas Seaton had emphasized *ab initio* calculations. Still more recently, the MQDT has been connected to the theoretical methods of configuration mixing through alternative forms of the Green's function for the motion of an electron in the optical potential field generated by the core.[4] (In our application the "optical" potential is real, local, isotropic, and designed to represent the average interaction of one particle with the rest of the system in a zeroth approximation.)

The developments of Refs. 3 and 4 rest mainly on the separate treatment of long- and short-range interactions and are thus independent of the Coulomb character of the long-range field that may bind an electron or merely deflect it near a core. Specifically, Ref. 3 mentions also applications to negative ions,[5] where the long-range Coulomb field is absent and the core-polarization field looms more important. However, such applications have proceeded thus far by analogy rather than by an explicit generalization of the formal MQDT. This paper aims at formulating the broader framework. We may keep referring to atomic electrons throughout the paper, for the sake of definiteness and familiarity, but we intend the entire treatment to apply in principle to the motion of other particles too.

A preliminary but lengthy development seems necessary to cast the properties of Coulomb field wave functions in a form convenient for extension to other fields (Sec. II). Analytical properties will be discussed for three types of asymptotic behavior of the potential: constant, $-1/r$, and $-1/r^2$. The latter two are singled out by yielding a nonzero density of continuum states in the zero-energy limit and an infinite series of bound levels converging to this same limit. Any other attractive field departs from one of these three laws by amounts that converge to zero faster than $1/r^2$. The effect of these departures will be represented, in Sec. II E, by phase shifts and by analogous parameters which modify the analytical laws pertaining to a field $-1/r^p$ with $p=0, 1, 2$. These parameters are smooth functions of energy across the ionization threshold but their energy dependence is often nonanalytic, i.e., it produces discontinuities in derivatives higher than the first. The threshold behavior of parameters representing departures from our three basic fields is the subject of effective-range theories. The nonanalyticity of these parameters will be touched upon but lies otherwise outside our scope.

Section III will then extend the customary treatments[6] of the Green's function of a particle in an optical potential so as to utilize the flexibility of QDT procedures for dealing with the nonlocal but short-range aspect of exchange interactions. Full application to multichannel problems follows finally in Sec. IV. Aspects of the Green's-function analysis that had not been identified in Ref. 4 will thus be brought out. To remedy deficiencies of that earlier work, to the point of superseding it, is in fact a second aim of the present paper.

Some vagueness had also resulted in Ref. 4 from an attempt to maximize generality. Here instead we shall restrict our scope to dealing with long-range potentials that are local and centrally symmetric. (Recall that nonlocal fields are, in fact, confined to the interior of the core, as long as one disregards the escape of two or more electrons from the core.) Noncentral, local fields do occur at long ranges and are currently treated laboriously by close-coupling calculations. The need to remove the restrictions to the escape of a single electron and—in the present paper—to central symmetry is currently acute but will not be addressed here. We shall also restrict ourselves for simplicity to many-electron wave functions constructed from eigenfunctions of a single-electron radial Hamiltonian $h(\vec{r})$ with a screening potential $v^{\rm scr}(r)$ common to all electrons, without exploring to what extent $h(\vec{r})$ might usefully differ for different channels. No restriction will be placed, however, on the number of configurations included in the complete wave function. We shall refer explicitly to single atoms, but molecular applications are also in order; the main adaptation required is mentioned at the end of Sec. I.

A. Analytical framework

Accordingly we consider, for an N-electron atom or ion, wave functions constructed from eigenfunctions of a single-particle Hamiltonian

$$h(\vec{r}) = p^2/2m - Ze^2/r + v^{\rm scr}(r) . \tag{1.1}$$

The N-electron Hamiltonian then has the form

$$H^{(N)} = \sum_{\alpha=1}^{N} h(\vec{r}_\alpha) + \sum_{\alpha>\beta=1}^{N} e^2/r_{\alpha\beta} - \sum_{\alpha=1}^{N} v^{\rm scr}(r_\alpha) . \tag{1.2}$$

Spin-orbit and spin-spin terms may be added to (1.1) and (1.2). Core eigenstates Φ_i will be regarded as solutions of

$$H^{(N-1)}\Phi_i(\vec{r}_1, \ldots, \vec{r}_{N-1}) = E_i\Phi_i \tag{1.3}$$

constructed from an unrestricted number of Slater determinants of eigenfunctions of $h(\vec{r})$. The occurrence of a continuous spectrum of E_i is disregarded in this paper, as noted above.

Close-coupling expansions of an eigenfunction of $H^{(N)}$ have the general form $\sum_i M_i(\vec{r}_N)\Phi_i(\vec{r}_1, \ldots, \vec{r}_{N-1})$. These expansions have to be antisymmetrized with respect to the Nth electron, i.e., the function M_i has to be entered as the Nth row of each Slater determinant included in Φ_i and with a different variable $\vec{r}_\alpha$ in each column. Since the index i serves as a channel index and must identify not only an eigenstate of $H^{(N-1)}$ but also its orbital and spin coupling with the Nth electron, one usually transfers the orbital and spin parts of $M_i(\vec{r}_N)$ from M_i into Φ_i. We shall also transfer to Φ_i the factor $1/r$ of M_i whose removal eliminates the term $(1/r)d/dr$ from the kinetic energy operator. Accordingly we shall indicate the complete eigenfunctions to be constructed by

$$\Psi = \sum_i \{M_i(r)\Phi_i(\omega)\}, \tag{1.4}$$

where the braces stand for antisymmetrization and ω includes $\hat{r}$ and the spin variables of the Nth electron. The goal of theory at this point is to construct the radial functions $M_i(r)$; it will be implemented in Sec. IV. The single-electron term of $H^{(N)}$ operating on this function will be indicated by $h(l_i, r)$, where l_i refers to the particular eigenvalue of the orbital angular momentum $\vec{l}^2$ whose eigenfunction is now included in $\Phi_i(\omega)$. The kinetic part of this operator reduces now to $-\frac{1}{2}d^2/dr^2$ in atomic units, with the understanding that it operates on $M_i(r)$ only and not on Φ_i.

On this basis we may formulate here the starting points of the QDT more explicitly. They are as follows:

(a) The finite spatial extent of the core implies that $\Phi_i(\omega)$ can be regarded as vanishingly small whenever any of the radial coordinates included in ω exceeds a "core radius" r_0.

(b) All interactions of the excited electron at $r > r_0$ are understood to be included in the central potential terms of $h(l_i, r)$; that is, the residual terms of $H^{(N)}$ are set to zero at $r > r_0$, however important they may be within the core.

Accordingly (i) each radial function $M_i(r)$ obeys the equation

$$[h(l_i, r) - \epsilon_i]M_i(r) = 0; \quad \epsilon_i = E - E_i; \quad \text{at } r > r_0 , \tag{1.5}$$

where E and E_i are the relevant eigenvalues of the full Hamiltonians $H^{(N)}$ and $H^{(N-1)}$, respectively, and where the zero value of ϵ_i coincides, as usual, with the potential of $h(\vec{r})$ at $r = \infty$.

(ii) For all "strongly closed" channels i whose core energies E_i are sufficiently larger than E, the function $M_i(r)$ decays so rapidly with in-

creasing r as to be itself vanishingly small at $r>r_0$. The $\sum_i$ can thus be restricted at $r>r_0$ to a finite subset of terms representing "open" or "weakly closed" channels; the sum thus restricted will be indicated by a prime, $\sum_i'$.

The emphasis in this paper is on proceeding without stating the analytical form of the potential term in $h(\vec{r})$ explicitly. As noted above, our treatment might be further extended to remove some of its limitations, such as our excluding noncentral terms in $h(\vec{r})$ and channel-coupling terms beyond r_0. (The QDT loses most of its import unless r_0 remains sufficiently small.) The close-coupling form of the wave function (1.4) is essential only for the treatment outside the core, i.e., for its subset of terms included in the $\sum_i'$. Therefore, the remainder of this sum—which is required for representing short-range correlations—may well be represented more flexibly; this would be important, e.g., for inclusion of short-range multicenter terms in molecular cores.

II. RADIAL WAVE FUNCTIONS

The QDT gives a primary role to analytical properties of independent solutions of the radial equation, in atomic units,

$$[h(l,r)-\epsilon]f(\epsilon,l,r)=\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+v(r)-\epsilon\right)f(\epsilon,l,r)=0\,,$$

$$v(r)\underset{r\to 0}{\longrightarrow}-Ze^2/r\,, \qquad (2.1)$$

$$v(r)\underset{r\to\infty}{\longrightarrow}v_p(r)\propto -1/r^p \quad (p=0,1,2)\,,$$

where any convergence at large r with $p>2$ is rated as equivalent to zero field (i.e., to $p=0$). The relevant properties have been developed in detail by Seaton[2] for the Coulomb field Hamiltonian but are actually largely independent of detailed properties of this field. We shall deal initially with solutions of the general Eq. (2.1), then specialize the treatment to the cases where $v(r)$ *coincides* with $v_p(r)$ at all r, in Sec. II B–II D. Finally Sec. II E will apply the QDT to the potential $v(r)$ specified in Eq. (2.1), which departs from its large-r form by amounts that vanish faster than $1/r^2$.

A first property of the solutions of (2.1) is, of course, that each of them is a linear combination of any chosen base pair of independent solutions. Alternative base pairs, identified by boundary properties at $r=0$ or at $r=\infty$, are suitable in different contexts. We shall study the linear transformations between such base pairs and particularly their dependence on the energy ϵ across the ionization threshold $\epsilon=0$ and in the bound-state range $\epsilon<0$.

More generally, the QDT involves the energy dependence of certain key parameters across the ionization threshold. This dependence may display a nonanalytic behavior for two separate reasons. First, the asymptotic behavior of wave functions at large r depends on their wave number $k=(2\epsilon)^{1/2}$, which has a branch point at $\epsilon=0$. Second, attractive fields $v_p(r)$, with $p=1$ or 2, support infinities of bound states whose spectra converge at $\epsilon=0$, thus generating an essential singularity. Additional singularities occur in the dependence of wave functions on the orbital momentum l, just at the integral values of interest. The description of these combined effects—each of them familiar in mathematical analysis—becomes rather laborious but appears essential to the connection between the properties of bound and free particle states.

A. Base functions and Wronskians

The differential equation (2.1) depends linearly on the parameters ϵ and $l+1$; accordingly there exist solutions that are entire functions of these parameters. We replace l by λ when it need not be an integer. The extension to noninteger λ is important not only for analytical purposes but also because a potential term $v_2(r)=-\frac{1}{2}a/r^2$ combines with the centrifugal term of Eq. (2.1) to yield $\frac{1}{2}\lambda(\lambda+1)/r^2$, with $\lambda(\lambda+1)=l(l+1)-a$; this parameter λ becomes complex in the interesting cases where the constant a is sufficiently large to bind a particle. The combination of a Coulomb field with a $-\frac{1}{2}a/r^2$ ("dipole") field leads to a Coulomb field equation with noninteger λ.[7]

In physical applications the potential function $v(r)$ includes no other singularity than a Coulomb term at $r=0$, whereby the indicial equation for this point has the roots $\lambda+1$ and $-\lambda$. We start from a basic solution, regular at $r=0$ for $\lambda\geq 0$ and analytic in ϵ,

$$f^0(\epsilon,\lambda,r)=a_0(\lambda)r^{\lambda+1}(1+c_1r+\cdots)\,. \qquad (2.2)$$

The normalization coefficient $a_0(\lambda)$ should be independent of energy and should ensure that its product by the series converges at all finite r for all λ; this convergence is nontrivial when the difference between the two roots, $2\lambda+1$, is an integer.[8] In the case of a Coulomb field critical values $\lambda=\lambda_c$ occur, such that the series in parentheses diverges when $-\lambda_c-1$ is a negative integer or half integer, while for zero field the series contains only even powers of r and diverges only when $-\lambda_c-1$ is a negative half integer. The solution (2.2) will then remain finite for all λ

only if the energy-independent coefficient $a_0(-\lambda-1)$ vanishes appropriately at $\lambda=\lambda_c$. To satisfy this criterion, we set $a_0(\lambda)=2^{\lambda+1}/\Gamma(2\lambda+2)$ for a Coulomb field and $a_0(\lambda)=[2^{\lambda+1/2}\Gamma(\lambda+\frac{3}{2})]^{-1}$ for zero field. Thereby $f^0(\epsilon,-\lambda-1,r)$ is also a nontrivial solution of (2.2) irregular for $\lambda>0$, and is independent of $f^0(\epsilon,\lambda,r)$ at all $\lambda\neq\lambda_c$ for which the Wronskian

$$W[f^0(\lambda),f^0(-\lambda-1)]=-(2\lambda+1)a_0(\lambda)a_0(-\lambda-1)$$
$$=-(2/\pi)\sin[\pi(p+1)(\lambda+\tfrac{1}{2})]\neq 0\,,$$
$$p=0 \text{ or } 1\,. \tag{2.3}$$

[The identity $\Gamma(z)\Gamma(1-z)=\pi/\sin\pi z$ is utilized here and frequently in the following.]

Adjustments of Eq. (2.2) and of its discussion are in order when $v_2(r)=-\frac{1}{2}a/r^2$ with a value of $a>l(l+1)+\frac{1}{4}$ and hence sufficient to bind a particle. For later convenience we denote this field as the "dipole field." In this event we have

$$\lambda=-\tfrac{1}{2}\pm i[a-(l+\tfrac{1}{2})^2]^{1/2}=-\tfrac{1}{2}\pm i\alpha\,, \tag{2.4}$$

and Eq. (2.2) represents two alternative, independent, complex conjugate solutions if we set $a_0=-i(2\pi/\alpha)^{1/2}$. This pair corresponds to $\{f^0_\lambda,f^0_{-\lambda-1}\}$ since $-\lambda-1=\lambda^*$ according to (2.4). We shall, however, replace this pair of solutions by their real and imaginary parts,

$$f^{0R}(\epsilon,\alpha,r)=\left(\frac{2}{\pi\alpha}\right)^{1/2}r^{1/2}\sin(\alpha\ln r)(1+c_1r+\cdots)\,,$$

$$f^{0I}(\epsilon,\alpha,r)=-\left(\frac{2}{\pi\alpha}\right)^{1/2}r^{1/2}\cos(\alpha\ln r)(1+\tilde{c}_1r+\cdots)\,,$$

$$W_{\epsilon\alpha}(f^{0R},f^{0I})=2/\pi\,. \tag{2.5}$$

Note that these functions oscillate wildly as $r\to 0$ since $\ln r$ is singular; however, this singularity has no physical importance as a dipole potential never actually extends to $r\sim 0$ where it would hold an infinite spectrum of deeply bound states.

In the opposite limit of large r we consider solutions expanded into powers of $1/r$; however, the expansion is only asymptotic because $r=\infty$ is an irregular point of the equation. Here we have generally a pair of independent solutions

$$f^\pm(\epsilon,\lambda,r)=e^{\pm ikr}r^{\pm\xi}(1+d_1/r+\cdots)\,, \tag{2.6}$$

where $k=(2\epsilon)^{1/2}$ (with $\mathrm{Im}\,k>0$ for $\epsilon<0$) and where

$$\pm\xi=\mp\frac{i}{k}\lim_{r\to\infty}\frac{dv}{d(1/r)}$$

are the roots of indicial-type equations[8]; ξ equals i/k when $v(r)\to -1/r$ as $r\to\infty$ and it vanishes when $v(r)$ vanishes faster than $1/r$. The systematics of the radial functions emerges from the connection between the solutions (2.2) and (2.6). Note that f^+ and f^- are independent, except at $\epsilon=0$, as seen by evaluating their Wronskian in the convenient limit $r\to\infty$,

$$W_\epsilon(f^-,f^+)=2ik\,. \tag{2.7}$$

The connection between nonindependent solutions of Eq. (2.1), such as (2.2) and (2.6), can be represented in terms of their Wronskians, utilizing the identities

$$W(a,b)c+W(b,c)a+W(c,a)b=0\,, \tag{2.8}$$

$$W(a,b)W(c,d)+W(b,c)W(a,d)$$
$$+W(c,a)W(b,d)=0\,, \tag{2.9}$$

which hold for any differentiable functions $\{a,b,c,d\}$. The first of these serves to represent any solution of (2.1) as a superposition of two base solutions. The second one, cast in the form

$$\frac{W(a,b)}{W(c,d)}=\begin{vmatrix} W(a,d)/W(c,d) & -W(a,c)/W(c,d)\\ W(b,d)/W(c,d) & -W(b,c)/W(c,d)\end{vmatrix}\,, \tag{2.10}$$

shows how the determinant of the transformation matrix from a base pair $\{c,d\}$ to a pair $\{a,b\}$ equals the ratio of the Wronskians of the final and initial base pairs.

Application of Eqs. (2.8) and (2.7) to the solutions $\{f^-,f^+,f^0\}$ yields

$$2ikf^0(\epsilon,\lambda,r)=W_{\epsilon\lambda}(f^-,f^0)f^+(\epsilon,\lambda,r)$$
$$-W_{\epsilon\lambda}(f^+,f^0)f^-(\epsilon,\lambda,r)\,. \tag{2.11}$$

The Wronskians in this equation coincide with the Jost functions J^- and J^+, to within the coefficient $2ika_0(\lambda)$. These parameters are constant in r but they link the small-r and large-r behavior of the wave functions and thus depend on the values of the potential $v(r)$ *at all* r. The analytical structure of the Wronskians for the three basic fields $v_p(r)$ $(p=0,1,2)$ is an essential part of our study and is described below.

