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General form of the quantum-defect theory. II

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An earlier paper by the same title recast the treatment of an electron in the field of an ionic core [quantum-defect theory (QDT)] into a form largely independent of the character of the long-range field. Analytical complexities and limitations of that paper are eliminated here by further reformulation. Qualitative aspects are highlighted. A WKB analysis interprets the QDT parameters as phase integrals over certain ranges of the radial coordinate; the limitations of the WKB analysis are then removed through the Milne approach to wave equations. The QDT analysis is connected to Jost's formulation of scattering, extended to long-range fields by explicit treatment of the relevant singularities. The effects of interactions confined to an internal many-body core are represented by QDT parameters wholly independent of the external region.

I. INTRODUCTION

Quantum-defect theory[1,2] (QDT) served initially to exploit a characteristic feature of an electron excited into a discrete or continuum state of an atomic system: The electron moves prevalently *outside* the residual ionic core, under the simple influence of the core's Coulomb field. The motion in this external region, which determines most of the spectral and scattering observables of the excited system, can be described with reference to standard Coulomb eigenfunctions. The motion *within* the multiparticle ionic core is, instead, more complicated, but is confined within a small region of space of the order of a molecular diameter. Owing to this confinement, the mutual influence of the motions in the internal and external regions can be represented by *a few* QDT parameters only—akin to scattering lengths—which can be determined either by fitting to experimental data or by *ab initio* calculations restricted to the core. QDT predicts spectral and scattering data on the basis of (1) this connection at the core's boundary and (2) the connection between the amplitude and phase of the outer-field wave function at the core's edge and at $r \to \infty$.

These two connections differ characteristically in their dependence on the excitation energy: Since strong interactions prevail in the core, the connection parameters at the core's edge depend on energy on a rather coarse scale; that is, it is generally sufficient to evaluate them at intervals of ~ 1 eV. Far outside the core, on the other hand, the forces are weak and the wave-function behavior may depend very sensitively upon energy. The connection between the wave functions at $r \to \infty$ and at the core's edge has then to be studied analytically.

The success of the QDT program in spectroscopy and scattering suggests an extension of its approach, not only to the electron motion in non-Coulomb outer potentials but also to the motion of *any pair of fragments* released by the breakdown of a compound system. With this aim an earlier paper, to be referred to as I,[3] has developed the QDT analysis for long-range interactions proportional to $1/r^2$ ("dipole field") or constant ("zero field"). The former occurs notably in electron plus excited hydrogen and electron plus polar molecule combinations, the latter in electron plus neutral scattering or in photodetachment from negative ions. Paper I dealt briefly with more general potentials in its Sec. II E.

QDT procedures were then extended to the $1/r^4$ polarization potential and to the interatomic potential in molecular dissociation.[4,5] More recently a QDT procedure has been applied to photoabsorption in a Stark field whose long-range potential does not vanish at infinity.[6] We underscore this further evidence of the flexibility of QDT's procedure without treating it explicitly.

Paper I considered different long-range fields

separately. Its analysis and its choice of parameters remained rather cumbersome owing to limited appreciation of several relevant factors. It now seems worthwhile to return to the subject, redeveloping most of Secs. II and IV of I, while its Introduction and its analysis of relevant Green's-function properties (Sec. III) remain serviceable. Notation will follow historical precedents except where new considerations recommend departures to be noted explicitly.

The present paper intends to be self-contained except for occasional references to paper I. The structure of QDT and the problems faced in implementing it, particularly in the definition and construction of its parameters, are reviewed in Sec. II. The results of paper I for the QDT parameters of specific long-range interactions are rederived in Sec. III in a unified way and combined into Jost functions. A general treatment is then developed in Sec. IV, having in mind potentials that may be known only numerically. A WKB procedure serves to identify the QDT parameters in terms of phase integrals over classically allowed or forbidden ranges of r. A phase-amplitude treatment, free from approximations, affords then a constructive procedure for the parameters. Finally, Sec. V replaces Sec. IV of paper I, which combines the parameters of separate fragmentation channels in the external region into a single multichannel treatment. The combination involves the QDT parameters discussed in previous sections, as well as those that arise from the internal region and provide the connection at the core's boundary.

II. MAJOR ELEMENTS OF QDT

Our development rests on the following circumstances.

(a) The QDT parameters serve to interconnect different solutions of a Schrödinger equation, identified by their behavior at short and large radial distances, respectively. Scattering phase shifts η are thus defined at positive energies $\epsilon=\frac{1}{2}k^2$ by connecting a solution $f^0(r)$, regular at the origin, to a pair of solutions $f^{\pm}(r)$ having the basic structure $\exp(\pm ikr)$ at $r\to\infty$,

$$f^0(r)=B^{-1/2}(2/\pi k)^{1/2}(f^+e^{i\eta}-f^-e^{-i\eta})/2i$$
$$=B^{-1/2}f(r)\ . \tag{2.1}$$

The function $f(r)$ is identified here as the real superposition of f^+ and f^- normalized per unit energy in atomic units and proportional to f^0.

The amplitude factor $B^{-1/2}$ arises as follows: The solution $f^0(r)$ of a single-particle Schrödinger equation is generally controlled at small r by the centrifugal term of the potential $l(l+1)/r^2$, which causes $f^0(r)\to r^{l+1}$ as $r\to 0$. Since the energy term of the equation is dwarfed here by $l(l+1)/r^2$, $f^0(r)$ is appropriately normalized independently of ϵ. The factor $B^{-1/2}$ of (2.1) serves thus to connect the normalizations of f^0 and of $f^{\pm}$—or, rather, of f—which are controlled by different considerations; B is generally a function of ϵ, as the phase η also is. As we will see, the two functions f^0 and f are each useful in its own particular context. The dependence on wave-function behavior at large distances, introduced into f through B, makes f^0 the more useful form when the focus is on dependences at small r. On the other hand, for an item in (d) and (e) below and in Appendix B, it is more convenient to work with f. [The specification of $f^0(r)$ at small r differs in the presence of an attractive potential $-a/r^p$ with $p\geq 2$, which dwarfs in turn the centrifugal potential and causes $f^0(r)$ to oscillate faster and faster as $r\to 0$. In this event $f^0(r)$ is identified adequately by an arbitrary, but energy-independent, standardization of its amplitude and phase at an appropriately small value of r (see, e.g., Ref. 4).]

(b) In the bound-state part of the spectrum we have $\epsilon<0$ and the corresponding wave number is imaginary, $k=i\kappa$, whereby $f^{\pm}$ has the essential form $e^{\mp\kappa r}$. The amplitude corresponding to $B^{-1/2}$ is indicated here by $A^{-1/2}$ and the complex phases $\exp(\pm i\eta)$ are replaced by real coefficients $(D\cos\beta,\ D^{-1}\sin\beta)$. The factors $D^{\pm 1}$ are monotonic functions of ϵ which adjust the scale of $f^{\pm}$, respectively, while the oscillating factors $(\cos\beta,\ \sin\beta)$ correspond more closely to $\exp(\pm i\eta)$ as we shall see. The counterpart of (2.1) is thus

$$f^0(r)=A^{-1/2}(\pi\kappa)^{-1/2}(\sin\beta\, D^{-1}f^- -\cos\beta\, Df^+)$$
$$=A^{-1/2}f(r)\ . \tag{2.2}$$

Bound states occur at energies for which (2.2) remains finite at $r\to\infty$, as expressed by the condition that the coefficient of the rising exponential $f^-(r)$ vanishes,

$$\sin\beta=0\ . \tag{2.3}$$

(c) In the presence of a multiparticle core confined to radial distances $r<r_0$, the radial function of an electron (or other fragment) excited out of the core is analogous to $f^0(r)$ at $r>r_0$. However, this function differs generally from f^0 by a phase shift determined by its normal logarithmic derivative at r_0. We represent the function with a phase shift δ^0 by

$$F^0(r) \propto f^0(r)\cos\delta^0 - g^0(r)\sin\delta^0 , \tag{2.4}$$

where $g^0(r)$ is an independent solution of the same equation as $f^0(r)$, to be identified appropriately. The value of δ^0 is fitted to experimental data or calculated by solving the Schrödinger equation within the core and fitting (2.4) to the excited electron's wave function at the core's edge. The considerations that underlie the definition of $g^0(r)$ are central to the present paper.

(d) Briefly, the structure of Eq. (2.4) suggests that $g^0(r)$ should lag $f^0(r)$ in phase by 90°, in order that δ^0 combine additively with η in Eq. (2.1). However, neither f^0 nor g^0 oscillates in general as $r \to 0$. [This difficulty does not arise in the case noted at the end of (a) when a strong attractive field caused $f^0(r)$ to oscillate rapidly as $r \to 0$.] QDT traditionally identifies an oscillation 90° out of phase with reference to oscillatory behavior at $r \to \infty$ for $\epsilon > 0$. One might thus define $g^0(r)$ as $\propto B^{1/2}(f^+ e^{i\eta} + f^- e^{-i\eta})$, where the + sign in the parentheses provides the desired phase lag and the exponent $\frac{1}{2}$ of B is adjusted to remove B from the Wronskian $W(f^0, g^0)$. However, the presence of the phase shift η in this tentative definition of $g^0(r)$ introduces an unwanted dependence of g^0 on phenomena occurring at large r and an equally unwanted sensitivity to the energy near the threshold $\epsilon = 0$. Accordingly one includes in $g^0(r)$ an additional term proportional to f^0, which does not contribute to $W(f^0, g^0)$, with a coefficient $\mathcal{G}(\epsilon)$ designed to remove the unwanted dependence on large-r and threshold effects, setting

$$\begin{aligned} g^0(r) &= -B^{1/2}(2/\pi k)^{1/2}[f^+(r)e^{i\eta} + f^-(r)e^{-i\eta}]/2 - \mathcal{G}f^0 = B^{1/2}g(r) - \mathcal{G}f^0 , \quad \epsilon > 0 \\ &= -A^{1/2}(\pi\kappa)^{-1/2}(\cos\beta\, D^{-1}f^- + \sin\beta\, Df^+) - \mathcal{G}f^0 = A^{1/2}g(r) - \mathcal{G}f^0 , \quad \epsilon < 0 . \end{aligned} \tag{2.5}$$

[The function $g(r)$ is normalized like $f(r)$ in (2.1) and lags it by 90° at $r \to \infty$.]

It remains awkward to define a solution to be utilized at small r starting from its behavior at $r \to \infty$. There is indeed in general a second independent solution besides f^0 near the origin, but the linear independence fails at just the physical values of the orbital angular momentum as we shall see in Sec. III. This complication is well known in the theory of special functions but the standard remedy will be seen to lead back to Eq. (2.5).

(e) The definition of g^0, and the actual construction of the coefficient $\mathcal{G}$, are but a part of a broader problem that has emerged in the QDT development, namely, that an irregular solution of a wave equation is not readily identified because addition of a regular solution fails to modify it appreciably near the singular point. This difficulty of defining a function through boundary conditions at a point of singularity bears as well on the identification of f^- at $\epsilon < 0$. Inadequate appreciation of this fact has been troublesome in the past (see I, Appendix A); dealing with it occupies much of the present paper. Two different avenues will be pursued for this purpose in Secs. III and IV, namely, reliance on analytical forms of the initial Eqs. (2.1) and (2.2), where this form is available, and alternative approaches akin to the WKB analysis under more general circumstances.

(f) QDT treatments have been expressed in terms of the six parameters B, η, A, β, D, and $\mathcal{G}$, originally for the Coulomb field and in the extensions of paper I. More compactly, however, solutions specified at small r are connected to those specified at large r by Jost functions $J^{\pm}(\epsilon, l)$, which embody all those parameters,

$$f^0 = J^+ f^+ + J^- f^- . \tag{2.6}$$

Section III will concern itself particularly with $J^{\pm}$. The two Jost functions are related by the symmetry property[7]

$$J^-(k) = [J^+(k^*)]^* . \tag{2.7}$$

For $\epsilon > 0$, i.e., k real, Eq. (2.7) amounts to the obvious complex conjugation symmetry of the two terms of (2.6), $J^- = J^{+*}$, but the meaning of (2.7) is nontrivial for $\epsilon < 0$.

The Jost functions pertaining to the wave function $F^0(r)$, Eq. (2.4), embody as well the additional parameter δ^0, which represents the effect of core interaction and is equivalent to the quantum defect μ, the namesake of QDT. The calculation of δ^0 is essential to QDT applications, of course, but is regarded as a problem of core dynamics to be pursued separately. The excitation of an electron (or other core fragment) by photoabsorption is similarly regarded as a core phenomenon to be studied separately; QDT itself takes into account the events

at large radial distances subsequent to photoabsorption.

(g) We have dealt thus far with radial wave functions of a particle, or fragment, at $r > r_0$ pertaining to a *single* mode of excitation (i.e., to a "single channel"). In fact, QDT deals generally with multichannel situations. Paper I's approach to a multichannel process started from the close-coupling representation of a system's complete wave function $\Psi = \sum_i \{M_i(r)\Phi_i(\omega)\}$, and reduced its Schrödinger equation laboriously to Eq. (I.4.14) for a reaction matrix $K^{(s0)}$, which represents the effect of short-range interactions. It then directed attention to the eigenvalues $\tan\delta_\alpha^{(s0)}$ and eigenfunctions $U_{i\alpha}^{(s0)}$ of the matrix $K^{(s0)}$, which combine with the QDT parameters for the several excitation channels i to predict observable results. Viewing the problems of core dynamics as a separate problem, we shall indicate instead, in Sec. V, how an R-matrix treatment of the multiparticle interactions at $r \le r_0$ determines the parameters $\delta_\alpha^{(s0)}$ and $U_{i\alpha}^{(s0)}$ without reference to circumstances prevailing at large radial distances. These parameters serve then as input for QDT treatments of outer-region phenomena.

III. QDT PARAMETERS OF ANALYTIC WAVE FUNCTIONS

We consider here the QDT properties of solutions of the radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{\lambda(\lambda+1)}{2r^2}-\frac{b}{r}-\epsilon\right]f(\epsilon,\lambda,b,r)=0\ , \tag{3.1}$$

in atomic units. This equation applies to a free particle for $\{\lambda=l,\ b=0\}$, to an electron in a Coulomb field for $\{\lambda=l,\ b=Z\}$, and to an electron in a combined Coulomb and dipole field for

$$\{\lambda(\lambda+1)=l(l+1)-a,\ b=Z\}\ .$$

Its analytic solutions thus contain all the elements developed in Sec. II of paper I, whose Eq. (I.2.1) is analogous to (3.1).

We depart from I, however, by normalizing the basic solution f^0 of (3.1) as

$$f^0(\epsilon,\lambda,b,r)\underset{r\to 0}{\to} r^{\lambda+1}\ ,\quad \lambda \ge -\tfrac{1}{2} \tag{3.2}$$

because the coefficient $a_0(\lambda)$ introduced in I proves unnecessary here. The normalization (3.2) does not apply for a strongly attractive dipole field, with $a > l(l+1)+\frac{1}{4}$, i.e., $\lambda(\lambda+1) < -\frac{1}{4}$, because λ becomes complex

$$\lambda = -\tfrac{1}{2} \pm [a - l(l+1)]^{1/2} = -\tfrac{1}{2} \pm i\alpha\ . \tag{3.3}$$

In this case the solutions of (3.1) oscillate at $r \to 0$, as noted in Sec. II at the end of (a); since $\lambda(\lambda+1)=\lambda^*(\lambda^*+1)$, we shall utilize the real standard solution

$$\tfrac{1}{2}[f^0(\epsilon,\lambda,b,r)+f^0(\epsilon,\lambda^*,b,r)]\underset{r\to 0}{\to} r^{1/2}\cos(\alpha \ln r)\ . \tag{3.4}$$

[This convention differs from that of (I.2.5).]

The familiar solution of (3.1) with the boundary condition (3.2) is

$$f^0(\epsilon,\lambda,b,r)=r^{\lambda+1}e^{-br/\nu}F(\lambda+1-\nu,2\lambda+2,2br/\nu)\ ; \tag{3.5}$$

for real values of λ, with

$$\nu = \begin{cases} ib/k\ , & \epsilon = \frac{1}{2}k^2 > 0\ ; \quad (3.6a) \\ b/\kappa\ , & \epsilon = -\frac{1}{2}\kappa^2 < 0\ . \quad (3.6b) \end{cases}$$

For complex values of λ, the combination (3.4) of solutions (3.5) applies.

The solutions $f^\pm$ introduced in Eq. (2.1) are characterized by their asymptotic form

$$f^\pm(\epsilon,\lambda,b,r)\underset{r\to\infty}{\to} e^{\mp br/\nu}r^{\pm\nu} \tag{3.7}$$

with the notation (3.4) and for either sign of ϵ. The connection (2.6), or (2.1), between f^0 and $f^\pm$ takes now the explicit form

$$f^0(\epsilon,\lambda,b,r)=J^+(\epsilon,\lambda,b)f^+(\epsilon,\lambda,b,r) + J^-(\epsilon,\lambda,b)f^-(\epsilon,\lambda,b,r)\ ; \tag{3.8}$$

when λ is complex, $J^\pm$ is defined as

$$\tfrac{1}{2}[J^\pm(\epsilon,\lambda,b)+J^\pm(\epsilon,\lambda^*,b)]\ . \tag{3.9}$$

The Jost functions in (3.8), which are equivalent to the Wronskians utilized in paper I, have explicit expressions obtained by comparing Eq. (3.8) to the asymptotic representation at $r \to \infty$ of the confluent hypergeometric functions in (3.5),

$$J^{\pm}(\epsilon,l,b)=\pm W(f^{\mp},f^{0})/2ik$$

$$=\begin{cases}\dfrac{\Gamma(2\lambda+2)}{\Gamma(\lambda+1\pm\nu)}\left[\dfrac{1}{2k}\right]^{\lambda+1\mp\nu} e^{i(1/2)\pi[\nu\mp(\lambda+1)]}, & \epsilon>0 \qquad (3.10a)\\ \dfrac{\Gamma(2\lambda+2)}{\Gamma(\lambda+1\pm\nu)}\left[\dfrac{1}{2\kappa}\right]^{\lambda+1\mp\nu}\begin{cases}\cos[\pi(\lambda+1-\nu)],\\ 1,\end{cases} & \epsilon<0\,. \qquad (3.10b)\end{cases}$$

Whereas (3.10a) explicitly satisfies the general analytic condition (2.7), it is clear that (3.10b), in general, does not. However, for all physically meaningful values of ν, i.e., at the bound-state eigenvalues when $\epsilon<0$, the relation (2.7) is indeed valid.