Here we stress only a few general properties of the pair of functions $W^\pm_{\epsilon\lambda}=W(f^\pm,f^0)$ for positive and for negative values of the energy ϵ. For $\epsilon>0$, W^+ and W^- are complex conjugate, because $f^\pm$ are complex conjugate while f^0 is real; this is also seen from Eq. (2.9). For negative values of the energy ϵ, instead, the solutions (2.4) no longer oscillate at large r but are real and take the exponential behavior

$$f^\pm(\epsilon,\lambda,r)=e^{\mp r/\nu}r^{\pm\xi}(1+d_1/r+\cdots)\,, \tag{2.12}$$

where $\nu=i/k=(-2\epsilon)^{-1/2}$. The Wronskians $W^\pm_{\epsilon\lambda}$ will then be real, with different functional forms. Solutions of Eqs. (2.1), in particular the radial

functions $M_i(r)$ of Eq. (1.4), remain bounded at large r only when the coefficient of the rising exponential f^- vanishes in their expansion (2.11). That is, boundedness requires that

$$W(f_i^+, M_i)=0\,, \tag{2.13}$$

for all closed channels with $\epsilon_i<0$. For our single-channel Eq. (2.1) with the potential $v(r)$, the discrete energy levels are identified by the eigenvalue equation

$$W_{\epsilon\lambda}(f^+, f^0)=0, \quad \text{for } \epsilon<0\,. \tag{2.14}$$

Recall finally how in scattering theory, with $\lambda=l$, discrete energy levels are identified as poles of the scattering matrix $S_{\epsilon l}$. The S matrix represents departures of the wave functions for a given field from zero-field functions and is represented in our notation by

$$S_{\epsilon l}=(W_{\epsilon l}^-/W_{\epsilon l}^+)/(W_{\epsilon l}^-/W_{\epsilon l}^+)_{v_0(r)=0}\,, \tag{2.15}$$

showing how its poles are indeed given by (2.14). For $\epsilon>0$ we have quite generally the familiar relation

$$S_{\epsilon l}=\exp 2i\,[\eta(k,l)-\eta(k,l)_{v_0=0}]\,,$$

where η is the phase of the complex Wronskian $W_{\epsilon l}^-$ and $\eta_{v_0=0}=-l\pi/2$.

B. Analytical expressions of the basic Wronskians

The Wronskians $W_{\epsilon\lambda}^\pm$ which appear in Eq. (2.9) play a role even more extensive than has been indicated thus far, particularly in their combinations $W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+$ and $W_{\epsilon\lambda}^-/W_{\epsilon\lambda}^+$. Their analytical form is determined by comparing Eq. (2.11) with the large-r expansion of the solutions $f^0(\epsilon,\lambda,r)$ of Eq. (2.1) which are known analytically for the basic potentials $v_p(r)$, $p=0,1,2$. The branch point of the wave number k at $\epsilon=0$ causes the form of $W_{\epsilon\lambda}^\pm$ to differ for $\epsilon\gtrless 0$. Simple analytic continuation does not suffice to round the branch point for reasons that have not been widely appreciated and are discussed in the Appendix. (That is, the $\epsilon<0$ expressions do not derive from the $\epsilon>0$ expressions simply by setting $k=i/\nu$.) Here we complement analytic continuation by stipulating that the rising exponential solution f^-, defined by Eq. (2.12), includes no additional term proportional to the decaying f^+. We give here the expressions of $W_{\epsilon\lambda}^\pm$ for nonintegral values of λ, even though the integral values of $\lambda=l$ are of greatest interest.

a. Zero field ($p=0$). In this simplest case we have

$$W_{\epsilon\lambda}^\pm=(2/\pi)^{1/2}(\pm i/k)^\lambda, \quad \epsilon>0\,, \tag{2.16}$$

$$W_{\epsilon\lambda}^+=(2/\pi)^{1/2}\nu^\lambda, \quad W_{\epsilon\lambda}^-=(2/\pi)^{1/2}\nu^\lambda\cos\pi\lambda, \quad \epsilon<0\,, \tag{2.17}$$

$$W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+=(2/\pi)k^{-2\lambda}, \quad W_{\epsilon\lambda}^-/W_{\epsilon\lambda}^+=e^{-i\pi\lambda}, \quad \epsilon>0\,, \tag{2.18}$$

$$W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+=(2/\pi)\nu^{2\lambda}\cos\pi\lambda, \quad W_{\epsilon\lambda}^-/W_{\epsilon\lambda}^+=\cos\pi\lambda, \quad \epsilon<0\,. \tag{2.19}$$

Substitution of Eqs. (2.16), (2.17), and (2.6) into (2.11) yields the large-r expressions

$$f^0(\epsilon,\lambda,r)\xrightarrow[r\to\infty]{}\begin{cases} k^{-\lambda-1/2}(2/\pi k)^{1/2}\sin(kr-\lambda\pi/2)\,, \\ \epsilon>0\,, \\ \nu^{\lambda+1/2}\,(\nu/2\pi)^{1/2}\,[e^{r/\nu}-\cos\pi\lambda e^{-r/\nu}]\,, \\ \epsilon<0\,. \end{cases} \tag{2.20}$$

The expression for $\epsilon>0$ differs by the factor $k^{-\lambda-1/2}$ from the familiar energy-normalized form of the radial functions. The square of this factor, $k^{-2\lambda-1}=(\pi/2k)W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+$, represents the reciprocal density of states $f_{\epsilon\lambda}^0$ for $\epsilon>0$, as will be discussed further.

b. Coulomb field, $v_1(r)=-1/r$. Here the analytical structure of the Wronskians derives from the large-r expression of confluent hypergeometric functions in terms of Γ functions and of exponentials, using again the relation $\Gamma(z)\Gamma(1-z)=\pi/\sin\pi z$:

for $\epsilon>0$

$$W_{\epsilon\lambda}^\pm=2(2k)^{\mp i/k}\exp(-\pi/2k)(\pm i/k)^\lambda/\Gamma(\lambda+1\mp i/k); \tag{2.21}$$

for $\epsilon<0$

$$W_{\epsilon\lambda}^+=(2/\pi)(2/\nu)^{-\nu}\nu^\lambda\sin\pi(\nu-\lambda)\Gamma(\nu-\lambda)\,, \qquad W_{\epsilon\lambda}^-=2(2/\nu)^\nu\nu^\lambda\cos\pi(\nu-\lambda)/\Gamma(\lambda+1+\nu)\,; \tag{2.22}$$

for $\epsilon>0$

$$W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+=4e^{-\pi/k}k^{-2\lambda}\left|\Gamma(\lambda+1-i/k)\right|^{-2}=(2k/\pi)/B(\epsilon,\lambda)\,, \qquad W_{\epsilon\lambda}^-/W_{\epsilon\lambda}^+=\exp\left[2i(k^{-1}\ln k-\lambda\pi/2+\sigma_\lambda)\right]; \tag{2.23}$$

for $\epsilon<0$

$$W_{\epsilon\lambda}^- W_{\epsilon\lambda}^+=(2/\pi\nu)\sin 2\pi(\nu-\lambda)/A(\nu,\lambda)\,, \qquad W_{\epsilon\lambda}^-/W_{\epsilon\lambda}^+=D^2(\nu,\lambda)\,\mathrm{cotan}\pi(\nu-\lambda)\,; \tag{2.24}$$

where we have set, following Seaton,[2]

$$\begin{aligned} B(\epsilon,\lambda)&=k^{2\lambda+1}e^{\pi/k}\left|\Gamma(\lambda+1-i/k)\right|^2/2\pi \\ &=A(i/k,\lambda)/[1-e^{-2\pi/k-2\pi i\lambda}]\,, \\ D(\nu,\lambda)&=\pi^{1/2}(2/\nu)^\nu\left[\Gamma(\nu-\lambda)\Gamma(\lambda+1+\nu)\right]^{-1/2}\,, \\ \sigma_\lambda&=\arg\Gamma(\lambda+1-i/k)\,, \\ A(\nu,\lambda)&=\Gamma(\lambda+1+\nu)/\nu^{2\lambda+1}\Gamma(\nu-\lambda) \\ &\xrightarrow[\lambda\to l]{}\prod_{j=0}^{l}(1-j^2/\nu^2)\,. \end{aligned} \tag{2.25}$$

Note that B is real for noninteger λ and $\epsilon>0$, even though $A(i/k,\lambda)$ is complex. Below threshold $A(\nu,\lambda)$ is real and reduces to the polynomial

form when λ is an integer.

The large-r form of f^0, analogous to Eq. (2.20), is

$$f^0(\epsilon,\lambda,r)\underset{r\to\infty}{\longrightarrow}\begin{cases}[B(\epsilon,\lambda)]^{-1/2}(2/\pi k)^{1/2} \\ \quad\times\sin(kr+k^{-1}\ln 2kr-\lambda\pi/2+\sigma_\lambda), & \epsilon>0 \\ [A(\nu,\lambda)]^{-1/2}(\nu/\pi)^{1/2} \\ \quad\times[\sin\pi(\nu-\lambda)D^{-1}e^{r/\nu}\nu^{-\nu} \\ \quad\quad-\cos\pi(\nu-\lambda)De^{-r/\nu}\nu^{\nu}], & \epsilon<0\,.\end{cases} \tag{2.26}$$

For $\epsilon>0$ the coefficient $B^{-1/2}$, which corresponds to $k^{-\lambda-1/2}$ of Eq. (2.20), reduces in fact to $k^{-\lambda-1/2}(2\pi)^{1/2}/\Gamma(\lambda+1)$ in the limit of $\epsilon\gg 1$, as it should, while it reduces to unity—instead of vanishing—at the threshold $\epsilon=0$; the coefficient $(2\pi)^{1/2}/\Gamma(\lambda+1)$ stems from the normalization of f^0 at $r=0$. For $\epsilon<0$ the coefficients of the rising and falling exponentials oscillate sinusoidally as functions of ν, but the amplitude of these oscillations is scaled by the coefficients D^{-1} and D which diverge and vanish, respectively, as ν increases toward the condensation point $\epsilon=0$. The discrete energy levels, roots of Eq. (2.14), occur here when $\nu-\lambda$ is a *positive* integer, whereas the elementary QDT equation $\sin\pi\nu=0$ is satisfied by any integer ν since it was derived for the special case $\lambda=l$ and without regard to the coefficient D. Note that Eq. (2.26) should be restructured for $\nu<\lambda$ where $A^{-1/2}$ and D may become imaginary.

c. Dipole field, $v_2(r)=-\frac{1}{2}a/r^2$. Here the basic solution $f^0(\epsilon,\lambda,r)$ is of the Bessel class, whose large-r expansion involves primarily exponentials and related functions. The centrifugal parameter λ is expressed in terms of α by Eq. (2.4); a Γ function appears in a parameter $\chi_\alpha=\arg\Gamma(1-i\alpha)$. The Wronskian expressions are as follows:

for $\epsilon>0$

$$W^{\pm}_{\epsilon\alpha}=(4k/\pi)^{1/2}e^{\pm i3\pi/4} \times\sin(\alpha\ln\tfrac{1}{2}k\mp\tfrac{1}{2}i\alpha\pi+\chi_\alpha)/\sinh^{1/2}\pi\alpha\,; \tag{2.27}$$

for $\epsilon<0$

$$W^{+}_{\epsilon\alpha}=(4/\pi\nu)^{1/2}\sin(\alpha\ln 2\nu-\chi_\alpha)/\sinh^{1/2}\pi\alpha\,, \qquad W^{-}_{\epsilon\alpha}=(4/\pi\nu)^{1/2}\cos(\alpha\ln 2\nu-\chi_\alpha)\sinh^{1/2}\pi\alpha\,; \tag{2.28}$$

for $\epsilon>0$

$$W^{-}_{\epsilon\alpha}W^{+}_{\epsilon\alpha}=(2k/\pi)[\cosh\pi\alpha-\cos 2(\alpha\ln\tfrac{1}{2}k+\chi_\alpha)]/\sinh\pi\alpha\,, \qquad W^{-}_{\epsilon\alpha}/W^{+}_{\epsilon\alpha}=\frac{i\sin(\alpha\ln\frac{1}{2}k+i\alpha\pi/2+\chi_\alpha)}{\sin(\alpha\ln\frac{1}{2}k-i\alpha\pi/2+\chi_\alpha)}\,; \tag{2.29}$$

for $\epsilon<0$

$$W^{-}_{\epsilon\alpha}W^{+}_{\epsilon\alpha}=(2/\pi\nu)\sin 2(\alpha\ln 2\nu-\chi_\alpha)\,, \qquad W^{-}_{\epsilon\alpha}/W^{+}_{\epsilon\alpha}=\operatorname{cotan}(\alpha\ln 2\nu-\chi_\alpha)\sinh\pi\alpha\,. \tag{2.30}$$

These parameters differ characteristically from those of the Coulomb field in that their oscillations depend on the logarithm of the energy. Thus the discrete energy levels occur when $\alpha\ln 2\nu-\chi_\alpha$ is a multiple of π and converge to the threshold exponentially, $\epsilon_n=2\exp[-2\alpha^{-1}(n\pi+\chi_\alpha)]$, in contrast to Rydberg series. [A quantum defect must be added to χ_α in this formula in any application because the attractive dipole potential $v_2(r)$ never extends to $r=0$.]

The large-r forms of f^0, analogous to Eqs. (2.20) and (2.26), are here

$$f^0(\epsilon,\alpha,r)\underset{r\to\infty}{\longrightarrow}\left(\frac{\cosh\pi\alpha-\cos 2(\alpha\ln\frac{1}{2}k+\chi_\alpha)}{\sinh\pi\alpha}\right)^{1/2}\times(2/\pi k)^{1/2}\sin[kr-\tfrac{1}{4}\pi+\phi(k,\alpha)]\,, \quad \epsilon>0\,,$$

$$\underset{r\to\infty}{\longrightarrow}(\nu/\pi)^{1/2}[\sin(\alpha\ln 2\nu-\chi_\alpha)\sinh^{-1/2}(\pi\alpha)e^{r/\nu}-\cos(\alpha\ln 2\nu-\chi_\alpha)\times\sinh^{1/2}(\pi\alpha)e^{-r/\nu}]\,, \quad \epsilon<0\,,$$

$$\operatorname{cotan}\phi(k,\alpha)=-\tanh(\pi\alpha/2)\operatorname{cotan}(\alpha\ln\tfrac{1}{2}k+\chi_\alpha). \tag{2.31}$$

(ϕ is in the same quadrant as $\alpha\ln\frac{1}{2}k+\chi_\alpha$.) Throughout the range $\epsilon>0$ the amplitude of this wave function is itself an oscillatory logarithmic function of energy. Thus it does not coincide with the amplitude for zero field in the high-energy limit, but this result is an artifact of our model potential which remains unrealistically $\propto -1/r^2$ as $r\to 0$. The oscillations at low energies are instead a realistic property of the long-range dipole field, related to the exponential convergence of the series of discrete levels at $\epsilon<0$.[9] The oscillations extend across the condensation point at $\epsilon=0$; note how the coefficient $\sinh^{1/2}\pi\alpha$ plays here a role analogous to that of D in the Coulomb case.

C. Alternative base pairs of solutions

The solutions $f^{\pm}(\epsilon,\lambda,r)$ introduced in Eq. (2.6) form a convenient base pair at large r because they are complex conjugate for $\epsilon>0$ and falling and rising at large r for $\epsilon<0$. The pair consisting of $f^0(\epsilon,\lambda,r)=f^0_\lambda$ and of $f^0_{-\lambda-1}$, regular and irregular at $r=0$, is analytic in ϵ and in λ but it does not form a convenient base because these functions do not remain independent at $\lambda=\lambda_c$. Accordingly we consider, besides $f^0_{-\lambda-1}$, a second irregular solution, $\bar{g}(\epsilon,\lambda,r)\equiv\bar{g}_\lambda$, designed to form a convenient pair with f^0_λ, by specifying that for $\epsilon>0$, it oscillates at large r out of phase with respect to

f^0_λ irrespective of the value of λ.

We write $\bar{g}_\lambda$ as a superposition of $\{f^-, f^+\}$, as f^0_λ is expressed in Eq. (2.11),

$$2ik\bar{g}(\epsilon,\lambda,r) = W_{\epsilon\lambda}(f^-,\bar{g})f^+ - W_{\epsilon\lambda}(f^+,\bar{g})f^- . \tag{2.32}$$

Our definition of $\bar{g}$ will be completed by specifying that $\bar{g}$ *lags* in phase by 90° with respect to f^0 at large r and by the convenient normalization convention,

$$W(f^0_\lambda, \bar{g}_\lambda) = 2/\pi . \tag{2.33}$$

The values of the Wronskians of Eq. (2.32) that meet these requirements are then determined by inspection of the large r Eqs. (2.20), (2.26), and (2.31). Note that these equations show $f^\pm$ to be effectively renormalized, for $\epsilon<0$, by the coefficient $D^{\pm1}$ for the Coulomb field and by $\sinh^{\pm1/2}\pi\alpha$ for the dipole field. Thus we obtain

$$W_{\epsilon\lambda}(f^\mp,\bar{g}) = \begin{cases} \mp(2ik/\pi)/W^\pm_{\epsilon\lambda}, & \epsilon>0, \\ \dfrac{\pm(4/\pi\nu)D^{\pm2}W^\pm_{\epsilon\lambda}}{(D^{-1}W^-_{\epsilon\lambda})^2+(DW^+_{\epsilon\lambda})^2}, & \epsilon<0, \end{cases} \tag{2.34}$$

where D is given by Eq. (2.25) for the Coulomb field, $D=1$ for zero field, and $D=\sinh^{1/2}\pi\alpha$ for the dipole field. The transformation matrix from $\{D^{-1}f^-, Df^+\}$ to $\{f^0,\bar{g}\}$ at $\epsilon<0$ is thus orthogonal to within normalization. The large-r forms of $\bar{g}$ are as follows:

zero field,

$$\bar{g}(\epsilon,\lambda,r) \xrightarrow[r\to\infty]{} \begin{cases} -k^{\lambda+1/2}(2/\pi k)^{1/2}\cos(kr-\lambda\pi/2), & \epsilon>0 \\ -\nu^{-\lambda}(1+\cos^2\pi\lambda)^{-1}(2/\pi)^{1/2}[\cos(\pi\lambda)e^{r/\nu}+e^{-r/\nu}], & \epsilon<0; \end{cases} \tag{2.35}$$

Coulomb field,

$$\bar{g}(\epsilon,\lambda,r) \xrightarrow[r\to\infty]{} \begin{cases} -[B(\epsilon,\lambda)]^{1/2}(2/\pi k)^{1/2}\cos(kr+k^{-1}\ln 2kr-\lambda\pi/2+\sigma_\lambda), & \epsilon>0 \\ -[A(\nu,\lambda)]^{1/2}(\nu/\pi)^{1/2}[\cos\pi(\nu-\lambda)D^{-1}e^{r/\nu}r^{-\nu}+\sin\pi(\nu-\lambda)De^{-r/\nu}r^{\nu}], & \epsilon<0; \end{cases} \tag{2.36}$$

dipole field,

$$\bar{g}(\epsilon,\alpha,r) \xrightarrow[r\to\infty]{} \begin{cases} -\{[\cosh\pi\alpha-\cos2(\alpha\ln\tfrac{1}{2}k+\chi_\alpha)]/\sinh\pi\alpha\}^{-1/2}(2/\pi k)^{1/2}\cos[kr-\pi/4+\phi(k,\alpha)], & \epsilon>0 \\ -(\nu/\pi)^{1/2}[\cos(\alpha\ln2\nu-\chi_\alpha)\sinh^{-1/2}(\pi\alpha)e^{r/\nu}+\sin(\alpha\ln2\nu-\chi_\alpha)\sinh^{1/2}(\pi\alpha)e^{-r/\nu}], & \epsilon<0. \end{cases} \tag{2.37}$$