A. Connections of $J^{\pm}$ across the $\epsilon=0$ threshold

Equations (3.10) are connected, in the main, by analytical continuation of the various ϵ-dependent parameters, indicated by (3.6) for ν and by $k\to i\kappa$. Indeed the ratio of Γ functions maintains the same form as a function of ν. The factor $(1/2k)^{\lambda+1\mp\nu}$ spins off a coefficient $\exp[-i\frac{1}{2}\pi(\lambda+1\mp\nu)]$ as $k\to i\kappa$. This coefficient merges into the last factor on the right of Eq. (3.10), but the result of this merger is nontrivial for J^{+} and has given rise to misunderstandings in the literature as detailed in Appendix A of I. The key element here is that the function f^{0} should remain real. Accordingly the last factor of (3.10b), resulting from this merger, has been set at $\mathrm{Re}\{\exp[-i\pi(\lambda+1-\nu)]\}$ in the expression of J^{+} as it was in paper I. This nontrivial aspect of the connection from $\epsilon>0$ to $\epsilon<0$ relates to the branch point of $k=(2\epsilon)^{1/2}$ at $\epsilon=0$ and further to the essential singularity of the wave function at $\{\epsilon=0,r=\infty\}$. The values of J^{-} remain, instead, simply connected across $\epsilon=0$, because in this case the power of i spun off from $(1/2k)^{\lambda+1+\nu}$ simply cancels the last factor of Eq. (3.10a).

This connection of $J^{\pm}$ across the threshold relates to the broader question of the specification of J^{+} at $\epsilon<0$, which has been introduced in Sec. II (e) and will be discussed extensively in Sec. IV. For the limited purposes of the present section we have bypassed the broader question by following the procedure of paper I.

B. QDT parameters as functions of $J^{\pm}$

The parameters B, η, A, β, D introduced in Sec. II are expressed simply in terms of the Jost functions $J^{\pm}$, as one sees by comparing Eqs. (2.1)–(2.3) with (2.6) and (2.7). The phase shift contributed by the potential of Eq. (3.1) over the whole range $0\le r\le\infty$ is obtained from

$$e^{2i\eta}=-\frac{J^{+}(\epsilon,\lambda,b)}{J^{-}(\epsilon,\lambda,b)}\,,\quad \epsilon>0 \qquad (3.11a)$$

where the $-$ sign originates from the sign difference in Eqs. (2.1) and (2.6). The phase η includes a term $(b/k)\ln(2k)$, which combines with the factor $r^{\pm\nu}$ of (3.7) to yield the diverging phase contribution of the Coulomb field (not included in the usual phase shift). The counterpart of (3.11a) for $\epsilon<0$ is

$$D^{2}\cot\beta=-\frac{J^{+}(\epsilon,\lambda,b)}{J^{-}(\epsilon,\lambda,b)}\,,\quad \epsilon<0\,. \qquad (3.11b)$$

Recall that the ratio J^{+}/J^{-} must be replaced, when λ is complex, by its more general form

$$\frac{J^{+}}{J^{-}}\to\frac{J^{+}(\epsilon,\lambda,b)+J^{+}(\epsilon,\lambda^{*},b)}{J^{-}(\epsilon,\lambda,b)+J^{-}(\epsilon,\lambda^{*},b)}\,.$$

The separation of the factors D and $\cot\beta$ in (3.11b) requires an additional consideration relating to their respective physical interpretations which emerge in Sec. IV. We note here that $\beta=\pi(\nu-\lambda)$ when λ is real.

The amplitude coefficients are obtained, instead, from the products of J^{+} and J^{-}, utilizing their relation (2.7),

$$B=\frac{1}{J^{+}(\epsilon,\lambda,b)J^{-}(\epsilon,\lambda,b)}\,,\quad \epsilon>0 \qquad (3.12a)$$

$$A\csc(2\beta)=\frac{1}{J^{+}(\epsilon,\lambda,b)J^{-}(\epsilon,\lambda,b)}\,,\quad \epsilon<0\,. \qquad (3.12b)$$

The separation of the factors A and $\csc(2\beta)$ relates to that of D and $\cot\beta$ noted above. For complex values of λ one must again substitute

$$\frac{1}{J^+J^-}\rightarrow\frac{4}{[J^+(\epsilon,\lambda,b)+J^+(\epsilon,\lambda^*,b)][J^-(\epsilon,\lambda,b)+J^-(\epsilon,\lambda^*,b)]}\ . \tag{3.13}$$

Substitution of the explicit form of $J^{\pm}$, Eqs. (3.10), yields readily the well-known expressions of the amplitudes and phases in the particular cases of the Coulomb field and zero field. For complex values of λ, instead, the reduction of the results to manifestly real form is somewhat laborious. A procedure for this purpose is developed in Appendix A and the combined results are presented in Tables I and II.

Large-r expressions of the standing-wave radial function f^0 in terms of the out- and in-going functions $f^{\pm}$ and of the QDT parameters are

$$f^0(\epsilon,\lambda,b,r)\underset{r\rightarrow\infty}{\rightarrow}[B(k,\lambda)]^{-1/2}\left[\frac{2}{\pi k}\right]^{1/2}\sin[kr+(b/k)\ln r+\eta]\ ,\quad \epsilon>0 \tag{3.14a}$$

$$f^0(\epsilon,\lambda,b,r)\underset{r\rightarrow\infty}{\rightarrow}[A(\kappa,\lambda)]^{-1/2}(\pi\kappa)^{-1/2}(D^{-1}\sin\beta\, e^{\kappa r}r^{-\nu}-D\cos\beta\, e^{-\kappa r}r^{\nu})\ ,\quad \epsilon<0\ . \tag{3.14b}$$

Because of the similar roles of the parameters A and B and of β and η at $\epsilon<0$ and $\epsilon>0$, respectively, we shall occasionally indicate each of these pairs by a single symbol, namely,

$$\mathscr{B}_\lambda=\begin{cases}A(\kappa,\lambda)\ , & \epsilon<0\\ B(k,\lambda)\ , & \epsilon>0\end{cases} \tag{3.15}$$

or

$$\delta_\lambda=\begin{cases}\beta(\kappa,\lambda)\ , & \epsilon<0\\ \eta(k,\lambda)\ , & \epsilon>0\ .\end{cases} \tag{3.16}$$

The remaining QDT parameter $\mathscr{G}(\epsilon,\lambda,b)$ has been introduced in Eq. (2.5) to remove from $g^0(\epsilon,\lambda,b,r)$ all effects of propagation at large r. As indicated in Sec. II (d), a second solution of Eq. (3.1) identified by an energy-independent boundary condition at the origin, is available and is generally independent of $f^0(\epsilon,\lambda,b,r)$. Since Eq. (3.1) is invariant under the substitution $\lambda\rightarrow-(\lambda+1)$, the function $f^0(\epsilon,-\lambda-1,b,r)$ is such a solution. Its independence is verified by constructing the Wronskian $W(f^0_\lambda,f^0_{-\lambda-1})$, which is seen from Eq. (3.2) to equal $-(2\lambda+1)$. [We have introduced here the symbol f^0_λ for $f^0(\epsilon,\lambda,b,r)$.] The Wronskian vanishes when $\lambda=-\frac{1}{2}$. In addition, however, the power expansion of $f^0_{-\lambda-1}$ from Eq. (3.5) shows that the coefficients of all terms beyond the one in r^λ are divergent for critical values $\lambda=\lambda_c$. In general, the values of λ_c are integers or half-integers, but only the half-integers occur for $b=0$. This divergence was formally avoided in paper I by introducing a coefficient $a_0(\lambda)$ in the definition (3.2). This meant, however, that $a_0(\lambda)f^0_{-\lambda-1}\propto f^0_\lambda$ at $\lambda=\lambda_c$, whereby its linear independence was lost anyhow. In addition, the coefficients A and B, which reflect the dependence of f^0 on large r, appear automatically in the power expansion of $f^0_{-\lambda-1}$, a function identified by an energy-independent boundary condition at the origin. The definition of the irregular function g^0 with a smooth dependence both on ϵ and λ thus requires an appropriate subtraction from $f^0_{-\lambda-1}$ of its singularities in λ and of its nonanalytic dependences on ϵ at $\epsilon=0$. Details of this subtraction are given in Appendix B. The result takes the form given in Eq. (2.5) with

$$\mathscr{G}_\lambda=-\mathscr{B}_\lambda\cot(\delta_\lambda-\delta_{-\lambda-1})\ , \tag{3.17}$$

except at the critical values $\lambda=\lambda_c$ where the above expression becomes singular. We refer to Appendix B for the result in those special cases and for the details of the derivation.

IV. GENERAL TREATMENT

The analytical representation of QDT parameters in Sec. III relates the amplitude and phase of wave functions in the asymptotic range, $r\rightarrow\infty$, to the corresponding values at shorter distances. Indeed we had noted in Sec. I that weak long-range interactions have great influence on the motion of slow particles and that the energy dependence of this influence has to be studied analytically. It was a main point of paper I that the long-range field of Eq. (3.1) encompasses all the characteristic asymptotic situations. A broader range of potentials that are relevant at shorter ranges was considered briefly in Sec. II E of I, namely, potentials that depart from the form (3.1) at intermediate ranges of r, $r_0<r<\infty$. Here we deal with QDT parameters of

a general medium-range potential regardless of its very long-range behavior.

It should also be contemplated that different portions of radial range external to the core may be treated separately. For example, an electron at very large distances from a neutral atom can be regarded as moving in a zero, or purely centrifugal, potential. Yet, down to much smaller radii, the electron-atom interaction is well represented by a $1/r^4$ polarization potential. Consequently, the phase shifts referred to the zero-field basis (spherical Bessel functions) can change fairly rapidly over a small range of energies near a threshold, even after the standard k^{2l+1} dependence of the centrifugal potential is removed; phase shifts referred to the exact Mathieu-function solutions of the Schrödinger equation with an r^{-4} potential vary far more slowly and smoothly with the energy. This has been demonstrated clearly in both single-channel and multichannel problems.[4,8]

Indeed the QDT procedures apply even when the potential does not converge to zero at large distances. For example, in the theory of the Stark effect, these procedures have been applied with great success by expressing the wave functions (f^+,f^-) or (f,g) in terms of Airy functions.[6] We shall not concern ourselves here any further with this flexibility of QDT, but concentrate instead on refining and implementing the remarks of Sec. II on identifying, interpreting, and interrelating the QDT parameters.

A. WKB analysis

We take advantage here of the WKB approximation which is appropriate to the treatment of long-range fields including the Coulomb field, at least in the absence of sharp field variations. The breakdown of WKB near a nucleus can be bypassed by the Langer procedure[9]; one first avoids the singularity by replacing r by $\ln r$ and then shows that the correct phase is obtained in any case in the r variable by adding a mock-centrifugal potential $1/4r^2$ and then following the WKB routine.[10]

Note that the WKB method is generally applicable in the outer region of atomic fields, barring only sharp irregularities. In particular, the analytic condition for applicability of WKB is seen to hold for the potential (3.1), even as $\epsilon\to 0$, particularly for large r. Consider that the rate of change of the wavelength $\lambda\!\!\!^{-}$

$$\frac{d\lambda\!\!\!^{-}}{dr}=\frac{d}{dr}\left[2\epsilon+\frac{2b}{r}-\frac{\lambda(\lambda+1)}{r^2}\right]^{-1/2}$$

vanishes at sufficiently large r, irrespective of the value of ϵ. For $\lambda\neq 0$ any centrifugal barrier can also be treated within a WKB framework.

Accordingly we combine here a long-range potential of interest with the centrifugal term and with the "Langer correction" into the effective potential, setting

$$U(r)=(\lambda+\tfrac{1}{2})^2/2r^2+V(r) \tag{4.1}$$

in a.u. For definiteness λ will be considered real in this section, and $U(r)$ will be assumed to have a single potential minimum and to vanish as $r\to\infty$. Three regions of interest, I, II, and III, are separated by two classical turning points $r_1(\epsilon)$ and $r_2(\epsilon)$ with r_2 taken to be infinite for $\epsilon\geq 0$. (Additional turning points may be considered, when relevant.) The regular solution, with behavior near $r=0$ of the form $f^0\to r^{\lambda+1}$ can be found immediately within the WKB approximation.

Region I, $0<r\ll r_1$

$$f_{\rm I}^0=\left[\frac{\lambda+\frac{1}{2}}{\kappa_{\rm I}}\right]^{1/2}e^{\varphi_{\rm I}(r)}, \tag{4.2}$$

where

$$\varphi_{\rm I}(r)=\int^r dr'\kappa_{\rm I}(r'), \tag{4.3}$$

and as usual

$$\kappa_{\rm I}(r)=[2U(r)-2\epsilon]^{1/2}. \tag{4.4}$$

When the centrifugal potential dominates near $r=0$ we can be more explicit about $\varphi_{\rm I}(r)$,

$$\varphi_{\rm I}(r)=\lim_{s\to 0}\left[\int_s^r\kappa_{\rm I}(r')dr'+(\lambda+\tfrac{1}{2})\ln s\right]. \tag{4.5}$$

These results adequately describe $f^0(r)$ in the classically forbidden region near $r=0$ and well inside the first turning point $r\ll r_1$. For $r\approx r_1$, where $\kappa_{\rm I}(r)$ approaches zero, this WKB wave function is a very poor approximation. Here the radial solution is replaced by a linear combination of Airy functions which are exact solutions to the Schrödinger equation for a linear potential. The explicit form of $f^0(r)$ near $r=r_1$ is not required here but will be needed to connect the approximate solution (4.2) at $r\ll r_1$ to an analogous expression at $r\gg r_1$ in region II. These connection formulas are given in standard texts.[10] Their use requires a transcription of (4.2):

$$f_{\rm I}^0(r)=\left[\frac{\lambda+\frac{1}{2}}{\kappa_{\rm I}}\right]^{1/2} e^{\varphi_{\rm I}(r_1)}\exp\left[-\int_r^{r_1}\kappa_{\rm I}(r')dr'\right] . \tag{4.6}$$

Region II, $r_1 \ll r \ll r_2$

The continuation of (4.6) into the classically allowed range is

$$f_{\rm II}^0(r)=2\left[\frac{\lambda+\frac{1}{2}}{k_{\rm II}}\right]^{1/2} e^{\varphi_{\rm I}(r_1)}\sin\left[\int_{r_1}^{r}k_{\rm II}(r')dr'+\frac{\pi}{4}\right] , \tag{4.7}$$

where the wave vector is now

$$k_{\rm II}(r)=[2E-2U(r)]^{1/2} . \tag{4.8}$$

At positive energies the outer turning point r_2 goes to ∞ and the asymptotic form is given by Eq. (3.14a), with B and η given in the WKB approximation by

$$B^{-1}=\pi(2\lambda+1)\exp[2\varphi_{\rm I}(r_1)] , \tag{4.9}$$

$$\eta=\lim_{r\to\infty}\left[\int_{r_1}^{r}k_{\rm II}(r')dr'-kr-(b/k)\ln r\right]+\frac{\pi}{4} . \tag{4.10}$$

For negative energies the wave function is extended into region III through the second turning point r_2, again using the WKB connection formulas. First we rewrite Eq. (4.7) as

$$f_{\rm II}^0(r)=-2\left[\frac{\lambda+\frac{1}{2}}{k_{\rm II}}\right]^{1/2} e^{\varphi_{\rm I}(r_1)} \times\sin\left[\int_r^{r_2}k_{\rm II}(r')dr'+\tfrac{1}{4}\pi-\beta\right] \tag{4.11}$$

with the phase shift

$$\beta(\kappa)=\int_{r_1}^{r_2}k_{\rm II}(r')dr'+\tfrac{1}{2}\pi . \tag{4.12}$$

Region III, $r_2 \ll r < \infty$ ($\epsilon<0$ only)

The connection formulas give, for r not too near r_2,

$$f_{\rm III}^0(r)=2\left[\frac{\lambda+\frac{1}{2}}{\kappa_{\rm III}}\right]^{1/2} \times e^{\varphi_{\rm I}(r_1)}(\sin\beta\, e^{\varphi_{\rm III}(r)}-\tfrac{1}{2}\cos\beta e^{-\varphi_{\rm III}(r)}) . \tag{4.13}$$

The exponent $\varphi_{\rm III}(r)$ is now defined through

$$\varphi_{\rm III}(r)=\int_{r_2}^{r}\kappa_{\rm III}(r')dr' \tag{4.14}$$

and

$$\kappa_{\rm III}(r)=[2U(r)-2E]^{1/2} . \tag{4.15}$$

To extract the asymptotic form of $f^0(r)$ and the negative-energy Jost functions, we cast once again $\varphi_{\rm III}(r)$ into the form

$$\varphi_{\rm III}(r)=\lim_{s\to\infty}\left[\kappa s-(b/\kappa)\ln s-\int_r^{s}\kappa_{\rm III}(r')dr'\right]+w(\kappa) \tag{4.16}$$

with

$$w(\kappa)=-\lim_{s\to\infty}\left[\kappa s-(b/\kappa)\ln s-\int_{r_2}^{s}\kappa_{\rm III}(r')dr'\right] . \tag{4.17}$$

Most importantly for our purposes, the large-r limit of $\varphi_{\rm III}(r)$ is simply

$$\varphi_{\rm III}(r)\underset{r\to\infty}{\longrightarrow}\kappa r-(b/\kappa)\ln r+w(\kappa) , \tag{4.18}$$

whereby the functions $\exp(\pm\varphi_{\rm III})$ in Eq. (4.13) are now identified with the exponential solutions $f^{\pm}$ of Eq. (3.7)

$$e^{\pm\varphi_{\rm III}(r)}=e^{\pm w(\kappa)}f^{\mp} . \tag{4.19}$$

The connection (2.2) between f^0 and $f^{\pm}$ accordingly takes the form given in Eq. (3.14b) with $\beta(\kappa)$ given in Eq. (4.12) and A coinciding with B in Eq. (4.9). Finally the rescaling amplitude D is given by

$$D=(\tfrac{1}{2})^{1/2}\exp[-w(\kappa)] . \tag{4.20}$$

These results represent the QDT parameters in terms of WKB phase or tunneling integrals. The essential physical origin of each parameter is thus identified, and, in particular, the range of integration that contributes to it, regardless of the accuracy of the WKB approximation. Accordingly we have gathered the parameters and will discuss each in turn.

$B(k)$. The amplitude coefficient $B^{-1/2}$ of the asymptotic form (4.13) of f^0 represents the ratio of this function, normalized as $r^{\lambda+1}$ at $r\to 0$, to the energy-normalized wave function $(2/\pi k)^{1/2}\sin(kr+\ldots)$ for $\epsilon>0$. For our potential with a single minimum, B involves only the tunneling integral from $r=0$ to $r=r_1$, Eq. (4.9). The centrifugal barrier at large r would introduce an additional factor near threshold in the absence of a countervailing long-range attraction. Tunneling under this second barrier would then add to B the additional factor $k^{2\lambda+1}$ which appears in Wigner's threshold law.