The function $\bar{g}(\epsilon,\lambda,r)$ thus introduced is not generally an analytic function of the energy ϵ, owing to nonanalyticities of the Wronskian coefficients. To make the nonanalyticity explicit we express $\bar{g}$ in terms of the analytic pair $\{f^0_\lambda, f^0_{-\lambda-1}\}$, using Eq. (2.8),

$$W\{f^0_\lambda, f^0_{-\lambda-1}\}\bar{g}(\epsilon,\lambda,r) = (2/\pi)f^0(\epsilon,-\lambda-1,r) + W(\bar{g}_\lambda, f^0_{-\lambda-1})f^0(\epsilon,\lambda,r) . \tag{2.38}$$

Here only the $W(\bar{g}_\lambda, f^0_{-\lambda-1})$ may be nonanalytic; its explicit forms, obtained by replacing $\bar{g}_\lambda$ and $f^0_{-\lambda-1}$ by their respective expressions in terms of $\{f^-, f^+\}$, are as follows:

zero field,

$$W(\bar{g}_\lambda, f^0_{-\lambda-1}) = \begin{cases} -(2/\pi)k^{2\lambda+1}\cos\pi(\lambda+\tfrac{1}{2}), & \epsilon>0 \\ -(2/\pi)\nu^{-2\lambda-1}\dfrac{\cos^2\pi(\lambda+\frac{1}{2})}{(1+\cos^2\pi\lambda)}, & \epsilon<0; \end{cases} \tag{2.39}$$

Coulomb field,

$$W(\bar{g}_\lambda, f^0_{-\lambda-1}) = \begin{cases} -(2/\pi)\,\mathrm{Re}A(i/k,\lambda) \\ \quad\times\left(\dfrac{\cos\pi(2\lambda+1)+\sin^2\pi(2\lambda+1)}{e^{2\pi/k}+\cos\pi(2\lambda+1)}\right), & \epsilon>0 \\ -(2/\pi)A(\nu,\lambda)\cos\pi(2\lambda+1), & \epsilon<0 \end{cases} \tag{2.40}$$

dipole field,

$$W(\bar{g}_\alpha, f^{0I}_\alpha) = \begin{cases} \dfrac{-(2/\pi)\sin2(\alpha\ln\frac{1}{2}k+\chi_\alpha)}{[\cosh\pi\alpha-\cos2(\alpha\ln\frac{1}{2}k+\chi_\alpha)]}, & \epsilon>0 \\ 0, & \epsilon<0. \end{cases} \tag{2.41}$$

All these expressions are nonanalytic at $\epsilon=0$ for general values of λ or α.

Special consideration is required for the zero-field case at $\lambda=\lambda_c$=half integer and for the Coulomb case at $\lambda=\lambda_c$=integer or half integer, where f^0_λ and $f^0_{-\lambda-1}$ are no longer independent, and $W(f^0_\lambda, f^0_{-\lambda-1})$ vanishes according to (2.3). Here the expressions of $W(\bar{g}_\lambda, f^0_{-\lambda-1})$ become analytic in ϵ, with values equal to $-2/\pi$ times the ratio $f^0_\lambda/f^0_{-\lambda-1}$, whereby the two terms on the right-hand side of Eq. (2.38) cancel. The expression of $\bar{g}_{\lambda_c}$ in terms of f^0_λ and $f^0_{-\lambda-1}$ results then by applying de l'Hospital's theorem to Eq. (2.38):

zero field,

$$\bar{g}_{\lambda_c} = \begin{cases} \pi^{-1}[(-1)^{\lambda_c-1/2}(\partial f^0_{-\lambda-1}/\partial\lambda)_{\lambda_c}+k^{2\lambda_c+1}(\partial f^0_\lambda/\partial\lambda)_{\lambda_c} \\ \quad +2k^{2\lambda_c+1}\ln k f^0_{\lambda_c}], & \epsilon>0 \\ \pi^{-1}(-1)^{\lambda_c-1/2}[(\partial f^0_{-\lambda-1}/\partial\lambda)_{\lambda_c}-\nu^{-2\lambda_c-1}(\partial f^0_\lambda/\partial\lambda)_{\lambda_c} \\ \quad -2\nu^{-2\lambda_c-1}\ln\nu f^0_{\lambda_c}], & \epsilon<0; \end{cases} \tag{2.42}$$

Coulomb field

$$\bar{g}_{\lambda_c}=(2\pi)^{-1}\{(-1)^{2\lambda_c+2}(\partial f^0_{-\lambda-1}/\partial\lambda)_{\lambda_c} + A(\nu,\lambda_c)(\partial f^0_\lambda/\partial\lambda)_{\lambda_c}+2\pi\mathcal{G}(\nu,\lambda_c)f^0_{\lambda_c}\}, \tag{2.43}$$

where $\nu=i/k$ at $\epsilon>0$ and we set, in accordance with Seaton,[2]

$$\mathcal{G}(\nu,\lambda_c)=(2\pi)^{-1}\,\mathrm{Re}\,[\partial A(\nu,\lambda)/\partial\lambda]_{\lambda_c}\,. \tag{2.44}$$

The nonanalyticities are confined to the factor $\ln k$ (or $\ln\nu$) in Eq. (2.42) and to the factor $\mathcal{G}$ in (2.43).

The definition of $\bar{g}_{\lambda_c}$ by Eq. (2.42) for $\epsilon>0$, as well as that of $\bar{g}_\lambda$ for $\lambda\neq\lambda_c$ and zero field, coincides with the usual definition of the Neumann function to within a normalization factor. In the Coulomb case, our functions f^0_λ and $f^0_{-\lambda-1}$ coincide with Seaton's[2] y_1 and y_2, $\bar{g}_\lambda$ coincides with the real part of Seaton's y_3, except for $\lambda\neq\lambda_c$ and $\epsilon>0$ where the term of (2.40) proportional to $\sin^2\pi(2\lambda+1)$ is added here. [Because $\bar{g}_\lambda$ is explicitly real no equivalent of Seaton's $\mathcal{K}(\nu,\lambda)$ occurs in our formulation.] Following Seaton,[2] an irregular solution analytic in ϵ can be formed at $\lambda=\lambda_c$ by subtracting from Eqs. (2.42) and (2.43) the nonanalytic term proportional to $f^0_{\lambda_c}$. We write in general

$$g^0(\epsilon,\lambda_c,r)=\bar{g}(\epsilon,\lambda_c,r)-\mathcal{G}(\nu,\lambda_c)f^0(\epsilon,\lambda_c,r)\,, \tag{2.45}$$

where $\mathcal{G}$ is given for the Coulomb field by Eq. (2.44) and for zero field by

$$\mathcal{G}(\nu,\lambda_c)=\begin{cases}(2/\pi)k^{2\lambda_c+1}\ln k, & \epsilon>0\\ (2/\pi)(-1)^{\lambda_c+1/2}\nu^{-2\lambda_c-1}\ln\nu\,, & \epsilon<0\,.\end{cases} \tag{2.44'}$$

The subtraction of a term proportional to f^0 preserves the Wronskian value, $W(f^0_{\lambda_c},g^0_{\lambda_c})=2/\pi$. The $g^0_{\lambda_c}$ thus defined coincides for the Coulomb field with Seaton's y_4; Seaton also considers a function y_5 (Whittaker function) which coincides with our f^+ to within normalization.

Thus far we have shown first [in Eqs. (2.32) and (2.34)] how to construct the "out-of-phase" base pair $\{f^0_\lambda,\bar{g}_\lambda\}$ for any central potential in terms of the Wronskians $W_{\epsilon\lambda}(f^\pm,f^0)$. Then we have constructed the analytic solution g^0_λ for the *special case* $\lambda=\lambda_c$. For $\lambda\neq\lambda_c$ we may now extend Eq. (2.45) by redefining $\mathcal{G}(\nu,\lambda)$ suitably so that g^0_λ remains analytic in ϵ. Our redefinition, which reduces to Eqs. (2.44) and (2.44a) at $\lambda=\lambda_c$, is (for $p=0$ or 1 only)

$$\mathcal{G}(\nu,\lambda)=\frac{W(\bar{g}_\lambda,f^0_{-\lambda-1})-\cos^2[\pi(p+1)(\lambda-\tilde{\lambda}_c)]\,W(\bar{g}_{\tilde{\lambda}_c},f^0_{-\tilde{\lambda}_c-1})}{W(f^0_\lambda,f^0_{-\lambda-1})}, \tag{2.46}$$

where $\tilde{\lambda}_c$ is that critical value λ_c which lies closest to λ. The definition of $\mathcal{G}$ by Eq. (2.46), which is proposed here but is *not unique* rests on the following considerations. The role of $\mathcal{G}(\nu,\lambda)f^0_\lambda$ in Eq. (2.45) is to subtract from $\bar{g}$ the nonanalytic portion of the last term in (2.38), while still fulfilling the intent of superposing f^0_λ with $f^0_{-\lambda-1}$ for most values of λ. Subtraction of $\mathcal{G}f^0_\lambda$ in (2.45), with $\mathcal{G}$ as defined by (2.46) removes from $\bar{g}_\lambda$ the nonanalytic term $W(\bar{g}_\lambda,f^0_{-\lambda-1})\times f^0_\lambda/W(f^0_\lambda,f^0_{-\lambda-1})$ and replaces it with a term analytic in ϵ. The numerator of the analytic term is designed to cancel $W(\bar{g}_\lambda,f^0_{-\lambda-1})f^0_\lambda$ at $\lambda=\lambda_c$ leaving, however, a finite contribution through de l'Hospital's rule. The coefficient $\cos^2[\pi(p+1)(\lambda-\tilde{\lambda}_c)]$ of the analytic term reduces to unity at $\lambda=\lambda_c$, with zero derivative (which is required for the extended definition to reduce to the previous one at $\lambda=\lambda_c$). Further the $\cos^2[\cdots]$ coefficient vanishes at the value of $\lambda=\lambda^{\mathrm{mid}}=\lambda_c+1/2p$ where the argument $\tilde{\lambda}_c$ of $W(\bar{g}_{\tilde{\lambda}_c},f^0_{-\tilde{\lambda}_c-1})$ jumps discontinuously by $1/p$. Note also that at $\lambda=\lambda^{\mathrm{mid}}$, g^0_λ is proportional to $f^0_{-\lambda-1}$, where the proportionality constant only fixes $W(f^0_\lambda,g^0_\lambda)=2/\pi$.

The expressions of $\mathcal{G}(\nu,\lambda)$ are summarized in Table I A. Note that for the dipole field ($p=2$) the special case $\lambda=\lambda_c$ does not occur. The function f^{0I}_α assumes the joint roles of $f^0_{-\lambda-1}$ and of g^0_λ, and for $\epsilon<0$ f^{0I}_α also coincides with $\bar{g}_\alpha$. For $\epsilon>0$ however, f^{0I}_α must be superposed with f^{0R}_α to generate a $\bar{g}_\alpha$ that is 90° out of phase with f^{0R}_α. This superposition is still expressed by Eq. (2.45), with $\mathcal{G}(\nu,\alpha)$ given in Table I A.

D. Normalization

The normalization method to be followed here is much the same as was introduced in 1926[10] for Coulomb functions and applied later by Seaton[2] in the MQDT. Its remarkable flexibility will be highlighted here by a physical consideration, namely, by utilizing explicitly the continuity equation

$$\partial\rho/\partial t+\mathrm{div}\,\vec{j}=0 \tag{2.47}$$

for the probability density ρ and flux $\vec{j}$ pertaining to our many-particle wave functions Ψ

$=\sum_i \{M_i(r)\Phi_i(\omega)\}$ in configuration space.

Each state we consider is stationary and of standing-wave type; hence the $\partial\rho/\partial t$ and $\vec{j}$ constructed with its real Ψ vanish. Accordingly we start from a pair of states with different energies E and E' and with time-dependent wave functions $\Psi_E e^{-iEt}$ and $\Psi^*_{E'} e^{iE't}$, intending to take the limit $E' \to E$ later on. Both ρ and $\vec{j}$ are now proportional to $\exp i(E'-E)t$. We integrate Eq. (2.47) over a volume V of configuration space, with volume element $d\tau$, surface element dS, and normal to the surface $\hat{n}$, obtaining

$$\left(i(E'-E)\int_V d\tau\, \Psi^*_{E'}\Psi_E + \int_S dS\, \vec{j}\cdot\hat{n}\right) e^{i(E'-E)t} = 0\,, \tag{2.48}$$

where $\vec{j}$ is constructed with the time-independent factors $\Psi^*_{E'}$ and Ψ_E. The time dependence may now be factored out and the equation divided by $i(E'-E)$ to yield

$$\int_V d\tau\, \Psi^*_{E'}\Psi_E = \frac{i}{E'-E}\int_S dS\, \vec{j}\cdot\hat{n}\,. \tag{2.49}$$

A main idea is to apply Eq. (2.49) to a volume sufficiently large for the right-hand side to be represented by a simple asymptotic expression. The value of the normalization integral on the left-hand side is thus obtained *irrespective of complications* in the inner volume. In our MQDT application to a single particle emerging outside a core, the surface S in configuration space is defined as the locus of all points $\{\vec{r}_1, \ldots, \vec{r}_\alpha, \ldots\}$ with the largest radial coordinate r_α equal to a value R outside the core radius r_0. Accordingly we enter in Eq. (2.49) Ψ_E and $\Psi^*_{E'}$ from Eq. (1.4) setting $r=R$ and $dS=d\omega$. The expression of $\vec{j}\cdot\hat{n}$ consists then of the $M_i(R)$ factors of Ψ and of their radial derivatives, while the integration over ω reduces to orthonormality of the Φ_i yielding

$$\int_V d\tau\, \Psi^*_{E'}\Psi_E = \sum_i \frac{1}{2(\epsilon'_i-\epsilon_i)} \times W(M_i(\epsilon'_i,R), M_i(\epsilon_i,R))\,. \tag{2.50}$$

Each term on the right-hand side is to be evaluated having in mind an eventual double limiting process, firstly $\epsilon'_i \to \epsilon_i$ and then $R\to\infty$.

Dealing with one channel at a time, we drop the index i and expand each $M(R)$ into the base pair $\{f^+, f^-\}$, as in Eq. (2.11),

$$M(\epsilon,R) = (1/2ik)[W_\epsilon(f^-,M)f^+(\epsilon,R) - W_\epsilon(f^+,M)f^-(\epsilon,R)]\,. \tag{2.51}$$

Determination of the Wronskian coefficients $W_\epsilon(f^\pm,M)$ will be a separate task. This expansion reduces the Wronskian of Eq. (2.50) to a linear combination of the four Wronskians

$$W(f^+_{\epsilon'}, f^+_\epsilon) = -i(k'-k)\exp[i(k'+k)R]R^{\xi'+\xi} + O(1/R)\,, \tag{2.52a}$$

$$W(f^+_{\epsilon'}, f^-_\epsilon) = -i(k'+k)\exp[i(k'-k)R]R^{\xi'-\xi} + O(1/R)\,, \tag{2.52b}$$

$$W(f^-_{\epsilon'}, f^+_\epsilon) = i(k'+k)\exp[i(-k'+k)R]R^{-(\xi'-\xi)} + O(1/R)\,, \tag{2.52c}$$

$$W(f^-_{\epsilon'}, f^-_\epsilon) = i(k'-k)\exp[-i(k'+k)R]R^{-(\xi'+\xi)} + O(1/R)\,. \tag{2.52d}$$

Using these expressions, we substitute Eq. (2.51) into Eq. (2.50) and apply the double limiting process. Standard arguments serve to evaluate the limit, separately for the continuous[10] ($\epsilon>0$) and for the discrete[2] ($\epsilon<0$) spectrum and separately for the four terms of the expansion. Only two terms, from Eqs. (2.52b) and (2.52c), contribute to the limit for $\epsilon>0$; only term (2.52c) contributes for $\epsilon<0$. The results are

$$\lim_{R\to\infty}\lim_{\epsilon'\to\epsilon}\frac{1}{2(\epsilon'-\epsilon)}W(M(\epsilon',R),M(\epsilon,R)) = \begin{cases} \dfrac{\pi}{2k}W_\epsilon(f^-,M)W_\epsilon(f^+,M)\delta(\epsilon'-\epsilon), & \text{for } \epsilon>0\,, \\ \tfrac{1}{4}\nu W_\epsilon(f^-,M)\dfrac{d}{d\epsilon}W_\epsilon(f^+,M)\,, & \text{at } W_\epsilon(f^+,M)=0,\ \text{for } \epsilon<0\,. \end{cases} \tag{2.53}$$

The coefficient of $\delta(\epsilon'-\epsilon)$ in the formula for $\epsilon>0$ represents the reciprocal of the spectral density of states $M(\epsilon,r)$, and is reduced to unity by normalizing M per unit energy.

In our approach to QDT the radial functions M will be represented as superpositions of the base pair $\{f^0,g^0\}$ or of an analogous pair of wave functions for the asymptotic fields $v_\rho(r)$. The normalization integrals will accordingly be expressed in terms of the Wronskians for these fields given above in Sec. II B and II C. Observe then that the combination of Wronskians with $M\equiv f^0$, $(\pi/2k)W(f^-,f^0)W(f^+,f^0)$, indeed equals the reciprocal density of states $1/k^{2\lambda+1}$ for zero field according to Eq. (2.18). For a Coulomb field this same combination is indicated by $1/B(\epsilon,\lambda)$ in Eq. (2.23). It will be convenient to write in general

$$(\pi/2k)W_{\epsilon\lambda}(f^-,f^0)W_{\epsilon\lambda}(f^+,f^0) = 1/B(\epsilon,\lambda)\,, \tag{2.54}$$

extending our notation by setting

$$B(\epsilon,\lambda) = \begin{cases} k^{2\lambda+1}, & \text{zero field}\,, \\ \sinh\pi\alpha/[\cosh\pi\alpha - \cos 2(\alpha\ln\tfrac{1}{2}k - \chi_\alpha)]\,, & \text{dipole field}\,. \end{cases} \tag{2.54'}$$

TABLE I. Summary of formulas.