$\eta(k)$. The positive-energy phase measures the number of half-wavelengths of f^0 between $r=0$ and $r=\infty$. As this would be infinite at all $\epsilon \geq 0$, η is given by Eq. (4.10) as a finite complement to the infinite term represented by the phase $kr+(b/k)\ln r$ of f^+. Together with the usual phase shift, η included the centrifugal contribution $-\lambda\pi/2$.

$A(\kappa)$. This amplitude parameter is the negative-energy extension of B, which relates f^0 to an energy-normalized form in the classically allowed range. For our potential with a single minimum, A and B coincide, both of them representing the amplitude of tunneling under the centrifugal barrier from $r=0$ into the oscillatory region II. The WKB expression for A and B can be evaluated analytically for the potential of Eq. (3.1). The WKB result is not exact except in the limit of large λ, in contrast to Eq. (4.21).

$\beta(\kappa)$. This phase function measures the number of half-wavelengths of f^0 between $r=0$ and $r=\infty$ for $\epsilon<0$. Bound states are identified by the condition $\beta=(n+1)\pi$, $n=0,1,\ldots$. For a long-range Coulomb field, the WKB integral gives exactly the value obtained in Sec. II, namely,

$$\beta(\kappa)=\pi(-\lambda+b/\kappa)\ . \tag{4.21}$$

$D(\kappa)$. This is a "rescaling parameter" which multiplies and divides f^+ and f^-, respectively, at $\epsilon<0$, so that the resulting solutions $(Df^+, D^{-1}f^-)$ have a comparable amplitude near the outer classical turning point r_2. As Eq. (4.17) shows, D is analogous to A in that it depends on a tunneling integral from r_2 outward to infinity. The WKB expression for $D(\kappa)$ is again not identical to the exact expression in Table II for a Coulomb field, but the agreement becomes exact as the energy approaches threshold for all λ.

We conclude this WKB analysis with the identification of the function $g^0(r)$ which was introduced in Sec. II (d) as a second element of a base set $\{f^0,g^0\}$. No difficulty arises in selecting $g^0(r)$ "90° out of phase" with respect to f^0 *within the WKB approximation,* whose phase function $\varphi_{II}(r)$ is common to all solutions in the classically allowed range. We set then simply

$$g^0(\epsilon,\lambda,r)=-A^{1/2}\left[\frac{2}{\pi k_{II}}\right]^{1/2} \times\cos\left[\int_{r_1}^{r} k_{II}(r')dr'+\frac{\pi}{4}\right]\ . \tag{4.22}$$

Continuation of g^0 into region I or III is provided by connection formulas. An energy-normalized base pair is now obtained from $\{f^0,g^0\}$ as

$$f=A^{1/2}f^0\ ,\quad g=A^{-1/2}g^0\ ,\quad \epsilon<0\ , \tag{4.23}$$

where A is replaced by B at $\epsilon>0$. The parameter $\mathscr{G}$ of Eq. (2.5) vanishes in the WKB approximation when b is nonzero in Eq. (3.1). For potentials having a single minimum, the parameter $\mathscr{G}$ of Eq. (2.5) vanishes in the WKB approximation. However, $\mathscr{G}$ is generally nonzero when there are more than two classical turning points. Physically this results from the fact that two solutions which differ in phase by 90° in one potential well (e.g., at small r) will no longer differ in phase by exactly 90° after tunneling[6] [see Eq. (4.41)].

B. Full treatment by a phase-amplitude method

The WKB approach has illustrated the interplay between the amplitude and phase of a wave function and its contribution to the determination of QDT parameters. This approach is developed into an *exact,* if generally numerical, treatment by phase-amplitude procedures which yield the phase and amplitude of a wave function as solutions of a pair of coupled differential equations. These methods preserve the features that have afforded a direct and interpretable construction of QDT parameters.

The common element of these methods is to represent the solution of a wave equation in the form

$$y(r)=\alpha(r)\sin\phi(r)\ . \tag{4.24}$$

A subsidiary relation, necessary to determine the amplitude $\alpha(r)$ and the phase $\phi(r)$, can take different forms, characteristic of alternative methods. The most familiar of these methods, described by Babikov[11] and by Calogero,[12] originates from classical mathematical physics.[13] It reduces the wave equation to a pair of first-order nonlinear equations which are readily interpreted. For our purposes it presents two shortcomings, namely, that it does not conserve the phase difference of a base pair of solutions $\{f^0,g^0\}$ as r varies and that its phase function $\phi(r)$ becomes imaginary in the classically inaccessible regions. These difficulties are avoided by an alternative method, which we shall follow even though it is more complicated numerically.

Its key element is a transformation of the Sturm-Liouville differential equation first discovered by

Milne,[14] but interpreted and greatly clarified in later papers by Young[15] and Wheeler.[16] The present treatment relies heavily on the recent study by Korsch and Laurent.[17] In 1930 Milne showed that *all* independent solutions $y(r)$ to an equation

$$y''(r)+k^2(r)y(r)=0 \tag{4.25}$$

can be expressed in terms of *any* particular solution of the nonlinear equation

$$\alpha''(r)+k^2(r)\alpha(r)=\frac{1}{\alpha^3(r)} . \tag{4.26}$$

The general solution $y(r)$ is given by

$$y(r)=a\alpha(r)\sin\left[\int^r \alpha^{-2}(r')dr'+b\right] , \tag{4.27}$$

where a and b are arbitrary constants. Observe that the phase and amplitude of (4.27) are related precisely as they are in the WKB approximation by

$$\phi(r)=\int^r \alpha^{-2}(r')dr' . \tag{4.28}$$

The fact that $\alpha^{-2}(r)$ is the rate of phase accumulation prompted the labeling of

$$K(r)\equiv\alpha^{-2}(r) \tag{4.29}$$

as the "quantum momentum".[17] Once α and ϕ have been calculated from Eqs. (4.26) and (4.28), it is quite clear how to find two solutions 90° out of phase. That is, we can simply choose them to be

$$\begin{aligned} f&=(2/\pi)^{1/2}\alpha\sin\phi , \\ g&=-(2/\pi)^{1/2}\alpha\cos\phi . \end{aligned} \tag{4.30}$$

This formulation lends itself to a geometrical interpretation of pairs of independent solutions to any such Sturm-Liouville differential equation. The independent solutions (f,g) can be thought of as the real and imaginary parts of a complex number

$$-i(2/\pi)^{1/2}\alpha(r)\exp[i\phi(r)] .$$

The modulus of this function is just the amplitude

$$(2/\pi)^{1/2}\alpha(r)=(f^2+g^2)^{1/2} , \tag{4.31}$$

while its phase is expressed as

$$\phi(r)=-\tan^{-1}(f/g) . \tag{4.32}$$

Equation (4.28) implies that the complex number rotates at a speed proportional to $\alpha^{-2}(r)$. In this representation two solutions 90° out of phase are mapped onto points at right angles which rotate at equal speed.

There is, of course, no unique way to require two solutions to differ in phase by 90°, although this phase difference implies orthogonality of solutions that extend to large distances $r\to\infty$ at $\epsilon>0$. This ambiguity appears in the Milne approach through the fact that $\alpha(r)$ in Eq. (4.27) can be *any* solution to the nonlinear Eq. (4.26). Accordingly the definition of (f,g) is not complete until the boundary conditions used to find $\alpha(r)$ are spelled out. One sensible way to do this, though far from the only one, is to let our classical ideas guide us by choosing $\alpha(r_c)\sim k^{-1/2}(r_c)$ at some critical radius r_c. This boundary condition was used by Korsch and Laurent[17] in their treatment of potentials with a single minimum at $r=r_c$, and they showed that the resulting amplitude and phase functions vary quite smoothly with r as desired. Caution must be exercised if a much different boundary condition is adopted to define α, as it may result in a highly oscillatory amplitude which is usually *not* the desired behavior.

In any event, once $\alpha(r)$ has been chosen and $\phi(r)$ determined also, then each of the three QDT basis pairs of independent radial functions can be calculated at once. In the following we stipulate that the phase function ϕ vanishes at $r=0$, which yields the explicit form

$$\phi(r)=\int_0^r \alpha^{-2}(r')dr' \tag{4.33}$$

to be entered in (4.27). The condition for a bound level in the purely long-range potential then resembles the Bohr-Sommerfeld quantization condition

$$\begin{aligned} \phi(\infty)&=(n+1)\pi \\ &=\int_0^\infty \alpha^{-2}(r')dr' , \quad n=0,1,\ldots . \end{aligned} \tag{4.34}$$

Moreover, comparison with the definition of β in Eq. (4.12) shows that β is simply

$$\beta=\phi(\infty) , \quad \epsilon<0 . \tag{4.35}$$

Now we have the tools to construct (possibly numerically) the alternative base pairs of independent solutions (f^0,g^0), (f,g), and (f^+,f^-), and the coefficients B, η, A, β, D, and $\mathcal{G}$ which interrelate them. Section II emphasized that $f^0(\epsilon,\lambda,r)$ can be determined at all energies by taking the small-r form $f^0\approx r^{\lambda+1}$ and integrating outward to larger radii. When this is done at positive energies, the amplitude $B^{-1/2}$ and phase η of the asymptotic oscillations can be extracted. The energy-normalized regular solution f is then simply

$$f=B^{1/2}f^0\underset{r\to\infty}{\to}(2/\pi k)^{1/2}\sin[kr+(b/k)\ln r+\eta] . \tag{4.36a}$$

Next the energy-normalized irregular solution, g is constructed for $\epsilon>0$ by integrating inward from $r=\infty$, starting from the larger-r form of g:

$$g(\epsilon,\lambda,r)\underset{r\to\infty}{\to}-(2/\pi k)^{1/2}\cos[kr+(b/k)\ln r+\eta]\ . \tag{4.36b}$$

The construction of $f^{\pm}$ is then trivial. Each of these functions is thus determined in a straightforward manner without any reference to the phase-amplitude method.

At negative energies a phase-amplitude procedure serves to define all the QDT functions and parameters unambiguously. Once Eq. (4.26) for the amplitude function $\alpha(r)$ is solved with suitable boundary conditions at small radii (as discussed above), $\phi(r)$ is given by quadrature in Eq. (4.33). The energy-normalized solutions (f,g) are then *defined* by Eq. (4.30) for $\epsilon<0$ only. The coefficient A is thus defined as the ratio

$$A=(2/\pi)\alpha^2(r)\sin^2\phi(r)/[f^0(\epsilon,\lambda,r)]^2\ , \tag{4.37}$$

which can be evaluated at any convenient radius.

The second function of the base pair $\{f^0,g^0\}$ is now taken to be proportional to $\alpha\cos\phi$ at all energies, with the coefficient required to yield the Wronskian

$$W(f^0,g^0)=2/\pi\ . \tag{4.38}$$

We have

$$g^0(\epsilon,\lambda,r)=-(2/\pi)^{1/2}A^{1/2}\alpha(r)\cos\phi(r)\ . \tag{4.39}$$

This amounts to setting $\mathscr{G}=0$ below threshold, as in the WKB approach. At positive energies g^0 and g need not be proportional and hence $\mathscr{G}\neq0$ in general. Since the Eqs. (4.36) and (4.38) imply that

$$g^0(\epsilon,\lambda,r)\underset{r\to\infty}{\to}-B^{1/2}(2/\pi\kappa)^{1/2}\sec(\eta^0-\eta)\times\cos[kr+(b/k)\ln r+\eta^0]\ , \tag{4.40}$$

the parameter $\mathscr{G}$ is expressed in terms of the asymptotic phase difference between g and g^0:

$$\mathscr{G}=B\tan(\eta-\eta^0)\ ,\quad \epsilon>0\ . \tag{4.41}$$

Finally, we determine the exponential solutions $f^{\pm}$ and the rescaling parameter D for $\epsilon<0$. The decaying solution f^+ is identified as the result of numerical integration of the radial Schrödinger equation inward from $r=\infty$, starting from the boundary condition (3.7). On the other hand, we know the rescaled solutions are expressed in terms of (f,g) by

$$\begin{bmatrix} Df^+ \\ D^{-1}f^- \end{bmatrix}=-(\pi\kappa)^{1/2}\begin{bmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix}\ , \tag{4.42}$$

with the value of β given by Eq. (4.35). The constant parameter D and the radial solution $f^-(\epsilon,\lambda,r)$ are thus obtained from (4.42) in terms of the known solutions f, g,, and f^+, and of β.

This completes the phase-amplitude specification of the radial solutions and of their QDT parameters. To illustrate these ideas further, we show in Appendix C how they are applied to a specific problem.

V. QDT PARAMETERS AT THE CORE BOUNDARY

Sections III and IV have dealt with the construction of the QDT parameters that relate the amplitude and phase of radial wave functions at short and at very large radial distances. This section deals, instead, with the characterization and construction of the parameters that serve to match a radial wave function at the core boundary $r=r_0$ to the wave function of the whole system, inclusive of the core. As noted in Sec. II (g), the system of interest has generally several alternative channels of excitation. Its wave function at $r\sim r_0$ takes, accordingly, the general form

$$\Psi=\Sigma_i\{M_i(r)\Phi_i(\omega)\}\ , \tag{5.1}$$

where $M_i(r)$ is the radial function of the particle (or fragment) that separates from the core residue in the ith channel and $\Phi_i(\omega)$ represents the ith state of the core residue as well as the spin of the particle and the angular motion of particle plus residue about their center of mass. The braces in (5.1) represent the appropriate antisymmetrization. Equation (5.1) coincides with (1.4) of paper I, whose description includes additional details.

Parameters that connect the system's wave function $\bar{\Psi}$ at $r\le r_0$ with the wave function (5.1) appropriate to $r\ge r_0$, can be determined in two steps: One should first calculate $\bar{\Psi}$ by a procedure that requires it to be regular at the origin and to take the form (5.1) at $r\sim r_0$ and then cast each $M_i(r)$ in the form (2.4),

$$M_i(r_0)=C_i[f^0(r_i)\cos\delta_i^0-g^0(r_0)\sin\delta_i^0]\ ,$$

with an amplitude C_i and a phase shift δ_i^0 to be determined by matching the value and derivative of M_i. The values of C_i and δ_i^0 depend here, of course, upon the definition of the irregular function $g^0(r)$, which is not unique, as noted in Sec. II (e) and elsewhere in this paper. However, any arbitrariness in the definition of $g^0(r)$ is compensated in the determination of the corresponding $\mathcal{S}(\epsilon)$ function and has *no effect upon the physically significant relationship* between $\bar{\Psi}$ and the observable QDT parameters at $r\to\infty$, namely, β_i or η_i. That is, the QDT parameters pertaining to the pairs $\{f^0,g^0\}$ serve only as standard stepping stones for connecting parameters of $\bar{\Psi}$ at the core boundary, $r=r_0$, to observable parameters at $r\to\infty$.

The R-matrix variational methods[18,19] of calculating energy eigenfunctions within a limited volume of space represent $\bar{\Psi}$ as a superposition of Slater determinants akin to those of multiconfiguration (analytical) Hartree-Fock calculations. These wavefunctions are readily cast in the form (5.1) near the volume boundary $r=r_0$. In particular, the approach of Ref. 19 seeks eigenchannel solutions $\bar{\Psi}_\alpha$ characterized by having identical values of the normal derivative

$$\left.\frac{\partial \ln M_i^{(\alpha)}(r)}{\partial r}\right|_{r=r_0}, \quad i=1,2,\ldots, \tag{5.2}$$

in all channels. The value of the boundary parameter (5.2) can be determined as the eigenvalue of the variational procedure for any given total energy, instead of the familiar procedure that seeks an energy eigenvalue for a fixed value of the boundary parameter. Channel amplitudes

$$\{M_1^{(\alpha)}(r_0),M_2^{(\alpha)}(r_0),\cdots\} \tag{5.3}$$

are provided as eigenvectors of the variational procedure. At any given energy, the number of mutually orthogonal eigenchannels α equals the number of channels i. As outlined above, QDT represents each of the amplitudes (5.3) in the form

$$M_i^{(\alpha)}(r_0)=C_i^{(\alpha)}[f_i^0(\epsilon_0,r_0)\cos\delta_{\alpha i}^0 - g_i^0(\epsilon_i,r_0)\sin\delta_{\alpha i}^0]\,. \tag{5.4}$$

The parameters $\delta_{\alpha i}^0$ and $C_i^{(\alpha)}$ can then be determined to fit simultaneously the values of $M_i^{(\alpha)}(r_0)$ and of its derivative (5.2).

A variant of this procedure, convenient for QDT applications, has been utilized by Lee.[20] The variant selects eigenchannels α by requiring the phase shifts $\delta_{\alpha i}^0$ to be equal in all channels i, instead of requiring the derivatives (5.2) to be equal. The representation (5.4) of the eigenchannel radial functions takes then the form

$$\begin{aligned} M_i^{(\alpha)}(r_0)&=U_{i\alpha}^0[f_i^0(\epsilon_i,r_0)\cos\delta_\alpha^0 - g_i^0(\epsilon_i,r_0)\sin\delta_\alpha^0]\,,\\ &=U_{i\alpha}^0[f_i^0(\epsilon_i,r_0) - g_i^0(\epsilon_i,r_0)\tan\delta_\alpha^0]\cos\delta_\alpha^0\,, \end{aligned} \tag{5.5}$$

where the sets of coefficients $U_{i\alpha}^0$, with fixed α and different i, represent an eigenvector of a modified R matrix, $K^{(s0)}$. In the last expression (5.5) the factor $\cos\delta_\alpha^0$ has been separated out as a normalization coefficient, while $\tan\delta_\alpha^0$ is an eigenvalue of the reaction matrix that was indicated by $-\pi K^{(s0)}$ in Sec. IV C of paper I. [Reference 20 did not in fact proceed as indicated here, but represented $M_i^{(\alpha)}(r_0)$ in terms of radial wave functions $\{f,g\}$ normalized per unit energy at $r\to\infty$ instead of $\{f^0,g^0\}$. The corresponding eigenphases are then indicated by δ_α, eigenvalues of $\tan^{-1}(-\pi K^{(s)})$, and the eigenvectors by $U_{i\alpha}$; the parameters $\mu_\alpha=\delta_\alpha/\pi$ are the usual eigenquantum defects of QDT.]

The eigenfunctions Ψ_α, with the structure (5.1), serve in QDT as a base set whose elements are superposed with coefficients A_α to generate eigenfunctions

$$\Sigma_{i\alpha}\{\Phi_i(\omega)[f_i^0(\epsilon_i,r)\cos\delta_\alpha^0 - g_i^0(\epsilon_i,r)\sin\delta_\alpha^0]\}U_{i\alpha}^0 A_\alpha\,, \quad r\geq r_0 \tag{5.6}$$

that satisfy boundary conditions at $r\to\infty$ appropriate to any specific problem. To this end an initial step replaces the base pairs $\{f_i^0,g_i^0\}$ by $\{f_i,g_i\}$ or $\{f_i^+,f_i^-\}$ normalized at $r\to\infty$, using the transformations of Secs. III and IV. This casts (5.6) into an expression involving superpositions of $f_i^\pm$ with coefficients which are combinations of $U_{i\alpha}^0,\delta_\alpha^0$ and of the QDT parameters of the external region. Asymptotic boundary conditions appropriate to a given physical situation can then be applied.[21] As a first step, one sets to zero the coefficients of the radial functions $f_i^-(\epsilon_i,r)$ in all channels with $\epsilon_i<0$, the so-called "closed" channels. For the "open" channels with $\epsilon_i>0$, outgoing- or ingoing-wave boundary conditions on the coefficients of their $f^\pm$ will determine, respectively, scattering or photoabsorption cross sections in terms of the combined set of QDT parameters.