(A) Parameters

	Zero field ($p=0$)	Coulomb field ($p=1$)	Dipole field ($p=2$)
$A(\nu,\lambda)$	$\frac{2\nu^{-2\lambda-1}}{1+\cos^2\pi\lambda}$	$\frac{\Gamma(\lambda+1+\nu)}{\nu^{2\lambda+1}\Gamma(\nu-\lambda)}$	1
$B(\epsilon,\lambda)$	$k^{2\lambda+1}$	$\frac{1}{2\pi}k^{2\lambda+1}\lvert\Gamma(\lambda+1-i/k)\rvert^2$	$\frac{\sinh\pi\alpha}{\cosh\pi\alpha-\cos2(\alpha\ln\frac{1}{2}k+\chi_\alpha)}$
$D(\nu,\lambda)$	1	$\pi^{1/2}(2/\nu)^\nu[\Gamma(\nu-\lambda)\Gamma(\lambda+1+\nu)]^{-1/2}$	$\sinh^{1/2}\pi\alpha$
$\beta_\lambda(\nu)$	$\sin^{-1}[(1+\cos^2\pi\lambda)^{-1/2}]$	$\pi(\nu-\lambda)$	$\alpha\ln2\nu-\chi_\alpha$
$\eta(k,\lambda)$	$-\lambda\pi/2$	$k^{-1}\ln2k-\lambda\pi/2+\sigma_\lambda$	$-\pi/4+\phi(k,\alpha)$
			$\chi_\alpha=\arg\Gamma(1-i\alpha)$
		$\sigma_\lambda=\arg\Gamma(\lambda+1-i/k)$	$\tan\phi=-\coth(\frac{1}{2}\pi\alpha)\tan(\alpha\ln\frac{1}{2}k+\chi_\alpha)$
			(ϕ in same quadrant as $\alpha\ln\frac{1}{2}k+\chi_\alpha$)
ζ	0	$i/k=\nu$	0
$\tilde\lambda_c$	half integer nearest λ	integer or half integer nearest λ	
$\mathcal{G}(i/k,\lambda),\epsilon>0$	$k^{2\lambda+1}\cot\pi(\lambda+\frac{1}{2})$ $\times[1-k^{2(\tilde\lambda_c-\lambda)}\cos\pi(\lambda+\frac{1}{2})(-1)^{\tilde\lambda_c+1/2}]$	$\mathrm{Re}A(i/k,\lambda)\cot\pi(\lambda+\frac{1}{2})-\frac{A(i/k,\tilde\lambda_c)\cos^2\pi(2\lambda+1)(-1)^{2\tilde\lambda_c+1}}{\sin\pi(2\lambda+1)}$ $+\frac{\mathrm{Re}A(i/k,\lambda)\sin\pi(2\lambda+1)}{e^{2\pi/k}+\cos\pi(2\lambda+1)}$	$\frac{-\sin2(\alpha\ln\frac{1}{2}k+\chi_\alpha)}{\cosh\pi\alpha-\cos2(\alpha\ln\frac{1}{2}k+\chi_\alpha)}$
$\mathcal{G}(\nu,\lambda),\epsilon<0$	$\nu^{-2\lambda-1}\frac{\cos^2\pi(\lambda+\frac{1}{2})}{\sin\pi(\lambda+\frac{1}{2})}\left[\frac{1}{1+\cos^2\pi\lambda}-\nu^{2(\lambda-\tilde\lambda_c)}\right]$	$A(\nu,\lambda)\cot\pi(2\lambda+1)-A(\nu,\tilde\lambda_c)\frac{\cos^2\pi(2\lambda+1)}{\sin\pi(2\lambda+1)}(-1)^{2\tilde\lambda_c+1}$	0

(B) Transformation between base pairs

$$\begin{pmatrix}f\\g\end{pmatrix}=\begin{pmatrix}B^{1/2}(\epsilon,\lambda) & 0\\ B^{-1/2}(\epsilon,\lambda)\mathcal{G}(i/k,\lambda) & B^{-1/2}(\epsilon,\lambda)\end{pmatrix}\begin{pmatrix}f^0\\g^0\end{pmatrix},\ \epsilon>0;\quad \begin{pmatrix}f\\g\end{pmatrix}=\begin{pmatrix}A^{1/2}(\nu,\lambda) & 0\\ A^{-1/2}(\nu,\lambda)\mathcal{G}(\nu,\lambda) & A^{-1/2}(\nu,\lambda)\end{pmatrix}\begin{pmatrix}f^0\\g^0\end{pmatrix},\ \epsilon<0;$$

(C) Asymptotic forms ($r\to\infty$) of optical potential solutions

$$f(\epsilon,l,r)\to(2/\pi k)^{1/2}\sin[kr-i\zeta\ln r+\eta(k,\lambda)+\delta_{\epsilon l}]$$

$$g(\epsilon,l,r)\to-(2/\pi k)^{1/2}\cos[kr-i\zeta\ln r+\eta(k,\lambda)+\delta_{\epsilon l}];\ \epsilon>0\ .$$

$$f(\epsilon,l,r)\to(\nu/\pi)^{1/2}\{\sin[\beta_\lambda(\nu)+\delta_{\epsilon l}]D^{-1}e^{r/\nu}r^{-\zeta}-\cos[\beta_\lambda(\nu)+\delta_{\epsilon l}]De^{-r/\nu}r^{\zeta}\}$$

$$g(\epsilon,l,r)\to-(\nu/\pi)^{1/2}\{\cos[\beta_\lambda(\nu)+\delta_{\epsilon l}]D^{-1}e^{r/\nu}r^{-\zeta}+\sin[\beta_\lambda(\nu)+\delta_{\epsilon l}]De^{-r/\nu}r^{\zeta}\};\ \epsilon<0$$

With this notation each of the large-r forms of f^0 for $\epsilon>0$, Eqs. (2.20), (2.26), and (2.31), is seen to include a coefficient $B^{-1/2}(\epsilon,\lambda)$. Similarly each of the large-r forms of $\bar{g}$ for $\epsilon>0$, Eqs. (2.35)–(2.37), includes a coefficient $B^{1/2}(\epsilon,\lambda)$. This remark suggests the introduction of yet another base pair of radial functions, normalized now per unit energy,

$$f(\epsilon,\lambda,r)=B^{1/2}(\epsilon,\lambda)f^0(\epsilon,\lambda,r)\,,$$
$$g(\epsilon,\lambda,r)=B^{-1/2}(\epsilon,\lambda)\bar{g}(\epsilon,\lambda,r),\quad \epsilon>0\,. \tag{2.55}$$

These two functions oscillate at large r with equal amplitude, 90° out of phase and have $W_{\epsilon\lambda}(f,g)=2/\pi$; however, their coefficients B are generally nonanalytic functions of ϵ.

For $\epsilon<0$, the normalization integral (2.53) with $M=f^0$ is not immediately relevant for zero field, though it will apply to potential wells converging to zero field. For the other fields, the main factor to be evaluated is the derivative $dW^+_\epsilon/d\epsilon$ at a root of $W^+_\epsilon=0$; the only nonzero contribution arises from the derivative of the sine factor in the expressions (2.22) and (2.28) of W^+_ϵ. Thus we find for the Coulomb field

$$\begin{aligned}\tfrac{1}{4}\nu W_{\epsilon\lambda}(f^-,f^0)dW_{\epsilon\lambda}(f^+,f^0)/d\epsilon\,\big|_{\nu-\lambda=n>0}&\\ =A^{-1}(\nu,\lambda)d\nu/d\epsilon\,\big|_{\nu=n+\lambda}&\\ =A^{-1}(\nu,\lambda)\nu^3\,\big|_{\nu=n+\lambda}\,,&\end{aligned} \tag{2.56}$$

and for the dipole field

$$\begin{aligned}\tfrac{1}{4}\nu W_{\epsilon\lambda}(f^-,f^0)dW_{\epsilon\lambda}(f^+,f^0)/d\epsilon\,\big|_{\alpha\ln2\nu-\chi_\alpha=n\pi}&\\ =\pi^{-1}d(\alpha\ln2\nu-\chi_\alpha)/d\epsilon\,\big|_{\alpha\ln2\nu-\chi_\alpha=n\pi}&\\ =\pi^{-1}\alpha\nu^2\,\big|_{\nu=(1/2)\exp[(n\pi+\chi_\alpha)/\alpha]}\,.&\end{aligned} \tag{2.57}$$

These values are reciprocal to the interval of successive energy eigenvalues, much as the expression (2.54) for $\epsilon>0$ is reciprocal to the density of states. The simple structure of Eqs. (2.56) and (2.57) derives from the structure of the large-r expressions of f^0 for $\epsilon<0$ in Eqs. (2.26) and (2.31). Those expressions contain the sine and cosine coefficients which are characteristic of the QDT and contribute to the normalization integral only the derivative of their argument; the other coefficients of $f^\pm$, namely, $D^{\pm1}$ or $\sinh^{\pm1/2}\pi\alpha$, also cancel.

The simple structure of these results—and the major role that the large-r expressions of f^0 will play in the following sections—suggest that we reduce these expressions to a common form for all three basic fields, $v_\rho(r)$, analogous to the common Eqs. (2.54) and (2.55) for $\epsilon>0$. To this end we should symmetrize the zero-field expression of f^0 in Eq. (2.20) for $\epsilon<0$ by introducing a new parameter β_λ through the relation

$$\cos\pi\lambda=\cos\beta_\lambda/\sin\beta_\lambda,\quad \tfrac{1}{4}\pi\leq\beta_\lambda\leq\tfrac{3}{4}\pi\,. \tag{2.58}$$

The pair of expressions of $\{f^0,\bar{g}\}$, Eqs. (2.20) and (2.35), can thus be cast in the form, for $\epsilon<0$,

$$\begin{aligned}f^0(\epsilon,\lambda,r)=&[A(\nu,\lambda)]^{-1/2}(\nu/\pi)^{1/2}\\ &\times[\sin\beta_\lambda D^{-1}f^-_\epsilon-\cos\beta_\lambda Df^+_\epsilon]\,,\\ \bar{g}(\epsilon,\lambda,r)=&-[A(\nu,\lambda)]^{1/2}(\nu/\pi)^{1/2}\\ &\times[\cos\beta_\lambda D^{-1}f^-_\epsilon+\sin\beta_\lambda Df^+_\epsilon]\,,\end{aligned} \tag{2.59}$$

where we have set

$$A(\nu,\lambda)=\nu^{-(2\lambda+1)}2\sin^2\beta_\lambda,\quad D=1\,, \tag{2.60}$$

for zero field. The form of the Coulomb field Eqs. (2.26) and (2.36) also coincides with Eq. (2.59) if we use $A(\nu,\lambda)$ and D from Eq. (2.25), and set

$$\beta_\lambda(\nu)=\pi(\nu-\lambda)\,, \tag{2.61}$$

for Coulomb field. Finally Eq. (2.59) represents the dipole field expressions (2.31) and (2.37) as well if we set

$$\begin{aligned}&A(\nu,\alpha)=1,\quad \beta_\alpha(\nu)=\alpha\ln2\nu-\chi_\alpha\,,\\ &D=\sinh^{1/2}\pi\alpha\,,\end{aligned} \tag{2.62}$$

for dipole field. These notations reduce the expressions in Eqs. (2.56) and (2.57) to the common form $A^{-1}\pi^{-1}d\beta_\lambda/d\epsilon\,\big|_{\nu_n}$. The amplitude factors A drop out of all these expressions too if we renormalize the pair $\{f^0,\bar{g}\}$ for $\epsilon<0$ as was done in Eq. (2.55) for $\epsilon>0$ by setting

$$f(\epsilon,\lambda,r)=A^{1/2}(\nu,\lambda)f^0(\epsilon,\lambda,r)\,,$$
$$g(\epsilon,\lambda,r)=A^{-1/2}(\nu,\lambda)\bar{g}(\epsilon,\lambda,r),\quad \epsilon<0\,. \tag{2.63}$$

For reference the important equations of Sec. II are summarized in Table I.

E. QDT for optical potential fields

The treatment in Sec. II B–II D has provided us with essential tools for QDT applications but the basic potentials $v_\rho(r)$ are hardly ever realistic over the entire range $0\leq r\leq\infty$. The present Sec. II E will deal with an application of intermediate complexity, namely, to an electron in the single-channel, local, optical potential field $v(r)$ considered in Eq. (2.1). The more realistic applications, to atomic systems with nonlocal multichannel inner fields will be developed in Sec. IV. The applications to be considered here are the following:

(a) A formulation of Eq. (2.14) for the eigenvalues of the discrete spectrum, showing separate contributions of parameters related to the asymptotic potential $v_\rho(r)$ and to the shorter-range portion of $v(r)$. The latter contribution will take the form of a quantum defect $\mu_{\epsilon l}$ which

varies "slowly," i.e., on a scale of order 0.1 a.u., near the threshold $\epsilon=0$ for atomic Rydberg electrons.

(b) A corresponding formulation of the continuum wave functions $f(\epsilon,\lambda,r)$ at large r showing how the departure of $v(r)$ from $v_p(r)$ is reflected only in the introduction of a slowly varying phase shift $\delta_{\epsilon l}=\pi\mu_{\epsilon l}$ and of a "slowly" varying amplitude $\gamma_{\epsilon l}$.

(c) A factorization of matrix elements of *short-range* operators $T(\epsilon)$,

$$(nlm\,|\,T\,|\,n'l'm')=N_{nl}(\epsilon)(\epsilon lm\,|\,T\,|\,\epsilon' l'm')N_{n'l'}(\epsilon')\,, \tag{2.64}$$

in which the dependence on the principal quantum number n (or n') is split off into a normalization factor N independent of T and into a core factor normalized per unit energy and "slowly" dependent on ϵ and ϵ'. (Similar factorizations may be used to sort out normalization effects for $\epsilon>0$.) These formulations attain the aim of restricting the need of numerical calculations for any specific system to $\mu_{\epsilon l}$ or other functions of ϵ that vary slowly and can accordingly be tabulated only over a coarse mesh unrelated to the actual energy of discrete levels; occasionally a single energy will suffice. An energy range of 0.1 a.u. has been indicated here as a standard for "coarse" mesh, having in mind the usual application to a valence electron of an atom (or molecule) with which we deal explicitly. A different standard should be used for other applications, e.g., to molecular vibrations.

The considerations at the beginning of Sec. II imply that any solution of Eq. (2.1) can be represented at large r as a superposition of the base pair of solutions $\{f,g\}$ defined by Eqs. (2.55) and (2.63), for the appropriate value of p. We implement this program for a solution regular at the origin and normalized there with $a_0(l)=2^{l+1}/(2l+1)!$ as appropriate to the Coulomb field near a nucleus, in accordance with Sec. II A. This solution will be called $f^{\rm opt}$ throughout Sec. II E *only* and it will be represented at large r as

$$f^{\rm opt}(\epsilon,l,r)\xrightarrow[r\to\infty]{}\gamma_{\epsilon l}[\cos\delta_{\epsilon l}f(\epsilon,\lambda,r)-\sin\delta_{\epsilon l}g(\epsilon,\lambda,r)]\,. \tag{2.65}$$

The index λ has been used in the base pair functions to allow for the occurrence of a $1/r^2$ term at large r. The structure of the coefficients in Eq. (2.65) is designed to combine with the large-r forms of $\{f,g\}$ for $\epsilon<0$, Eqs. (2.63) and (2.59), to yield

$$f^{\rm opt}(\epsilon,l,r)\xrightarrow[r\to\infty]{}\gamma_{\epsilon l}(\nu/\pi)^{1/2}[\sin(\beta_\lambda+\delta_{\epsilon l})D^{-1}f^- -\cos(\beta_\lambda+\delta_{\epsilon l})Df^+],\ \epsilon<0\,. \tag{2.66}$$

Here $\delta_{\epsilon l}$, a slow function of ϵ, combines additively with β_λ which may vary extremely fast near a condensation point. For the Coulomb field, where β_λ takes the form $\pi(\nu-\lambda)$, $\delta_{\epsilon l}$ is generally represented as $\pi\mu_{\epsilon l}$, $\mu_{\epsilon l}$ being the quantum defect which adds to ν in the expression $\beta_\lambda+\delta_{\epsilon l}=\pi(\nu+\mu_{\epsilon l}-\lambda)$. At $\epsilon>0$ one obtains an expression where $\delta_{\epsilon l}$ adds to the phase of an oscillating function of kr and thus represents a phase shift. We proceed now to the QDT tasks, deferring that of calculating the coefficients $\gamma_{\epsilon l}$ and $\delta_{\epsilon l}$ for any given potential $v(r)$ as well as the task of removing the effects of nonanalyticity of the pair $\{f,g\}$ from this calculation.

The eigenvalue Eq. (2.14) requires, when applied to $f^{\rm opt}$, that the coefficient of f^- vanishes in Eq. (2.66). Since D^{-1} never vanishes and vanishing of $\gamma_{\epsilon l}$ would cause $f^{\rm opt}$ to vanish throughout, the eigenvalue equation requires the sine factor to vanish,

$$\beta_\lambda(\nu)+\delta_{\epsilon l}=n\pi\,, \tag{2.67}$$

a fundamental, if obvious, extension of results of Sec. II B. In applications with $p=1$ at large negative ϵ it should be recalled from Sec. II B, that the factorization of D utilized here must be modified at $\nu\leq\lambda$. These remarks dispose of task (a). The completion of task (b) amounts to writing explicitly the large-r expression of $f^{\rm opt}$ for $\epsilon>0$ in accordance with earlier remarks,

$$f^{\rm opt}(\epsilon,l,r)\xrightarrow[r\to\infty]{}\gamma_{\epsilon l}(2/\pi k)^{1/2}\sin[kr-i\zeta\ln r+\eta(k,\lambda)+\delta_{\epsilon l}],\ \epsilon>0\,. \tag{2.68}$$

Here ζ is the parameter of Eq. (2.6), which equals i/k for a Coulomb field and vanishes otherwise, and $\eta(k,\lambda)$ is the phase of $W^-_{\epsilon\lambda}$ for the reference potential $v_p(r)$, namely,

$$\eta(k,\lambda)=\begin{cases}-\lambda\pi/2, & \text{zero field},\\ -\lambda\pi/2+k^{-1}\ln 2k+\sigma_\lambda, & \text{Coulomb field},\\ -\pi/4+\phi(k,\alpha), & \text{dipole field},\end{cases} \tag{2.69}$$

with σ_λ and $\phi(k,\alpha)$ from Eqs. (2.25) and (2.31).