TABLE I. QDT parameters for a general angular momentum $\lambda \equiv \lambda_R + i\alpha$ and strength b of the Coulomb field in Eq. (3.1). The parameters (X,x), (Y,y), and (Z,z) represent the modulus and phase of ratios of gamma functions defined in Appendix A and simplify in special cases as tabulated in Table II.

$$\delta(\epsilon,\lambda)\equiv \begin{cases} \eta(k,\lambda) = -\frac{1}{2}\pi\lambda_R + (b/k)\ln(2k) + \phi(k,\lambda), \\ \qquad \phi = \frac{1}{2}(z_\alpha + z_{-\alpha}) + \tan^{-1}\left[\dfrac{Z_\alpha - Z_{-\alpha}}{Z_\alpha + Z_{-\alpha}}\tan[\tfrac{1}{2}z_\alpha - \tfrac{1}{2}z_{-\alpha} - \alpha\ln(2k)]\right], & \text{for } \epsilon > 0 \\ \beta(\kappa,\lambda) = \pi(b/\kappa - \lambda_R) + \tilde{\phi}(\kappa,\alpha), \\ \qquad \tilde{\phi} = \tan^{-1}\{\tanh(\pi\alpha)\tan[y - \alpha\ln(2\kappa)]\}, & \text{for } \epsilon < 0 \end{cases}$$

$$D^2(\kappa,\lambda)\equiv \tfrac{1}{2}X(2\kappa)^{2b/\kappa}(\cos x\cosh(\pi\alpha)\sin[\pi(b/\kappa - \lambda_R)] + \sin x\sinh(\pi\alpha)\cos[\pi(b/\kappa - \lambda_R)] + \{\sinh^2(\pi\alpha) + \sin^2[\pi(b/\kappa - \lambda_R)]\}^{1/2}), \quad \text{for } \epsilon < 0 \text{ only}$$

$$\mathscr{B}(\epsilon,\lambda)\equiv \begin{cases} B(k,\lambda) = (4/\pi)(2k)^{2\lambda_R+1}e^{b\pi/k}\{Z_\alpha^2 + Z_{-\alpha}^2 + 2Z_\alpha Z_{-\alpha}\cos[z_\alpha - z_{-\alpha} - 2\alpha\ln(2k)]\}^{-1}, & \text{for } \epsilon > 0 \\ A(\kappa,\lambda) = (4/Y^2)(2\kappa)^{2\lambda_R+1}\{\cosh(2\pi\alpha) + \cos[2y - 2\alpha\ln(2\kappa)]\}^{-1}, & \text{for } \epsilon < 0 . \end{cases}$$

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APPENDIX A: QDT PARAMETERS FOR COULOMB AND DIPOLE POTENTIALS

This appendix works out the details of the analytical reduction of the Jost functions $J^{\pm}(\epsilon,\lambda,b)$ to the QDT parameters B, η, A, β, and D for the potential in (3.1). It deals, therefore, with the subject addressed in Sec. II of paper I, but whereas I considered Coulomb, dipole, and zero fields separately, we deal with them here as a combined entity. Also, in amalgamating them into a single whole, we have found it necessary to depart somewhat from the definitions of these parameters in I, particularly for the case of dipole and zero fields.[22]

As a generalization of (3.3), we set

$$\lambda = \lambda_R + i\alpha , \tag{A1}$$

so that appropriate choices for (λ_R,α) reduce to dipole $(\lambda_R = -\frac{1}{2}, \alpha \neq 0)$ and to Coulomb and zero fields with real angular momentum $(\alpha = 0)$, respectively. We begin with $\epsilon > 0$ and from (3.9) and (3.10a), and have

$$J^{\pm} = \frac{1}{2}\left[\frac{1}{2k}\right]^{\lambda_R + 1 \mp \nu} \exp\{\mp i\tfrac{1}{2}\pi[\nu \mp (\lambda_R + 1)]\} \times \left[\frac{\Gamma(2\lambda+2)}{\Gamma(\lambda+1\pm\nu)}e^{(1/2)\pi\alpha}e^{-i\alpha\ln(2k)} + (\alpha \leftrightarrow -\alpha)\right], \tag{A2}$$

where the last symbol in the large parentheses means that the previous term is repeated with α replaced everywhere by $-\alpha$. It is convenient to separate the ratio of gamma functions into its modulus and argument

$$\frac{\Gamma(2\lambda+2)}{\Gamma(\lambda+1+\nu)} = Z_\alpha e^{-(1/2)\pi\alpha}e^{iz_\alpha} , \tag{A3}$$

where Z_α and z_α are real functions of λ_R and ν. From (2.1) and (3.8), it follows that the expression in (A2) coincides with

$$(2\pi k)^{-1/2}B^{-1/2}\exp[\pm i(\eta - \tfrac{1}{2}\pi)] .$$

Separating out the modulus and argument of (A2) leads, therefore, to the identification of B and η. Table I records the general form and Table II the specific expressions in the limiting cases of the three kinds of long-range fields.

TABLE II. QDT parameters for zero, Coulomb, and dipole fields. This table is similar to the one in paper I except for some redefinition. The parameter ϕ defined here equals $-\frac{1}{2}\pi$ plus the ϕ of paper I.

	Parameter	Zero	Coulomb	Dipole
	λ_R	λ	λ	$-\frac{1}{2}$
	α	0	0	α
	b	0	b	0
$\epsilon<0$	X	1	$\Gamma(\lambda+1-b/\kappa)/\Gamma(\lambda+1+b/\kappa)$	1
	x	0	0	0
	D^2	$\sin(-\pi\lambda)$	$\pi(2\kappa)^{2b/\kappa}/[\Gamma(\lambda+1+b/\kappa)\Gamma(-\lambda+b/\kappa)]$	$\cosh(\pi\alpha)$
	Y	$\Gamma(\lambda+\frac{3}{2})2^{2\lambda+1}/\sin^{1/2}(-\pi\lambda)$	$\Gamma(2\lambda+2)[\Gamma(-\lambda+b/\kappa)/\Gamma(\lambda+1+b/\kappa)]^{1/2}$	$[2\pi\alpha/\sinh(2\pi\alpha)]^{1/2}$
	y	0	0	$2\alpha\ln 2-\chi_\alpha$, $\chi_\alpha=\arg\Gamma(1-i\alpha)$
	β	$-\pi\lambda$	$\pi(b/\kappa-\lambda)$	$\frac{1}{2}\pi+\tilde{\phi}$ $\tan\tilde{\phi}=\tanh(\pi\alpha)\tan\left[\alpha\ln\frac{2}{\kappa}-\chi_\alpha\right]$
	A	$\frac{2}{[\Gamma(\lambda+\frac{3}{2})]^2}(\frac{1}{2}\kappa)^{2\lambda+1}\sin(-\pi\lambda)$	$\frac{2\Gamma(\lambda+1+b/\kappa)}{[\Gamma(2\lambda+2)]^2\Gamma(-\lambda+b/\kappa)}(2\kappa)^{2\lambda+1}$	$\frac{2\sinh(2\pi\alpha)}{\pi\alpha\{\cosh(2\pi\alpha)+\cos[2\alpha\ln(2/\kappa)-2\chi_\alpha]\}}$
	Z_α	$\pi^{-1/2}2^{2\lambda+1}\Gamma(\lambda+\frac{3}{2})$	$\Gamma(2\lambda+2)/\lvert\Gamma(\lambda+1+ib/k)\rvert$	$[\alpha e^{\pi\alpha}/\sinh(\pi\alpha)]^{1/2}$
	z_α	0	$\arg\Gamma(\lambda+1-ib/k)\equiv\sigma_\lambda$	$2\alpha\ln 2-\chi_\alpha$
$\epsilon>0$	ϕ	0	σ_λ	$\tan\phi=\tanh(\frac{1}{2}\pi\alpha)\tan\left[\alpha\ln\frac{2}{k}-\chi_\alpha\right]$
	B	$[\Gamma(\lambda+\frac{3}{2})]^{-2}(\frac{1}{2}k)^{2\lambda+1}$	$\frac{\lvert\Gamma(\lambda+1+ib/k)\rvert^2}{[\Gamma(2\lambda+2)]^2}\frac{e^{\pi b/k}}{\pi}(2k)^{2\lambda+1}$	$\frac{2\sinh(\pi\alpha)}{\pi\alpha\{\cosh(\pi\alpha)+\cos[2\alpha\ln(2/k)-2\chi_\alpha]\}}$