With regard to (c), the factorization of matrix elements indicated in Eq. (2.64), we recall that the normalization integrals, Eqs. (2.56) and (2.57), for the basic fields $v_p(r)$ were condensed in the form $A^{-1}\pi^{-1}d\beta_\lambda/d\epsilon\,|_{\nu_n}$ following Eqs. (2.60)–(2.62). The factor A^{-1} in this formula has now been removed by the replacement of $\{f^0,\bar g\}$ by $\{f,g\}$, but

a factor $\gamma_{\epsilon l}^2$ has been introduced in Eq. (2.65). The phase β_λ is now adjusted by the optical field contribution $\delta_{\epsilon l}$. The normalization coefficient appearing in Eq. (2.64) is thus

$$N_{nl}(\epsilon)=[\gamma_{\epsilon l}^2\pi^{-1}d(\beta_\lambda+\delta_{\epsilon l})/d\epsilon]_{\nu=\nu_n}^{-1/2}. \tag{2.70}$$

Now this equation also applies when the optical potential converges to zero field at large r. Whereas the eigenvalue Eq. (2.67) had no root $\nu<\infty$ for $p=0$ and $\delta_{\epsilon l}=0$, it indeed has roots, in general, for $v(r)<0$; to such roots correspond nonzero values of $d(\beta_\lambda+\delta_{\epsilon l})/d\epsilon\big|_{\nu_n}=d\delta_{\epsilon l}/d\epsilon\big|_{\nu_n}$.

Turning now to the determination of $\gamma_{\epsilon l}$ and $\delta_{\epsilon l}$, one must generally calculate $f^{\rm opt}(\epsilon,l,r)$ by integrating Eq. (2.1) numerically, with the given $v(r)$, from $r=0$ to a value of r sufficiently large for the representation (2.65) to be sufficiently accurate. The integration may proceed by standard methods (e.g., Numerov's) but a WKB or a phase amplitude method[11] (PAM) may be appropriate. A test of convergence to the form (2.65) is to express $\delta_{\epsilon l}$ in terms of Wronskians

$$\tan\delta_{\epsilon l}=W(f_{\epsilon\lambda},f_{\epsilon l}^{\rm opt})/W(g_{\epsilon\lambda},f_{\epsilon l}^{\rm opt}). \tag{2.71}$$

This ratio should vary slowly with increasing r at large r; accordingly it may be evaluated at different r values until it has become constant to the required accuracy. The PAM procedure, whose applications to atomic radial functions have been reviewed recently,[11] utilizes a pair of comparison functions which may coincide with the pair $\{f,g\}$ in our problem. In this event $f^{\rm opt}$ is represented by Eq. (2.65) for all r values but $\gamma_{\epsilon l}$ and $\delta_{\epsilon l}$ become functions of r and constitute a new pair of dependent variables that replaces $f^{\rm opt}$. The equations for $\gamma_{\epsilon l}$ and $\delta_{\epsilon l}$ are nonlinear and of first order, and involve the potential difference $v_p(r)-v(r)$. In particular $\delta_{\epsilon l}$ is obtained by integrating the Volterra equation

$$\delta_{\epsilon l}(r)=\pi\int_0^r dr'\,[v_p(r')-v(r')]\times[f_{\epsilon\lambda}(r')\cos\delta(r')-g_{\epsilon\lambda}(r')\sin\delta(r')]^2, \tag{2.72}$$

which is equivalent to Eq. (2.71) at all r and indicates automatically the progress of $\delta_{\epsilon l}(r)$ toward its eventual value. Once $\delta_{\epsilon l}(r)$ has been evaluated, $\gamma_{\epsilon l}$ is obtained by quadrature. Reference 11 discusses aspects of the practical calculation of $\delta_{\epsilon l}$ but additional ones have emerged from recent extensive calculations and will be reported elsewhere.

F. Example and Addendum

As an example of an optical potential consider a square well of depth $V_0<0$ and radius r_0. For simplicity we discuss only $l=0$. The solution $f^{\rm opt}$ is regular at the origin; in the absence of any short-range Coulomb field we choose $a_0(0)=[2^{1/2}\Gamma(\frac{3}{2})]^{-1}$. Within the inner well the radial wave function is then

$$f^{\rm opt}(\epsilon,l=0,r)=(2/\pi\kappa^2)^{1/2}\sin\kappa r,\quad r<r_0, \tag{2.73}$$

where $\kappa^2=2(\epsilon-V_0)$. With integer l and zero field in the outer region the appropriate base functions are taken to be $\{f_l,g_l\}$, given by

$$f(\epsilon,l=0,r)=\begin{cases}(2/\pi k)^{1/2}\sin kr, & \epsilon>0,\\ (2\nu/\pi)^{1/2}\sinh(r/\nu), & \epsilon<0,\end{cases}$$
$$g(\epsilon,l=0,r)=\begin{cases}-(2/\pi k)^{1/2}\cos kr, & \epsilon>0,\\ -(2\nu/\pi)^{1/2}\cosh(r/\nu), & \epsilon<0,\end{cases} \tag{2.74}$$

where $k^2=-1/\nu^2=2\epsilon$. This problem is solved once the coefficients $\delta_{\epsilon l}$ and $\gamma_{\epsilon l}$ of Eq. (2.65) are determined. First we evaluate the Wronskians in Eq. (2.71) to obtain

$$\tan\delta_{\epsilon 0}=\begin{cases}\dfrac{\kappa\sin kr_0\cos\kappa r_0-k\cos kr_0\sin\kappa r_0}{-\kappa\cos kr_0\cos\kappa r_0-k\sin kr_0\sin\kappa r_0}, & \epsilon>0,\\ \dfrac{\kappa\nu\sinh(r_0/\nu)\cos\kappa r_0-\cosh(r_0/\nu)\sin\kappa r_0}{-\kappa\nu\cosh(r_0/\nu)\cos\kappa r_0+\sinh(r_0/\nu)\sin\kappa r_0}, & \epsilon<0.\end{cases} \tag{2.75}$$

Similarly continuity at r_0 requires that

$$\gamma_{\epsilon 0}=\begin{cases}\left(\dfrac{k}{\kappa^2}\right)^{1/2}\dfrac{\sin\kappa r_0}{\sin(kr_0+\delta_{\epsilon 0})}, & \epsilon>0,\\ \left(\dfrac{1}{\kappa^2\nu}\right)^{1/2}\dfrac{\sin\kappa r_0}{\cos\delta_{\epsilon 0}\sinh(r_0/\nu)+\sin\delta_{\epsilon 0}\cosh(r_0/\nu)}, & \epsilon<0.\end{cases} \tag{2.76}$$

The eigenvalue equation (2.67) can be written for this example as

$$\delta_{\epsilon 0}+\pi/4=n\pi, \tag{2.77}$$

whose roots coincide with those of the more familiar expression $\tan\kappa r_0+\kappa\nu=0$. Finally the normalization integral is given in Eq. (2.70) so that the wave function in the outer field takes the simple form

$$f^{\rm opt}(\epsilon_n,l=0,r)/N_n=(-1)^{n+1}[\pi^{-1}d\delta_{\epsilon 0}/d\epsilon]_{\epsilon_n}^{-1/2}\times(\nu_n/\pi)^{1/2}e^{-r/\nu_n},\quad r>r_0. \tag{2.78}$$

The outer wave function is thus completely specified by a single parameter $\delta_{\epsilon 0}$. This formula will also represent the wave functions in the exterior field for an s-wave electron scattered by a neutral core or for an atom-atom collision; the values of $\delta_{\epsilon 0}$ depend of course on the specific field at shorter range.

There remain to be considered the effects of

nonanalyticity of the base pair $\{f,g\}$ at $\epsilon=0$. In accordance with Sec. II C these effects are made explicit by expressing $\{f,g\}$ in terms of the analytic base pair $\{f^0,g^0\}$. The replacement of $\{f,g\}$ by $\{f^0,g^0\}$ is performed conveniently in Eq. (2.71), using Eqs. (2.55) and (2.45) which yields

$$\tan\delta_{\epsilon l}=A(\nu,\lambda)/[\cot\delta^0_{\epsilon l}+\mathcal{G}(\nu,\lambda)]\,,$$
$$\tan\delta^0_{\epsilon l}=W(f^0_{\epsilon\lambda},f^{\rm opt}_{\epsilon l})/W(g^0_{\epsilon\lambda},f^{\rm opt}_{\epsilon l}),\quad \epsilon<0\,, \tag{2.79}$$

and the same formula with B in place of A for $\epsilon>0$. The parameter $\delta^0_{\epsilon l}$, which depends on ϵ analytically, is the one to be calculated. The corresponding modification of $\gamma_{\epsilon l}$ is

$$\gamma_{\epsilon l}=\gamma^0_{\epsilon l}A^{1/2}(\nu,\lambda)(\sin\delta^0_{\epsilon l}/\sin\delta_{\epsilon l})$$
$$=\gamma^0_{\epsilon l}A^{-1/2}\sin\delta^0_{\epsilon l}[A^2+(\cot\delta^0_{\epsilon l}+\mathcal{G})^2]^{1/2}\,. \tag{2.80}$$

The effects of nonanalyticity, expressed through $\mathcal{G}$ and A, are rather mild for the case of Coulomb fields ($p=1$) but are essential otherwise. For zero field, A and B vanish at $\epsilon=0$, causing $\delta_{\epsilon l}$ to vanish there and introducing the well-known Wigner threshold effects. For the dipole field B oscillates wildly and $\delta_{\epsilon l}$ diverges as $k\to 0$; on the other hand $\mathcal{G}$ vanishes here and δ coincides with δ^0 for $\epsilon<0$.

When $v_p(r)-v(r)$ converges at large r slower than a decreasing exponential (e.g., as r^{-n} with $n>2$), the transformation to the analytic base pair $\{f^0,g^0\}$ does not ensure that $\delta^0_{\epsilon l}$ is analytic in ϵ. The most important example arises for the polarization field $v(r)=-\beta^2/2r^4$ at large radii. The $l=0$ phase shifts contributed by this optical potential may be expanded at $\epsilon\sim 0$ as[12]

$$\cot\delta^0_{\epsilon,l=0}=\cot\delta^0_{\epsilon=0,l=0}+C_1(\beta)k$$
$$+C_2(\beta)k^2\ln(\beta k/4)+\cdots\,, \tag{2.81}$$

with $C_1(\beta)$ and $C_2(\beta)$ independent of k. For this potential the phase amplitude Eq. (2.72) shows that the expression (2.79) approaches its large-r limit as

$$\tan\delta^0_{\epsilon l}(r)\underset{r\to\infty}{\longrightarrow}\tan\delta^0_{\epsilon l}(r=\infty)+O(r^{-3})\,. \tag{2.82}$$

Optical potentials $1/r^n$ with $n>2$ are thus seen to introduce nonanalyticities which have not yet been separated out systematically in the manner of Sec. II C. However these effects are weak and should not present major numerical problems.

In the remainder of this paper no further reference will be necessary to the solutions of Eq. (2.1) for the basic fields $v_p(r)$. Henceforth we shall then indicate $f^{\rm opt}$ by $f^0(\epsilon,l,r)$. The corresponding solution $\bar g(\epsilon,l,r)$ is then identified by its large-r form, obtained from Eqs. (2.66) and (2.68) by introducing the phase lag through subtraction of $\frac{1}{2}\pi$ from $\delta^0_{\epsilon l}$ and inverting the amplitude $\gamma_{\epsilon l}$ into $1/\gamma_{\epsilon l}$. The pair $\{f,g\}$ is obtained by removal of the amplitudes $\gamma^{\pm1}_{\epsilon l}$. The function $g^0(\epsilon,l,r)$ for the optical potential is obtained in a similar fashion, by replacing, in the asymptotic expression of $f^0(\epsilon,l,r)$, $\gamma^0_{\epsilon l}$ by $1/\gamma^0_{\epsilon l}$ and $\delta^0_{\epsilon l}$ by $\delta^0_{\epsilon l}-\pi/2$. Since $\gamma^0_{\epsilon l}$ and $\delta^0_{\epsilon l}$ are analytic in ϵ, as are $\{f^0,g^0\}_p$ for the reference potential $v_p(r)$ used, the irregular g^0 so defined is also analytic in ϵ. We further define the quantities A, B, and $\mathcal{G}$ for the optical potential by

$$f(\epsilon,l,r)/f^0(\epsilon,l,r)=B^{1/2}(k,l),\quad \epsilon>0$$
$$=A^{1/2}(\nu,l),\quad \epsilon<0 \tag{2.83}$$
$$[\bar g(\epsilon,l,r)-g^0(\epsilon,l,r)]/f^0(\epsilon,l,r)=\mathcal{G}(\nu,l)$$

When these definitions are adopted, the transformation given in Table I B applies to the optical potential solutions as well as to the basic field solutions ($p=0,1,2$). The transformation parameters are then *defined* by Eq. (2.83), and do not reduce to a simple analytical form because $v(r)$ is left unspecified. Unless otherwise stated $A(\nu,\lambda)$ is to be replaced by $B(\epsilon,\lambda)$ at $\epsilon>0$ throughout the remainder of this paper.

G. Connection with Seaton's notation

We have followed Seaton's notation[2] in most respects, but we have reduced slightly the number of distinct parameters. In particular we have dropped Seaton's distinction between δ and $\pi\mu$ for $\epsilon>0$ and we have defined B for $\epsilon>0$ only. The resulting differences are summarized for integer $\lambda=l$, by the equations

Reference 2		Present paper
$-I^{-1}J\equiv\beta$	=	$\tan\delta^0_{\epsilon l}$,
$Y\equiv\tan\pi\eta$	=	$[\cot\delta^0_{\epsilon l}+\mathcal{G}(\nu,l)]^{-1}$
$A^{1/2}YA^{1/2}\equiv\tan\pi\mu$	=	$\begin{cases}(A/B)\tan\delta_{\epsilon l}, & \epsilon\geq 0\,,\\ \tan\delta_{\epsilon l}, & \epsilon\leq 0\,,\end{cases}$ (2.84)

$$R\equiv B^{1/2}YB^{1/2}\equiv\tan\delta=\tan\delta_{\epsilon l}\equiv\tan\pi\mu_{\epsilon l},\quad \epsilon\gtrless 0\,.$$

Reference 2 deals with a multichannel situation throughout, whereby its expressions are regarded as matrices; the present Sec. II deals instead with a single channel only. As noted above, in Sec. II C, $\mathcal{G}(\nu,\lambda)$ in the present paper is the real part of Seaton's $\mathcal{G}$; for $\epsilon<0$ and integer $\lambda=l$, $\mathcal{G}$ is real in either case and no distinction is necessary. The parameter B was defined in Ref. 2 to be identical to A for $\epsilon<0$.

III. SMOOTH GREEN'S FUNCTION

Green's functions serve to represent general solutions of *inhomogeneous* linear equations, such as

$$[h(r)-\epsilon]\psi_\epsilon(r)=-F_\epsilon(r)\,, \tag{3.1}$$

in terms of the solution for a standard unit inhomogeneity,

$$[h(r)-\epsilon]G_\epsilon(r,r')=-\delta(r-r')\,. \tag{3.2}$$

A Green's function G_ϵ that satisfies (3.2) can be represented in terms of any pair of independent solutions of the homogeneous equation $[h(r)-\epsilon]y(r)=0$, but the choice of this pair depends on the boundary conditions to be imposed on the solution of (3.1). We shall point out here how this choice is to be made in the QDT, for closed channels in particular.

Scattering theory utilizes the Green's function approach to recast *homogeneous* Schrödinger equations into an integral form. For a single-channel problem with a potential $V(r)$, the Schrödinger equation $[h(r)+V(r)-\epsilon]\psi_\epsilon(r)=0$ is rewritten in the form (3.1) with $F_\epsilon(r)=V(r)\psi_\epsilon(r)$, and then in integral form by means of the Green's function,

$$\psi_\epsilon(r)=f_\epsilon(r)+\int_0^\infty dr'\,G_\epsilon(r,r')V(r')\psi_\epsilon(r')\,, \tag{3.3}$$

where f_ϵ satisfies $[h(r)-\epsilon]f_\epsilon=0$ and is regular at $r=0$. Familiar treatments of scattering theory include in $h(r)$ only the kinetic energy operator; here we include also a $v(r)$ term such that $V(r')$ vanishes for $r'>r_0$. This departure from common practice implies a second one, namely, the use of Green's functions for $\epsilon<0$; the study of alternative boundary conditions at $r=\infty$ for G_ϵ in this range constitutes the main novelty of this section. The multichannel aspects of Eq. (3.3) will be dealt with in Sec. IV.

For negative values of ϵ one would normally require the Green's function to be bounded both at $r=0$ and at $r=\infty$. The solution of Eq. (3.2) in the notation of Sec. II—but dropping the index λ or l—is then

$$G_\epsilon(r,r')=2f^+_\epsilon(r_>)f_\epsilon(r_<)/W_\epsilon(f,f^+)\,, \tag{3.4}$$

where $r_>(r_<)$ indicates the larger (smaller) of (r,r') [see, e.g., Ref. 6(b), p. 82–83]. Note, however, that $f_\epsilon(r)$ and $f^+_\epsilon(r)$ are *no longer* linearly independent when ϵ coincides with an eigenvalue ϵ_n of $h(r)$. At these values, $\epsilon=\epsilon_n$, the Wronskian in (3.4) vanishes causing G_ϵ to be singular. This singularity can be isolated by representing f^+ in terms of the pair $\{f,g\}$ with Wronskian $2/\pi$ by means of Eq. (2.8),

$$f^+_\epsilon(r)=\tfrac{1}{2}\pi\{-W_\epsilon(g,f^+)f_\epsilon(r)+W_\epsilon(f,f^+)g_\epsilon(r)\}\,. \tag{3.5}$$

The Green's function takes then the form

$$G_\epsilon(r,r')=\pi g_\epsilon(r_>)f_\epsilon(r_<)-\pi\frac{W_\epsilon(g,f^+)}{W_\epsilon(f,f^+)}f_\epsilon(r)f_\epsilon(r')\,. \tag{3.6}$$

The first term of this expression is now *free of the singularity* at ϵ_n and its two factors are always linearly independent. The second factor has a pole at each $\epsilon=\epsilon_n$, where $W_\epsilon(f,f^+)$ vanishes in accordance with Eq. (2.13); the characterization of the singularity of G_ϵ in the form (3.6) will prove important.

Equation (3.6) shows the Green's function G_ϵ to depend nonanalytically on the energy ϵ at the threshold $\epsilon=0$, as neither $\{f,g\}$ nor the Wronskians are analytic. The behavior of the Wronskians at $\epsilon=0$ has been discussed in Sec. II and its implications for our purposes will be considered below. The nonanalyticity of G_ϵ can be made explicit by substituting in Eq. (3.6) $g(r)=A^{-1/2}[g^0+\mathcal{G}f^0]$, in accordance with Eqs. (2.63) and (2.83), where as usual A is replaced by B for $\epsilon>0$. The pair $\{f^0,g^0\}$ is now analytic in ϵ and the nonanalyticity of $\mathcal{G}(\nu,l)$ has been discussed in Sec. II. Thus, we write, using Eq. (2.83),

$$G_\epsilon(r,r')=\pi g^0_\epsilon(r_>)f^0_\epsilon(r_<)-\pi\frac{W_\epsilon(g^0,f^+)}{W_\epsilon(f^0,f^+)}f^0_\epsilon(r)f^0_\epsilon(r')\,, \tag{3.6'}$$

where only the Wronskians remain nonanalytic.

Following these considerations on the singularity of the Green's function G_ϵ, we turn now to the problem of solving the integral equation (3.3) for the wave function $\psi_\epsilon(r)$. This problem would be complicated by the occurrence of the singularities whenever the energy ϵ of interest approaches one of the discrete eigenvalues ϵ_n. However, the QDT can eliminate the singularities because they result, as we have seen, from imposing the boundedness of G_ϵ at $r=\infty$, whereas the QDT does not impose this condition on its wave function at the outset. Removal of this condition permits us to use a different Green's function which is "smooth," i.e., free of poles. We define this function as consisting of the first term only of Eq. (3.6), setting

$$G^{(s)}_\epsilon(r,r')=\pi g_\epsilon(r_>)f_\epsilon(r_<)\,. \tag{3.7}$$

Should it be desirable for the Green's function to be not only free from poles at ϵ_n but also analytic in ϵ, one could restrict it instead to the first term of Eq. (3.6'), setting

$$G^{(s0)}_\epsilon(r,r')=\pi g^0_\epsilon(r_>)f^0_\epsilon(r_<)\,. \tag{3.7'}$$

We shall return to this option later, while concentrating here on $G^{(s)}_\epsilon$.

Substitution of the smooth Green's function in

Eq. (3.3) gives now, for $r > r_0$,

$$\psi_\epsilon(r) = f_\epsilon(r) + g_\epsilon(r)\pi \int_0^{r_0} dr' f_\epsilon(r') V(r') \psi_\epsilon(r')$$
$$= f_\epsilon(r) + g_\epsilon(r)\pi (f_\epsilon^0 | V | \psi_\epsilon), \qquad (3.8)$$

where the integral is now limited to $r' < r$ by the finite range of $V(r')$. This equation thus expresses the wave function $\psi_\epsilon(r)$ at $r > r_0$ in terms of an integral over its values at $r < r_0$, an essential gain deriving from the factorized form of $G_\epsilon^{(s)}$. The problem of solving the Schrödinger equation for ψ_ϵ resolves now into two separate ones: (a) the calculation of the matrix element $(f_\epsilon | V | \psi_\epsilon)$ for arbitrary ϵ, which implies determining the solution within the core region only, $r < r_0$, and (b) the application of the boundary condition at $r = \infty$ which determine the discrete eigenvalues of $h(r) + V(r)$.

Note that the form (3.8) of the Schrödinger equation has been considered routinely in scattering theory, i.e., for $\epsilon > 0$, without any need for distinguishing the Green's functions G_ϵ and $G_\epsilon^{(s)}$.[6] In the continuum there is wide freedom of choice for the boundary condition on G_ϵ at $r = \infty$, and it proves convenient to require $G_\epsilon(r, r')$ to oscillate at large r with a lag of 90° with respect to $f_\epsilon(r)$. One is thus led to define G_ϵ so as to coincide with the function we have called $G_\epsilon^{(s)}$. Note also that the form of the solution (3.8) at $\epsilon > 0$ identifies the quantity $(f_\epsilon | V | \psi_\epsilon)$ as a *reaction matrix* element; we shall extend this terminology to the range $\epsilon < 0$ in accordance with Ref. 4.

Of the two problems indicated above, (a) and (b), the first one will be dealt with in Sec. IV by expanding the wave function $\psi_\epsilon(r)$ into eigenfunctions f_ϵ of $h(r)$. This expansion will lead us to use an expanded form of the Green's function $G^{(s)}$, which remains to be discussed here. It is instead straightforward to formulate problem (b), i.e., the boundedness condition on $\psi_\epsilon(r)$ at $r = \infty$, for $\epsilon < 0$, by entering the large-r form of $\psi_\epsilon(r)$, namely, Eq. (3.8) in place of $M_l(r)$ in Eq. (2.13),

$$W(f^+, \psi_\epsilon) = W_\epsilon(f^+, f) + W_\epsilon(f^+, g)\pi (f_\epsilon | V | \psi_\epsilon) = 0. \qquad (3.9)$$

The Wronskians on the right-hand side are to be obtained from Sec. II, whereby problem (b) reduces to (a), the calculation of the reaction matrix.

A. Eigenfunction expansion of $G_\epsilon^{(s)}(r, r')$

A familiar solution to the Green's function equation (3.2) is readily expressed in terms of the complete set of eigenfunctions $f_n(r)$ of the operator $h(r)$. These eigenfunctions $f_n(r)$ are of course regular at both $r = 0$ and $r = \infty$. Accordingly the solution constructed in this manner satisfies the same boundary conditions as the singular Green's function $G_\epsilon(r, r')$ and is

$$G_\epsilon(r, r') = \sum_n f_n(r) \frac{1}{\epsilon - \epsilon_n} f_n(r'), \qquad (3.10)$$

as can be verified by substitution in (3.2) [see, e.g., Ref. 6(b) Chap. 4, Sec. 3]. The sum over n runs here over the entire spectrum—discrete and continuum—of normalized eigenfunctions $f_n(r)$, thus including an integration over the range $\epsilon_n > 0$. The function (3.10) is indeed singular whenever ϵ coincides with an eigenvalue ϵ_n. The expansion of $G_\epsilon^{(s)}(r, r')$ which we seek is obtained by combining Eq. (3.7) and Eq. (3.10) with (3.6),

$$G_\epsilon^{(s)}(r, r') = \sum_n f_n(r) \frac{1}{\epsilon - \epsilon_n} f_n(r')$$
$$+ f_\epsilon(r)\pi \frac{W_\epsilon(g, f^+)}{W_\epsilon(f, f^+)} f_\epsilon(r'). \qquad (3.11)$$

We shall now verify that the singularities of the two terms of this expansion at $\epsilon = \epsilon_n$ cancel exactly, a result that was utilized in Ref. 4 without detailed analysis.

To this end we use Eq. (2.55) to replace $W_\epsilon(g, f^+)$ in the last term of Eq. (3.11) by $-B^{-1/2} W_\epsilon(f^+, \bar{g})$; further $W_\epsilon(f^+, \bar{g})$ is written in the form (2.34) and $W_\epsilon(f, f^+)$ is replaced by $-B^{1/2} W_{\epsilon l}^+$, which gives

$$\pi \frac{W(g, f^+)}{W(f, f^+)} = \frac{1}{B(\epsilon, l)} \frac{2D^{-2} |W_{\epsilon l}^-|^2}{|D^{-1} W_{\epsilon l}^-|^2 + |D W_{\epsilon l}^+|^2} \frac{2ik}{W_{\epsilon l}^- W_{\epsilon l}^+},$$
$$= \begin{cases} i\pi, & \epsilon > 0, \\ -\pi \cot(\beta_\lambda + \delta_{\epsilon l}), & \epsilon < 0. \end{cases} \qquad (3.12)$$

Here the parameters $W_{\epsilon l}^\pm$ and $\delta_{\epsilon l}$ pertain to the function called f^{opt} in Sec. IIE. The index λ is replaced by an integer l for all parameters that reflect departures of the optical potential from its asymptotic form $v_p(r)$; however, all parameters pertaining to v_p itself remain labeled by λ. Equation (3.12) has been cast in a form that holds for both $\epsilon < 0$ and $\epsilon \geq 0$. Thus the $|\cdots|$ notation is required because $W^\pm$ is complex for $\epsilon > 0$; on the other hand $D = 1$ in this range. Similarly i/k appears in place of ν. The final expressions in Eq. (3.12) follow from the relations among f, g, and f^+ implicit in Table IC. Note how the imaginary unit i, which occurs in the positive energy expression, extrapolates for $\epsilon < 0$ into an oscillating function having poles at the roots of Eq. (2.67). The poles of the complete expression (3.12) thus coincide with the zeros of $W_{\epsilon l}^+$ at $\epsilon = \epsilon_n$, as expected. To compare the first term of Eq. (3.11) with the second one, we express its normalized wave

functions f_n in terms of the standard $f_{\epsilon_n} \equiv f(\epsilon_n, l, r)$ and of the normalization integrals (2.70), where we set $M = f_{\epsilon l}$, obtaining

$$\sum_n^{\epsilon_n<0} f_n(r)\frac{1}{\epsilon-\epsilon_n} f_n(r') = \sum_n^{\epsilon_n<0} f_{\epsilon_n}(r)\frac{1}{\epsilon-\epsilon_n} f_{\epsilon_n}(r')\,\pi\left(\frac{d}{d\epsilon}(\beta_\lambda+\delta_{\epsilon l})\right)^{-1}_{\epsilon=\epsilon_n}, \tag{3.13a}$$

$$\sum_n^{\epsilon_n>0} f_n(r)\frac{1}{\epsilon-\epsilon_n} f_n(r') = \left(\int_0^\infty d\epsilon' f_{\epsilon'}(r)\frac{1}{\epsilon-\epsilon'} f_{\epsilon'}(r')\right)_{\mathrm{Im}k'=0^+}. \tag{3.13b}$$

Here we have had to specify the sign of $\mathrm{Im}k'$, because the coefficient k' in the density of states has a branch cut along the real axis of integration; the upper edge of this cut has been specified in keeping with the connection $k \to i/\nu$ across the branch point $\epsilon = 0$ adopted in Sec. II. To verify that the singularities at $\epsilon \sim \epsilon_n < 0$ in the separate terms of Eq. (3.11) cancel exactly, consider that by Eq. (3.12),

$$\pi\frac{W_{\epsilon l}(g,f^+)}{W_{\epsilon l}(f,f^+)} \xrightarrow[\epsilon\to\epsilon_n]{} -\frac{1}{\epsilon-\epsilon_n}\,\pi\left(\frac{d}{d\epsilon}(\beta_\lambda+\delta_{\epsilon l})\right)^{-1}_{\epsilon_n} \tag{3.14}$$

which is indeed the negative of the coefficient multiplying $f_{\epsilon_n}(r) f_{\epsilon_n}(r')$ in the negative energy sum of Eq. (3.13a). For $\epsilon > 0$, on the other hand we first write $f_\epsilon(r) f_\epsilon(r')$ in terms of the analytic product as

$$f_\epsilon(r) f_\epsilon(r') = f^0_\epsilon(r) f^0_\epsilon(r')(2k/\pi W^-_{\epsilon l} W^+_{\epsilon l}).$$

This gives the useful identity

$$\frac{2ik}{W^-_{\epsilon l} W^+_{\epsilon l}} f^0_\epsilon(r) f^0_\epsilon(r') = -\lim_{\delta\to 0}\left(\int_{\epsilon-\delta}^{\epsilon+\delta} d\epsilon' \frac{2k'}{\pi W^-_{\epsilon' l} W^+_{\epsilon' l}} \times \frac{f^0_{\epsilon'}(r) f^0_{\epsilon'}(r')}{\epsilon-\epsilon'}\right)_{\mathrm{Im}k'=0^+}, \tag{3.15}$$

whereby the addition of the second term of (3.11) reduces the integral in (3.13b) to the familiar principal part integration to be denoted by P. The expression of $G^{(s)}_\epsilon$, fully factorized in the variables r and r', thus takes the final form

$$G^{(s)}_\epsilon(r,r') = \sum_n^{\epsilon_n<0} f_{\epsilon_n}(r)\frac{1}{\epsilon-\epsilon_n} f_{\epsilon_n}(r') \times \pi\left(\frac{d}{d\epsilon}(\beta_\lambda+\delta_{\epsilon l})\right)^{-1}_{\epsilon_n} - [f_\epsilon(r) f_\epsilon(r')\cot(\beta_\lambda+\delta_{\epsilon l})]_{\epsilon<0} + P\int_0^\infty d\epsilon' f_{\epsilon'}(r)\frac{1}{\epsilon-\epsilon'} f_{\epsilon'}(r'). \tag{3.16}$$

This differs from the standard expressions of Ref. 6 only by the explicit introduction of its middle term which has the same effect at $\epsilon < 0$ as the principal part symbol P at $\epsilon > 0$. Indeed the sum of the first two terms could be approximated by a principal part integral when ϵ approaches a condensation point.

The nonanalyticities of the Green's function $G^{(s)}_\epsilon$ should be treated explicitly for long-range dipole and zero fields owing to the behavior of the normalization coefficients A and B. Firstly, each function f_ϵ in Eq. (3.16) should be expressed as $A^{1/2} f^0_\epsilon$ (or $B^{1/2} f^0_{\epsilon'}$ for $\epsilon' > 0$) whereby a coefficient A or B emerges in each term of $G^{(s)}_\epsilon$. Secondly, comparison of Eqs. (3.6) and (3.6′) with Eq. (2.83) shows that

$$G^{(s0)}_\epsilon(r,r') = G^{(s)}_\epsilon(r,r') - \pi\vartheta(\nu,l) f^0_\epsilon(r) f^0_\epsilon(r'). \tag{3.17}$$

IV. SOLUTION OF THE SCHRÖDINGER EQUATION

In this final section we construct eigenfunctions of $H^{(N)}$, in the close-coupling form (1.4) and for positions of the Nth particle outside the core, $r > r_0$, by determining the appropriate form of the functions $M_i(r)$. These functions will be expressed in terms of standard pairs of solutions of the radial Eq. (2.1) and of a "smooth" reaction matrix $K^{(s)}$. Smoothness is achieved by determining $K^{(s)}$ through an equation that makes explicit use of the smooth Green's function $G^{(s)}$ of Sec. III but conforms to standard practice in other respects. Imposing boundedness conditions at $r = \infty$ on the $M_i(r)$ for closed channels (i.e., for channels with $\epsilon_i < 0$) will then yield the discrete spectra of bound and autoionizing levels in a form that constitutes the desired generalization of the MQDT.

A. Coupled equations for the $M_i(r)$

Consider the Schrödinger equation $(H^{(N)} - E)\sum_i \{M_i(r)\Phi_i(\omega)\} = 0$ and its projections on the various core functions $\Phi_j(\omega)$. Owing to the symmetry of the $\{M_i\Phi_i\}$, it is sufficient to specify the core particle coordinates in Φ_j as $(\vec{r}_1, \ldots, \vec{r}_{N-1})$ and to perform the projection by integrating over all these coordinates. The projection takes into account that each Φ_i obeys Eq. (1.3); furthermore

each $M_i(r)$ may be regarded as orthogonal to all single-electron orbitals in Φ_i, since any nonorthogonal components of M_i would cancel in the antisymmetrized product $\{M_i\Phi_i\}$. Thus we have

$$\sqrt{N}\int\prod_{\alpha=1}^{N-1} d\vec{r}_\alpha\,\Phi_j(\omega)[H^{(N)}-E]\sum_i\{M_i(r)\Phi_i(\omega)\}$$

$$=[h(l_j,r_N)-\epsilon_j]M_j(r_N)$$

$$+\sqrt{N}\int\prod_{\alpha=1}^{N-1} d\vec{r}_\alpha\,\Phi_j(\omega)\left(\sum_{\alpha=1}^{N-1}\frac{e^2}{r_{\alpha N}}-v^{\mathrm{scr}}(r_N)\right)$$

$$\times\sum_i\{M_i(r)\Phi_i(\omega)\}=0\,, \qquad (4.1)$$

where $\epsilon_j=E-E_j$ and where the factor $\sqrt{N}$ cancels the corresponding factor in the expansion of the determinants in $\{M_i\Phi_i\}$. The term with $v^{\mathrm{scr}}(r_N)$ in (4.1) yields only $v^{\mathrm{scr}}(r_N)M_i(r_N)\delta_{ij}$ owing to orthogonalities. Further, since the $N-1$ terms of the $\sum_\alpha$ yield equal contributions, we may deal explicitly with $\alpha=N-1$ only. Orthogonalities permit us then to replace the antisymmetrization $\{M_i\Phi_i\}$ by a permutation operator $P_{N,N-1}$. Thereby Eq. (4.1) reduces to

$$[h(l_j,r_N)-\epsilon_j]M_j(r_N)+\sum_i(\Phi_j|V|\Phi_i)M_i(r_N)=0\,, \qquad (4.2)$$

where

$$V(r_N,r_{N-1})=(N-1)(1-P_{N,N-1})e^2/r_{N,N-1}-v^{\mathrm{scr}}(r_N)\,. \qquad (4.3)$$

and the matrix symbol $(\Phi_j|V|\Phi_i)$ involves integration over $\vec{r}_1,\ldots,\vec{r}_{N-1}$. This matrix symbol is still a function of r_N which operates on $M_i(r_N)$; indeed it operates as a nonlocal exchange potential because V includes the operator $P_{N,N-1}$. To stress this operator property we introduce the notation

$$\bar{V}_{ji}(r_N)=(\Phi_j|V|\Phi_i)\,. \qquad (4.3')$$

whereby Eq. (4.2) takes the form

$$[h(l_j,r)-\epsilon_j]M_j(r)+\sum_i\bar{V}_{ji}(r)M_i(r)=0 \qquad (4.2')$$

of a coupled system to be solved for the $M_i(r)$. Recall that $\bar{V}_{ji}(r)$ *vanishes* for $r>r_0$, as per stipulation (b) of Sec. I; all integrations will be limited to $r<r_0$ whenever $\bar{V}_{ji}$ is a factor in the integrand.

In accordance with Sec. III, this system will be solved formally in terms of the smooth Green's function $G^{(s)}_{\epsilon_j l_j}$ of the operator $h(l_j,r)-\epsilon_j$, as though the last term of (4.2′) represented an inhomogeneity. That is, we regard Eq. (4.2′) as a multichannel analog of (3.1) and write the analog of Eq. (3.3) as

$$M_j(r)=f(\epsilon_j,l_j,r)C_j+\int_0^{r_0}dr'\,G^{(s)}_{\epsilon_j l_j}(r,r')$$

$$\times\sum_i\bar{V}_{ji}(r')M_i(r')\,. \qquad (4.4)$$

Here $f(\epsilon_j,l_j,r)$ is the solution of $[h(r)-\epsilon_j]u(r)=0$ regular at $r=0$ and normalized per unit energy according to Eq. (2.55); the coefficient C_j allows adjusting of the relative amplitudes of the coupled radial functions M_i as required to solve the system (4.4). As we shall see, the coefficients C_j must eventually be determined so as to enforce boundedness of the $M_j(r)$ at $r=\infty$; at this point the $f(\epsilon_j,l_j,r)$ themselves generally diverge at $r=\infty$ for all closed channels, i.e., when $\epsilon_j<0$. To verify that $M_j(r)$, as given by Eq. (4.4), satisfies (4.2′), note that applications of $h(l_j,r)-\epsilon_j$ yields no contribution from the first term on the right-hand side of (4.4) and reduces its second term to $-\sum_i\bar{V}_{ji}(r)M_i(r)$.

B. Coupled equations for the smooth reaction operator $K^{(s)}$

The representation of $M_j(r)$ by Eq. (4.4), in terms of a Green's function, follows the Lippmann-Schwinger approach to scattering theory. Continuing along this approach, notice that Eq. (4.4) constitutes a linear system with inhomogeneous terms proportional to the coefficients C_j. Hence each $M_j(r)$ must be a linear function of the set $\{C_1,\ldots,C_j,\ldots\}$. This functional dependence is made explicit by replacing iteratively the M_i on the right-hand side of Eq. (4.4); the result is represented by a Born series of operators

$$M_j(r)=f_j(r)C_j+\sum_i\int_0^{r_0}dr'\left(G^{(s)}_j(r,r')\bar{V}_{ji}(r')\right.$$

$$\left.+\sum_k\int_0^{r_0}dr''\,G^{(s)}_j(r,r'')\bar{V}^{(s)}_{jk}(r'')G^{(s)}_k(r'',r')\bar{V}_{ki}(r')+\cdots\right)f_i(r')C_i\,, \qquad (4.5)$$

where we have replaced the subscripts $\epsilon_j l_j$ by the channel index j throughout. The sum of the series in large parentheses is often written as $G_j^{(s)}(r,r')\bar{K}_{ji}^{(s)}(r')$, where $\bar{K}_{ji}^{(s)}(r')$ is an element of a matrix of reaction operators that can also be defined directly through the operator equation

$$\sum_i \bar{V}_{ji}(r)M_i(r) = \sum_i \bar{K}_{ji}^{(s)}(r) f(\epsilon_i, l_i, r) C_i . \qquad (4.5')$$

Note that the $\bar{K}_{ji}^{(s)}(r)$ are *nonlocal* operators, like the $\bar{V}_{ji}(r)$, and *vanish* likewise for $r > r_0$. They are functions of the total energy E, on which they depend implicitly—through the channel energies $\epsilon_j = E - E_j$.

Elimination of the C_i. Equation (4.5′) represents the unknown solutions $M_i(r)$ in terms of the reaction operators $\bar{K}_{ji}^{(s)}(r)$ and of the coefficients C_i. Since these coefficients serve only to specify a particular solution in terms of boundary conditions, we derive firstly from Eq. (4.5) an equation for the $\bar{K}_{ji}^{(s)}(r)$ which is independent of C_i but incorporates the whole collision dynamics. To this end the following operations are performed: (i) multiply Eq. (4.5) by $\Phi_j(\omega)$ and sum over j; (ii) apply to the result the operator $V(r, r_{N-1})$ defined by Eq. (4.3); (iii) multiply again by $f(\tilde{\epsilon}_k, l_k, r)\Phi_k(\omega)$ and integrate over both r and ω. The integration turns the left-hand side of (4.5) into a matrix element indicated alternatively by

$$\int_0^\infty dr f(\tilde{\epsilon}_k, l_k, r) \sum_j \bar{V}_{kj}(r) M_j(r)$$

$$= \sum_j (f_{\tilde{\epsilon}_k} | \bar{V}_{kj} | M_j) \qquad (4.6)$$

$$= \sum_i (f_{\tilde{\epsilon}_k} | \bar{K}_{ki}^{(s)} | f_{\epsilon_i}) C_i . \qquad (4.7)$$

The tilde on $\tilde{\epsilon}_k$ specifies that this energy need not coincide with $\epsilon_k = E - E_k$. Insofar as $\tilde{\epsilon}_k$ may coincide with the eigenvalues of $h(l_k, r)$, the functions $f(\tilde{\epsilon}_k, l\ , r)\Phi_k(\omega)$ form a complete set. Accordingly the projection of Eq. (4.5) over all elements of this set—i.e., operation (iii)—preserves all the information of the initial equation. Equation (4.5) for $M_j(r)$ is thus transformed into

$$\sum_i (f_{\tilde{\epsilon}_k} | \bar{K}_{ki}^{(s)} | f_{\epsilon_i}) C_i - \sum_i \Bigg((f_{\tilde{\epsilon}_k} | \bar{V}_{ki} | f_{\epsilon_i}) - \sum_j \int_0^{r_0} dr \int_0^{r_0} dr' f(\tilde{\epsilon}_k, l_k, r) \bar{V}_{kj}(r)$$

$$\times G_{\epsilon_j l_j}^{(s)}(r, r') \bar{K}_{ji}(r') f(\epsilon_i, l_i, r') \Bigg) C_i = 0 . \qquad (4.8)$$

The structure of this new equation permits us now to leave aside the determination of the C_i by requiring instead that the coefficient of each C_i vanish, namely, that the operators $\bar{K}_{ji}^{(s)}(r)$ satisfy the system

$$(f_{\tilde{\epsilon}_k} | \bar{K}_{ki}^{(s)} | f_{\epsilon_i}) = (f_{\tilde{\epsilon}_k} | \bar{V}_{ki} | f_{\epsilon_i}) + \sum_j \int_0^{r_0} dr \int_0^{r_0} dr' f(\tilde{\epsilon}_k, l_k, r) \bar{V}_{kj}(r) G_{\epsilon_j l_j}^{(s)}(r, r')\, \bar{K}_{ji}^{(s)}(r') f(\epsilon_i, l_i, r') . \qquad (4.9)$$

Configuration mixing representation. This equation is still complicated by double integration over the two variables r and r', which remain entangled even when we factorize $G^{(s)}$ in the form $\pi g(r_>) f(r_<)$ since $r_> = \max(r, r')$. However, we can disentangle r and r' by substituting the eigenfunction expansion of $G^{(s)}$, (3.16), at the price of introducing a summation over all virtual levels of energy ϵ_{jn}. Separate integrals over r and r' are then represented as matrix elements and Eq. (4.9) takes the form

$$(f_{\tilde{\epsilon}_k} | \bar{K}_{ki}^{(s)} | f_{\epsilon_i}) = (f_{\tilde{\epsilon}_k} | \bar{V}_{ki} | f_{\epsilon_i})$$

$$+ \sum_j \Bigg[\sum_n^{\epsilon_{jn} < 0} (f_{\tilde{\epsilon}_k} | \bar{V}_{kj} | f_{\epsilon_{jn}}) \frac{1}{\epsilon_j - \epsilon_{jn}} (f_{\epsilon_{jn}} | \bar{K}_{ji}^{(s)} | f_{\epsilon_i}) \pi \Big(\frac{d}{d\epsilon} (\beta_{\lambda_j} + \delta_{\epsilon_j l_j}) \Big)^{-1}_{\epsilon_{jn}}$$

$$- \operatorname{cotan}(\beta_{\lambda_j} + \delta_{\epsilon_j l_j}) (f_{\tilde{\epsilon}_k} | \bar{V}_{kj} | f_{\epsilon_j}) (f_{\epsilon_j} | \bar{K}_{ji}^{(s)} | f_{\epsilon_i}) \big|_{\epsilon_j < 0}$$

$$+ P \int_0^\infty d\epsilon'_j (f_{\tilde{\epsilon}_k} | \bar{V}_{kj} | f_{\epsilon'_j}) \frac{1}{\epsilon_j - \epsilon'_j} (f_{\epsilon'_j} | \bar{K}_{ji}^{(s)} | f_{\epsilon_i}) \Bigg] . \qquad (4.10)$$

The first two terms in the large square brackets of this equation represent the extension to negative energies $\epsilon_j<0$ of the principal part integration over $\epsilon_j'>0$.

A final change to more standard notation can now be introduced in Eq. (4.10). The symbol $\overline{V}_{ji}(r)$ introduced in Eq. (4.3′) to indicate a one-particle operator was obtained by integration over several variables. Having now expressed Eq. (4.10) in terms of matrix elements of $\overline{V}_{ji}$ we can condense all integrations in the form of a matrix element of the two-particle operator $V(r_N, r_{N-1})$ over multielectron wave functions. Similarly the matrix elements of $\overline{K}^{(s)}_{ji}$ can be expressed in terms of a multielectron operator $K^{(s)}$. Thus we rewrite Eq. (4.10) more explicitly as

$$
\begin{aligned}
(f_{\tilde{\epsilon}_k}\Phi_k|K^{(s)}|f_{\epsilon_i}\Phi_i) = {} & (f_{\tilde{\epsilon}_k}\Phi_k|V|f_{\epsilon_i}\Phi_i) \\
& + \sum_j{}' \Bigg[\sum_n^{\epsilon_{jn}<0} (f_{\tilde{\epsilon}_k}\Phi_k|V|f_{\epsilon_{jn}}\Phi_j) \frac{1}{\epsilon_j-\epsilon_{jn}} (f_{\epsilon_{jn}}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i) \pi \left(\frac{d}{d\epsilon} (\beta_{\lambda_j}+\delta_{\epsilon_j l_j}) \right)^{-1}_{\epsilon_{jn}} \\
& - (f_{\tilde{\epsilon}_k}\Phi_k|V|f_{\epsilon_j}\Phi_j) \cot(\beta_{\lambda_j}+\delta_{\epsilon_j l_j}) (f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)\big|_{\epsilon_j<0} \\
& + P\int_0^\infty d\epsilon_j' (f_{\tilde{\epsilon}_k}\Phi_k|V|f_{\epsilon_j'}\Phi_j) \frac{1}{\epsilon_j-\epsilon_j'} (f_{\epsilon_j'}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i) \Bigg] .
\end{aligned}
\tag{4.11}
$$

This equation is equivalent to Eq. (20) of Ref. 4 which had been developed by more heuristic considerations. As indicated in Ref. 4, integral equations of this type for a reaction matrix have been reduced to an algebraic system and solved numerically. The introduction of the concept of a smooth reaction matrix here and in Ref. 4, with insertion of the middle term in the large square brackets for $\epsilon_j<0$, extends the practical calculation of K matrices to ranges of E where some or even all of the channels are closed. Moreover the explicit use of energy normalized base functions throughout Eq. (4.11) should expedite the numerical evaluation of the infinite $\sum_n$ and the calculation of the $K^{(s)}$ matrix on a mesh of channel energies which may be rather coarse. The prime has been inserted on the symbol $\sum_j'$ in Eq. (4.11) to implement the stipulation, in item (ii) at the end of Sec. I, that only a finite number of channels need be considered in practice because additional channels would not contribute appreciably.

Note in Eq. (4.11) the occurrence of matrix elements $(f_{\tilde{\epsilon}_k}\Phi_k|K^{(s)}|f_{\epsilon_i}\Phi_i)$ that are not diagonal in the energy label, since the values of $\tilde{\epsilon}_k$ are unrestricted whereas ϵ_i has the fixed value $E-E_i$. The eigenvalues ϵ_{jn} and ϵ_j' of $h(l_j,r)$ in the sum and integral on the right-hand side of the equation also need not coincide with the energy-shell value $\epsilon_j=E-E_j$. That is, Eq. (4.11) represents a system of equations linking all the elements of one column of the square matrix $(f_{\tilde{\epsilon}_k}\Phi_k|K^{(s)}|f_{\tilde{\epsilon}_i}\Phi_i)$. [The matrix elements with $\tilde{\epsilon}_i$ values off the energy shell would have to be obtained from separate equations adjoint to (4.11).] Introduction of off-shell elements of $K^{(s)}$ is a consequence of using the eigenfunction expansion of the Green's function in contrast to its form $G^{(s)}(r,r')$ in Eq. (4.9), even though our applications will require only the use of on-the-shell elements of $K^{(s)}$. Recall also that we introduced initially values of $\tilde{\epsilon}_k\neq\epsilon_k$ to ensure completeness of the set $(f_{\tilde{\epsilon}_k}\Phi_k|$. In fact Eq. (4.11) also involves a term with an on-shell value $\epsilon_j<0$ which need not be an eigenvalue of $h(l_j,r)$; this further extension of the range of $\tilde{\epsilon}_j$ accords with the QDT's removal of the boundedness condition which relaxes the restriction on the eigenvalue spectrum.

Treatment of nonanalyticity. As in the earlier sections, we shall now consider and separate out the influence upon Eq. (4.11) of the nonanalyticity of the density-of-states coefficients A and B, in the energy normalized functions f, and of the factor $\cot(\beta_{\lambda_j}+\delta_{\epsilon_j l_j})$. Recall that the nonanalyticities reflect the behavior of wave functions at very large radial distances and for small values of the channel energies ϵ_j, while the reaction operator $K^{(s)}$ represents the effect of interactions at short ranges, $r<r_0$. Accordingly it should be possible to remove any appreciable influence of the nonanalyticity from our calculation.

As in Secs. II and III we proceed by two steps. Firstly we transform the matrices of V and $K^{(s)}$ to the representation of analytical functions $|f^0_{\epsilon_i}\Phi_i)$ by separating out the normalization factors $A^{1/2}(\nu_i,l_i)$ or $B^{1/2}(\epsilon_i,l_i)$ according to Eq. (2.83). The factors arising from $(f_{\tilde{\epsilon}_k}\Phi_k|$ and from $|f_{\epsilon_i}\Phi_i)$ appear equally in all terms of Eq. (4.11) and accordingly factor out of this equation. On the other hand a factor $A(\nu_j,l_j)$ or $B(\epsilon_j',l_j)$ emerges in each term in the large square brackets of Eq. (4.11) and

cannot be eliminated because it represents the spectral density of virtual states $|f^0_{\epsilon_j}\Phi_j)$ which are being summed over in the process of configuration mixing. However, the very process of summation averages over the nonanalytic singularities of the factors A or B, thus reducing their effect.

The second and more fundamental step for removing nonanalyticities consists of deriving an alternative K-matrix equation using the analytic Green's function $G^{(s0)}$ instead of $G^{(s)}$ to determine a reaction matrix $K^{(s0)}$. The derivation differs from the development of this section only in the following respects. Analytic base functions $\{f^0,g^0\}$ replace $\{f,g\}$ throughout and density of state factors $A(\nu_j,l_j)$ or $B(\epsilon_j,l_j)$ appear in the large square brackets of Eq. (4.11). The substantive difference lies, however, in the occurrence of the additional second term in the eigenfunction expansion of $G^{(s0)}$, Eq. (3.17). There results an *additional term* in the equation corresponding to (4.11), namely,

$$\sum_j{}' (f^0_{\epsilon_k}\Phi_k|V|f^0_{\epsilon_j}\Phi_j)[-\pi\mathcal{G}(\nu_j,l_j)] \times (f^0_{\epsilon_j}\Phi_j|K^{(s0)}|f^0_{\epsilon_i}\Phi_i). \quad (4.12)$$

This term is designed to cancel the nonanalyticities remaining in the $\sum_j$ terms, performing the same role as the terms with a factor $\mathcal{G}$ in Eqs. (2.45) and (3.17). The matrix $K^{(s0)}$ constructed by this procedure need not be itself analytic (since, for example, tangents of phase shifts may diverge) but the unnormalized solutions $M_j(r)$ constructed with $K^{(s0)}$, (f^0,g^0), and the corresponding coefficients C_j must indeed be analytic functions of ϵ_j.

In the case of a long-range Coulomb field, the function $\mathcal{G}$ is smooth as $\epsilon\sim 0$, even though nonanalytic. One may then calculate $K^{(s)}$ directly, instead of $K^{(s0)}$. (In Ref. 2, a matrix $IJ^{-1}\equiv K^{(s0)}$ is treated nevertheless as fundamental.) For zero and dipole fields, on the other hand, $K^{(s0)}$ is smooth at threshold but $K^{(s)}$ is not owing to branch points of $\mathcal{G}$, A, and B. One should then calculate $K^{(s0)}$ first and then generate $K^{(s)}$ from it. The connection between these two matrices is illustrated by rewriting their respective equations [Eq. (4.11) and its analog] in a compact operator notation, namely,

$$K^{(s)} = V + VG^{(s)}K^{(s)}, \quad (4.13)$$

$$K^{(s0)} = V + VG^{(s)}K^{(s0)} + V(-\pi\mathcal{G})K^{(s0)}. \quad (4.14)$$

Multiplication of Eq. (4.14) by the operator $(1-\pi\mathcal{G}K^{(s0)})^{-1}$, from its right, shows now that the operator $K^{(s0)}(1-\pi\mathcal{G}K^{(s0)})^{-1}$ obeys the same linear inhomogeneous Eq. (4.13) as $K^{(s)}$ whereby

$$K^{(s)} = K^{(s0)}(1-\pi\mathcal{G}K^{(s0)})^{-1}. \quad (4.15)$$

Numerical calculation of $K^{(s)}$ from this equation should start from the matrix form of the operator

$$(1-\pi\mathcal{G}K^{(s0)})_{ji} = \delta_{ji} - \pi\mathcal{G}(\nu_j,l_j)(f^0_{\epsilon_j}\Phi_j|K^{(s0)}|f^0_{\epsilon_i}\Phi_i). \quad (4.16)$$

Inversion of this matrix presents no problem if the set of channels j is truncated as indicated by the $\sum_j'$ in Eq. (4.11). The $K^{(s)}$ matrix obtained from (4.15) should eventually be cast in the energy-normalized representation, yielding

$$(f_{\epsilon_k}\Phi_k|K^{(s)}|f_{\epsilon_i}\Phi_i) = A^{1/2}(\nu_k,l_k) \times (f^0_{\epsilon_k}\Phi_k|K^{(s0)}(1-\pi\mathcal{G}K^{(s0)})^{-1}|f^0_{\epsilon_i}\Phi_i)\ A^{1/2}(\nu_i,l_i), \quad (4.17)$$

where $A(\nu,l)$ is replaced by $B(\epsilon,l)$, as usual, for $\epsilon>0$.

C. Boundedness at $r=\infty$ and the coefficients C_i

There remains now to reinstate the condition that the radial functions $M_j(r)$ vanish at $r=\infty$ for all closed channels, with $\epsilon_j<0$, and to examine the consequences of this condition for the coefficients C_i. This amounts to translating Sec. III D of Ref. 4 into the present notation. To this end we return to the expression (4.4) of $M_j(r)$, setting $r>r_0$. Since $r'<r_0$, Eq. (3.17) becomes here $G^{(s)}_{\epsilon_j l_j} = \pi g(\epsilon_j,l_j,r)f(\epsilon_j,l_j,r')$, and we obtain for $r>r_0$, also using (4.5′),

$$M_j(r) = f(\epsilon_j,l_j,r)C_j + g(\epsilon_j,l_j,r)\sum_i{}'\pi(f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)C_i. \quad (4.18)$$

This is a multichannel analog of Eq. (3.18), with the reaction matrix *on the energy shell* and in energy-normalized form, whereas off-shell matrix elements would result from use of the eigenfunction expansion of $G^{(s)}$. Entering then the expression (4.18) of M_j into the boundary condition (2.13) gives our basic result, analogous to (3.9), and equivalent to Eq. (21) of Ref. 4,

$$W_{\epsilon_j}(f^+,M_j) = \sum_i{}'\{W_{\epsilon_j}(f^+,f)\delta_{ji} + W_{\epsilon_j}(f^+,g)\pi(f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)\}C_i = 0, \quad \epsilon_j<0. \quad (4.19)$$

The Wronskians which appear in this expression reduce to trigonometric functions of the energy since the base pair $\{f_{\epsilon j}, g_{\epsilon j}\}$ is related to the base pair $(\nu/\pi)^{1/2}\{D^{-1}f^-, Df^+\}$ by an orthogonal transformation. By inspecting the large-r expression Eq. (2.66) for $f^{\rm opt}$, and by recalling the connection between f, g, and $f^{\rm opt}$ discussed near the end of Sec. II F, we obtain for $\epsilon_j < 0$,

$$W_{\epsilon_j}(f^+, f) = (4/\pi\nu_j)^{1/2}[D(\nu_j, \lambda_j)]^{-1} \times \sin(\beta_{\lambda_j} + \delta_{\epsilon_j l_j}) = D_j^{-2} W_{\epsilon_j}(f^-, g),$$
$$W_{\epsilon_j}(f^+, g) = -(4/\pi\nu_j)^{1/2}[D(\nu_j, \lambda_j)]^{-1} \times \cos(\beta_{\lambda_j} + \delta_{\epsilon_j l_j}) = -D_j^{-2} W_{\epsilon_j}(f^-, f). \quad (4.20)$$

These expressions reduce Eq. (4.19) to the form

$$\sum_i{}' [\sin(\beta_{\lambda_j} + \delta_{\epsilon_j l_j})\delta_{ij} - \cos(\beta_{\lambda_j} + \delta_{\epsilon_j l_j})\pi(f_{\epsilon_j}\Phi_j | K^{(s)} | f_{\epsilon_i}\Phi_i)] C_i = 0, \quad \epsilon_j < 0. \quad (4.21)$$

The implications of Eq. (4.19) or (4.21) are only summarized here as they have been discussed in Ref. 4 and many times elsewhere in equivalent contexts. When all channels are closed, the matrix of the system (4.19) is square and solutions $\{C_i\}$ exist only for the discrete energy eigenvalues at which the determinant of this matrix vanishes. In the general case only some of the channels of the truncated set $\{M_j\}$ are closed, say, those with $1 \leq j \leq n$. The n equations (4.19) permit the elimination of n among the C_i, typically of all the C_j with $j \leq n$. The remaining C_i are to be determined by the boundary conditions at $r = \infty$, e.g., of the "outgoing-wave" or standing-wave type. However, the existence of closed channels manifests itself usually through resonances, i.e., through rapid variations of the C_i as functions of energy near the discrete levels at which a minor determinant of order $\leq n$ of the matrix in Eq. (4.21) vanishes or passes through a sharp minimum. In simple examples the off-diagonal elements of the $K^{(s)}$ matrix are small and the resonances occur near the zeros of diagonal elements of the matrix in Eq. (4.21).

The representation (4.18) of the radial functions M_j at $r > r_0$, in terms of the base sets $\{f_{\epsilon_j}, g_{\epsilon_j}\}$, of the $K^{(s)}$ matrix and of the C_i, permits also a corresponding representation of the normalization integrals developed in Sec. II D. For discrete levels of a multichannel system Eqs. (2.50) and (2.53) lead to

$$\int d\tau\, |\Psi_n|^2 = \sum_j{}' \tfrac{1}{4}\nu_{jn} W_{\epsilon_{jn}}(f^-, M_j) \times [dW_{\epsilon_j}(f^+, M_j)/d\epsilon_j]_{\epsilon_{jn}}, \quad (4.22)$$

where the energies $\epsilon_{jn} = E_n - E_j$ are determined by the roots E_n of the determinant of the square matrix in Eq. (4.21). The Wronskians in this equation are reduced by Eq. (4.18) to linear combinations of the explicit expressions (4.20). The coefficients C_i in the expansion of M_j are the eigenvectors of the matrix in Eq. (4.21). For states of the continuous spectrum the analog of Eq. (4.22) is

$$\int d\tau\, \Psi_{E'}\Psi_E = \sum_{j}^{\epsilon_j > 0}{}' (\pi/2k_j) W_{\epsilon_j}(f^-, M_j) \times W_{\epsilon_j}(f^+, M_j)\delta(E - E'). \quad (4.23)$$

Substitution of Eq. (4.18) reduces the Wronskians to their basic forms analogous to (4.20), namely,

$$W_{\epsilon_j}(f^\pm, f) = (2k_j/\pi)^{1/2} \exp[\mp i(\eta_{\lambda_j} + \delta_{\epsilon_j l_j})],$$
$$W_{\epsilon_j}(f^\pm, g) = (2k_j/\pi)^{1/2} \exp[\mp i(\eta_{\lambda_j} + \delta_{\epsilon_j l_j} - \pi/2)]. \quad (4.24)$$

Equation (4.23) becomes then an algebraic expression quadratic in the Wronskians (4.24), quadratic in matrix elements of $K^{(s)}$, and quadratic in the coefficients C_i. The C_i are determined, for any continuum state of interest, by specifying its boundary conditions at $r = \infty$. Their values vary rapidly at the resonant energies of the closed channels.

The complete expressions of the normalization integrals thus obtained remain sufficiently complicated to prevent analysis of their implication by simple inspection. The same holds in general for the closed-channel equation (4.21). Some progress is achieved in these respects by diagonalizing the matrix $K^{(s)}$ as we shall now discuss.

Eigenphase shifts and the MQDT. The quantum-defect treatments are characterized by the casting of Wronskians in the form of trigonometric functions, as in Sec. II C and in Eqs. (4.20)–(4.24). This procedure extends to multichannel treatments by expressing the information embodied in the $K^{(s)}$ matrix in terms of phase shifts. These are not the phase shifts of ordinary scattering theory but relate instead the phase of the radial functions $M_j(r)$ to those of the base set functions $f_{\epsilon_j}(r)$. The latter functions already involve phase shift contributed by the optical potentials. We aim here at incorporating the phase shifts contributed by $K^{(s)}$ together with those of the $f_{\epsilon_j}(r)$ into a trigonometric form of the boundedness Eq. (4.21) and of the normalization integral Eq. (4.22).

In single-channel problems the reaction matrix $K^{(s)}$ reduces, on the energy shell, to a single element given in terms of a phase shift $-\pi^{-1}\tan\delta$. In multichannel problems the same relation holds between the eigenvalues of the $K^{(s)}$ matrix on the energy shell and a corresponding set of eigenphase shifts. To extract these data one must diagonalize $K^{(s)}$ by solving the algebraic system

$$\sum_i{}' \pi(f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)U^{(s)}_{i\alpha} = -U^{(s)}_{j\alpha}\tan\delta^{(s)}_\alpha , \tag{4.25}$$

with eigenvectors $U^{(s)}_{i\alpha}$ normalized to form an orthogonal matrix. Expressing $\boldsymbol{K}^{(s)}$ in Eq. (4.21) in terms of $\delta^{(s)}_\alpha$ and $U^{(s)}_{i\alpha}$ then yields the condensed form of the boundedness condition

$$\sum_\alpha U^{(s)}_{i\alpha}\sin(\beta_{\lambda_i}+\delta_{\epsilon_i l_i}+\delta^{(s)}_\alpha)A_\alpha = 0, \tag{4.26}$$

where the set of coefficients

$$A_\alpha = \sum_j U^{(s)\dagger}_{\alpha j} C_j/\cos\delta^{(s)}_\alpha \tag{4.27}$$

replace the set $\{C_i\}$. Notice how the matrix $U^{(s)}_{i\alpha}\sin(\beta_{\lambda_i}+\delta_{\epsilon_i l_i}+\delta^{(s)}_\alpha)$ combines the contributions of parameters pertaining to *different* base sets. Inspection of the structure of this matrix, and of the energy dependence of its parameters, may readily reveal the occurrence of roots of its minor determinants.

In typical applications of MQDT the parameter β_{λ_i} varies rapidly with energy, when $\epsilon_i \sim 0$. In contrast the eigenphase shifts $\delta^{(s)}_\alpha$ vary slowly insofar as the matrix $(f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)$ represents interactions within the core which are unrelated to the threshold energies of the various channels. Rapid variations of $\delta^{(s)}_\alpha$ and of the eigenvectors $U^{(s)}_{i\alpha}$ may, however, result from the nonanalyticity of $K^{(s)}$ at the energy thresholds. In this event the threshold influence should be removed prior to diagonalization. Firstly the matrix $K^{(s)}$ should be transformed to the analytic frame $|f^0_{\epsilon_i}\Phi_i)$ prior to diagonalization, by factoring out the channel normalization factor $A^{1/2}(\nu_i, l_i)$ (or $B^{1/2}$) in each row and column of the initial $(f_{\epsilon_j}\Phi_j|K^{(s)}|f_{\epsilon_i}\Phi_i)$. More basically one should instead diagonalize the matrix of $K^{(s0)}$, obtaining eigenphase shifts $\delta^{(s0)}_\alpha$ and eigenvectors $U^{(s0)}_{i\alpha}$ that should vary slowly with energy. The expression of the $K^{(s)}$ matrix to be inserted into Eq. (4.21) would then be derived from the relationships (4.16) or (4.17) between $K^{(s)}$ and $K^{(s0)}$ or from their simpler form, in terms of reciprocal operators, $K^{(s)-1} = K^{(s0)-1} + \pi\mathcal{G}$. The occurrence of the nonunitary transformation factors $A^{1/2}$ in (4.17) prevents now the reduction of Eq. (4.21) to its compact form (4.26).

The analog of (4.26) in terms of $\delta^{(s0)}_\alpha$ and of $U^{(s0)}_{j\alpha}$ is instead

$$\sum_\alpha[\sin(\beta_{\lambda_i}+\delta_{\epsilon_i l_i})\cos\delta^{(s0)}_\alpha - \mathcal{G}(\nu_i, l_i)\sin(\beta_{\lambda_i}+\delta_{\epsilon_i l_i})\sin\delta^{(s0)}_\alpha + A(\nu_i, l_i)\cos(\beta_{\lambda_i}+\delta_{\epsilon_i l_i}) \times \sin\delta^{(s0)}_\alpha]U^{(s0)}_{i\alpha}A^{(0)}_\alpha = 0 . \tag{4.28}$$

The calculation of the normalization integrals, Eqs. (4.22) and (4.23), is also facilitated by diagonalizing the $K^{(s)}$, or $K^{(s0)}$, matrix but does not lead to expressions as compact as Eq. (4.26). General formulas have been developed by Lu,[13] and especially by Lee and Lu,[14] for the case of a long-range Coulomb field; a more limited treatment has been given by Lee for the zero-field case.[5(b)] The resonant effects due to the coupling of closed and open channels are embodied in these treatments.

V. CONCLUSIONS

The formulation of the MQDT in this paper rests primarily on separating the influence of short-range interactions, within an atomic or molecular core, from those of the long-range forces acting on an excited, ionized, or detached electron. From this point of view the long-range field need not be restricted to the Coulomb law which was characteristic of the original QDT. The basic formulas of the original QDT combined the energy parameter ν of Coulomb wave functions with a quantum defect μ (or phase shift $\pi\mu$) which represents the effect of short-range interactions; the parameter μ was then replaced by a reaction matrix in the multichannel version of the theory. The present version combines three, rather than two basic parameters:

(a) The main parameter of motion at extremely large radii remains ν for the Coulomb field, but it is replaced by $\alpha\ln 2\nu - \chi_\alpha$ for a dipole field and by a constant β_λ for zero field, Eqs. (2.58), (2.61), and (2.62). No other force law need be considered in this range.

(b) Motion outside the core but at less than asymptotic range contributes a phase shift $\delta_{\epsilon l}$ which adds to the asymptotic parameter (Sec. IIE). The dependence of this quantum defect on energy may be slow but it need not be negligible as, e.g., in the case of polarization potentials, and is essential when the field vanishes faster than $1/r^2$.

(c) The short-range interactions are then represented by a reaction matrix, much as in the traditional MQDT. However, the introduction of a

smooth Green's function, in Sec. III, has enabled us to construct a reaction matrix that is free from resonance effects and can be calculated nevertheless in the presence of closed channels, thus justifying the heuristic results of Ref. 4.

ACKNOWLEDGMENTS

We are indebted to J. L. Dehmer, M. Inokuti, and especially to A. F. Starace for a critical reading of the manuscript. This research was supported by the U.S. Dept. of Energy, Office of Basic Energy Sciences.

APPENDIX: LARGE-r EXPANSION OF f^0

We aim here at clarifying a persistent paradox in the QDT literature, namely, the occurrence of complex coefficients in the asymptotic forms of the manifestly real Coulomb functions $\{f^0, g^0\}$ for $\epsilon < 0$. This paradox appears also in the large-r forms of the confluent hypergeometric function $F(a, c, z)$ as given by standard references [e.g., p. 346 of Ref. 8, p. 608 of Ref. 15, and especially Eq. (13.5.1) on p. 508 of the NSB Tables[16]]. Even though the imaginary term was dropped by Eissner *et al.*,[17] it persisted in Fano's analysis of the H_2 spectrum[18] until it was again removed[19] at the suggestion of Dubau.

The solutions to Eq. (2.1) with $v_1 = -1/r$ and $v_0 = 0$ are given in terms of the confluent hypergeometric function $F(a, c, z)$ by the following:
for Coulomb field

$$f^0(\epsilon, \lambda, r) = \frac{(2r)^{\lambda+1} e^{-r/\nu}}{\Gamma(2\lambda+2)} F(\lambda+1-\nu, 2\lambda+2, 2r/\nu) ;$$

for zero field

$$f^0(\epsilon, \lambda, r) = \frac{r^{\lambda+1} e^{-r/\nu}}{2^{\lambda+1/2}\Gamma(\lambda+\frac{3}{2})} F(\lambda+1, 2\lambda+2, 2r/\nu) . \tag{A1}$$

(The dipole-field solutions are then linear combinations of the zero-field solutions but with λ complex. For simplicity we will discuss here only the case where λ is real.) The radial dependence of both expressions (A1) has the *real* integral representation [Ref. 15, Eq. (5.3.46)],

$$z^{c/2} e^{-z/2} F(a, c, z) = \frac{z^{c/2} e^{-z/2} \Gamma(c)}{\Gamma(a)\Gamma(c-a)} \times \int_0^1 dt [e^{zt} t^{a-1} (1-t)^{c-a-1}] . \tag{A2}$$

The integrand of this expression has two singular branch points, at $t = 0$ and $t = 1$, whenever $a - 1$ and $c - a - 1$ are not integers. At large z each of these two points makes a separate contribution to the solution which is proportional to f^- or f^+, respectively. The two contributions are separated in Ref. 15 by adding and subtracting a term $\int_0^{-\infty} dt [\cdots]$, giving

$$z^{c/2} e^{-z/2} F(a, c, z) = \frac{z^{c/2} e^{-z/2} \Gamma(c)}{\Gamma(a)\Gamma(c-a)} \times \left(\int_{-\infty}^1 dt + \int_0^{-\infty} dt \right) \times [e^{zt} t^{a-1} (1-t)^{c-a-1}] . \tag{A3}$$

Note, however, that the integral which has been added and subtracted is *complex*, as its integrand contains the factor $[-|t|]^{a-1}$, where a is generally not an integer.

A change of variables in the two integrals reduces (A3) to the form

$$z^{c/2} e^{-z/2} F(a, c, z) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \left(z^{a-c/2} e^{z/2} \int_0^\infty du\, e^{-u} u^{c-a-1} (1 - u/z)^{a-1} + (-z)^{-a} z^{c/2} e^{-z/2} \int_0^\infty d\omega\, e^{-\omega} \omega^{a-1} (1 + \omega/z)^{c-a-1} \right) . \tag{A4}$$

The leading terms in the asymptotic expansions of f^- and f^+ are obtained by setting the binomials in the integrals equal to unity. In the continuum the two contributions are complex conjugate as $z = -2ikr$ and $a - c/2$ is also imaginary in our case, so the function f^0 is real. Below threshold, though, this is no longer true. At large z the two integrals are approximately $\Gamma(c-a)$ and $\Gamma(a)$, respectively, so that the *apparent* large-z form becomes

$$z^{c/2} e^{-z/2} F(a, c, z) \xrightarrow[z\to\infty]{} \frac{\Gamma(c)}{\Gamma(a)} z^{a-c/2} e^{z/2} + e^{\pm i\pi a} \frac{\Gamma(c)}{\Gamma(c-a)} z^{c/2-a} e^{-z/2} . \tag{A5}$$

So for real, positive z the second term is com-

plex; its complex conjugate term fails to appear in the contribution of the first term at large z since it is converging to 0 exponentially.

The solution to the paradox thus appears to consist of stipulating that only the *real part* of the $\int_0^{-\infty} dt[\cdots]$ is to be added and subtracted when transforming Eq. (A2) into (A3). The factor $\exp(\pm i\pi a)$ in (A5) is thus replaced by $\cos\pi a$. This convention has been used in Sec. II of the present paper. It could presumably be justified in greater detail by adapting to the range of $\epsilon < 0$ the analysis originally conducted by Sommerfeld and Schur[10] for $\epsilon > 0$. That analysis utilizes a complex integral form of Eq. (A2) and the occurrence of branch cuts exiting from $t = 0$ and $t = 1$. At $\epsilon < 0$ *both* of these cuts would run alongside the negative real axis of t and the contributions to each term of (A3) would follow paths on either side of each cut. Altogether there would be four paths running between $t = 0$ and $t = -\infty$, one pair in opposite directions between the two cuts and another pair outside the cuts.

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