For $\epsilon<0$, the unraveling of the two parameters $J^{\pm}$ in (3.10b) into the three parameters A, D, and β in (2.2) is made unique by specifying that β represents the accumulation of phase over the whole range of r. This criterion coincides with the conventional choice of $\beta=\pi(\nu-\lambda)$ for the Coulomb field as in paper I. It differs from I for the other fields. The apparent asymmetry of the last term in (3.10b) between J^{+} and J^{-} is removed through the identity

$$\Gamma(z)\Gamma(1-z)=\pi/\sin\pi z \ .$$

Thus (3.10b) can be written

$$J^{\pm}=\mp\pi^{-1/2}\Gamma(2\lambda+2)\left[\frac{\Gamma(\nu-\lambda)}{\Gamma(\lambda+1+\nu)}\right]^{1/2} \times\left[\frac{\Gamma(\lambda+1-\nu)}{\Gamma(\lambda+1+\nu)}\sin\pi(\nu-\lambda)\right]^{\pm1/2} \times\left[\frac{1}{2\kappa}\right]^{\lambda+1\mp\nu}\begin{cases}\cos[\pi(\nu-\lambda)]\\ \sin[\pi(\nu-\lambda)]\end{cases} . \tag{A4}$$

This form permits a ready comparison with (3.11b) to identify D and β. In particular, the rescaling parameter D follows immediately from the terms involving $\pm$ in (A4), that is,

$$D^2=\mathrm{Re}\left[(2\kappa)^{2\nu}\frac{\Gamma(\lambda+1-\nu)}{\Gamma(\lambda+1+\nu)}\sin[\pi(\nu-\lambda)]\right] . \tag{A5}$$

In forming the real part when λ is complex, it is convenient to define

$$\Gamma(\lambda+1-\nu)/\Gamma(\lambda+1+\nu)\equiv Xe^{ix} , \tag{A6}$$

which reduces to unity in the absence of a Coulomb field, that is, when $b=0$. The explicitly real form of D^2 is given in Table I with special forms for Coulomb, zero, and dipole fields in Table II.

Once D has been so defined, the "rescaled Jost functions," $J^{\pm}/D^{\pm1}$ are equal to

$$\mp(\pi\kappa A)^{-1/2}\begin{cases}\cos\beta\\ \sin\beta\end{cases}$$

from (2.2). Upon forming the real part of the rescaled Jost functions, we have

$$A^{-1/2}\begin{cases}\sin\beta\\ \cos\beta\end{cases}=2^{-(\lambda_R+2)}\kappa^{-(\lambda_R+1/2)}Y\,\mathrm{Re}\left[e^{i[y-\alpha\ln(2\kappa)]}\begin{cases}\sin[\pi(\nu-\lambda_R-i\alpha)]\\ \cos[\pi(\nu-\lambda_R-i\alpha)]\end{cases}\right] , \tag{A7}$$

with

$$Ye^{iy}\equiv\Gamma(2\lambda+2)[\Gamma(\nu-\lambda)/\Gamma(\lambda+1+\nu)]^{1/2} . \tag{A8}$$

Table I gives the general expressions and Table II the specific values of A and β for the three limiting cases.

The entries in Table II differ from the results in I in the following respects. The phase parameters ζ and η are unchanged and $B(k,\lambda)$ differs only trivially from paper I because of our removal of the normalization factor $a_0(\lambda)$ in (3.2). Likewise, for the Coulomb field, $A(\kappa,\lambda)$ differs only in this factor, and D and β are exactly as before. All three parameters are, however, substantially different for the dipole and zero fields.

A point to be stressed is that the parameters A, D, and $\sin\beta$ vanish for the case of zero field when λ is an integer; their reciprocals appear in physically significant combinations, e.g., in (2.2), but these expressions remain finite. Similarly imaginary values of parameters may emerge in the tables, but their significant combinations are nevertheless real. The definitions of QDT parameters adopted in paper I may prove to be preferable for actual calculations when only the long-range dipole field or zero field are present.

APPENDIX B: DEFINITION OF $g^0(r)$ AND $\mathcal{G}(\epsilon)$

The notation introduced at the end of Sec. III, which sets $f^0(\epsilon,\lambda,b,r)\equiv f^0_\lambda$, etc., will be followed here. The reciprocal linear relations between the base pair $\{f^0_\lambda,g^0_\lambda\}$ normalized at $r\to0$ and the energy-normalized pair $\{f_\lambda,g_\lambda\}$, implied by (2.1), (2.5), etc., are then

$$\begin{bmatrix} f_\lambda \\ g_\lambda \end{bmatrix} = \begin{bmatrix} \mathscr{B}_\lambda^{1/2} & 0 \\ \mathscr{B}_\lambda^{-1/2}\mathscr{G}_\lambda & \mathscr{B}_\lambda^{-1/2} \end{bmatrix} \begin{bmatrix} f_\lambda^0 \\ g_\lambda^0 \end{bmatrix},$$
$$\begin{bmatrix} f_\lambda^0 \\ g_\lambda^0 \end{bmatrix} = \begin{bmatrix} \mathscr{B}_\lambda^{-1/2} & 0 \\ -\mathscr{B}_\lambda^{-1/2}\mathscr{G}_\lambda & \mathscr{B}_\lambda^{1/2} \end{bmatrix} \begin{bmatrix} f_\lambda \\ g_\lambda \end{bmatrix}. \tag{B1}$$

In accordance with Sec. III, and following the original approach of Seaton[1] adhered to in paper I, we start here from the base pair $\{f_\lambda^0, f_{-\lambda-1}^0\}$ of independent solutions of Eq. (3.1). Recall that this pair's independence fails for a set of values of $\lambda=\lambda_c$, as noted at the end of Sec. III, and that the λ_c include (for $b\neq 0$) the integer orbital quantum numbers $\lambda_c=l$ of greatest physical significance. We also recall, from Sec. II (e), that the definition of $g^0(r)$ involves rather arbitrary conventions which serve to articulate the theory but do not affect its final results. Since no single convention appears definitely preferable, we treat here separately the two cases $\lambda\neq\lambda_c$, $\lambda=\lambda_c$, without attempting to blend the separate results into a unified convention.

Properties of the base pair $\{f_\lambda^0, f_{-\lambda-1}^0\}$ emerge by calculating and comparing their Wronskian evaluated from their limiting forms at $r\to 0$ and $r\to\infty$,

$$W(f_\lambda^0, f_{-\lambda-1}^0) = -(2\lambda+1), \tag{B2}$$

from $f^0(r)\to r^{\lambda+1}$,

$$W(f_\lambda^0, f_{-\lambda-1}^0) = \mathscr{B}_\lambda^{-1/2}\mathscr{B}_{-\lambda-1}^{-1/2}(2/\pi)\sin(\delta_\lambda-\delta_{-\lambda-1}), \tag{B3}$$

from (2.1). The expression (B3) vanishes at $\lambda=\lambda_c$, where the phase difference is a multiple of π. This phase difference has a simple expression for potentials represented by (3.1) with *real* λ, namely,

$$\delta_\lambda-\delta_{-\lambda-1} = \begin{cases} \eta_\lambda-\eta_{-\lambda-1} = -\pi\lambda-\tan^{-1}\{\tan[\pi(\lambda+1)]\tanh(\pi b/k)\}, & \epsilon>0 \\ \beta_\lambda-\beta_{-\lambda-1} = -\pi(2\lambda+1), & \epsilon<0. \end{cases} \tag{B4}$$

[It should be pointed out that (B3) is valid at $\epsilon<0$ only if $D_\lambda=D_{-\lambda-1}$, which is satisfied in Table II.] The nonindependence of $\{f_\lambda^0, f_{-\lambda-1}^0\}$ at $\lambda=\lambda_c$ will manifest itself through the occurrence of the expression (B3) in the denominators of our results. Indeed we shall start from the expression of the solution $g_\lambda(r)$ in terms of $\{f_\lambda^0, f_{-\lambda-1}^0\}$,

$$g_\lambda(r) = \frac{f_{-\lambda-1}(r)-\cos(\delta_\lambda-\delta_{-\lambda-1})f_\lambda(r)}{\sin(\delta_\lambda-\delta_{-\lambda-1})}, \tag{B5}$$

an expression that lags 90° in phase behind $f_\lambda(r)$ with the Wronskian $W(f_\lambda,g_\lambda)=2/\pi$. Formulas applying at $\lambda=\lambda_c$ are then obtained by de l' Hospital's limiting procedure for $\lambda\to\lambda_c$, which is familiar, e.g., from the definition of the Neuman function

$$N_n(z) = \lim_{\nu\to n} N_\nu(z) = \lim_{\nu\to n} \frac{J_{-\nu}(z)-\cos(\pi\nu)J_\nu(z)}{-\sin(\pi\nu)}. \tag{B6}$$

(a) $\lambda\neq\lambda_c$. The function g_λ^0 can now be defined by entering in Eq. (B1) the functions $f_\lambda=\mathscr{B}_\lambda^{1/2}f_\lambda^0$ and g_λ from (B5),

$$g_\lambda^0 = -\mathscr{G}_\lambda f_\lambda^0(r) + \mathscr{B}_\lambda^{1/2}\frac{\mathscr{B}_{-\lambda-1}^{1/2}f_{-\lambda-1}^0-\cos(\delta_\lambda-\delta_{-\lambda-1})\mathscr{B}_\lambda^{1/2}f_\lambda^0}{\sin(\delta_\lambda-\delta_{-\lambda-1})}. \tag{B7}$$

The function f_λ^0 is seen to drop out of this expression upon setting

$$\mathscr{G}_\lambda = -\mathscr{B}_\lambda\cot(\delta_\lambda-\delta_{-\lambda-1}), \tag{B8}$$

the formula anticipated in (3.17). Comparison of (B2) and (B3) permits us now also to eliminate $\mathscr{B}_\lambda^{1/2}\mathscr{B}_{-\lambda-1}^{1/2}$ from (B7), thus reducing that equation to

$$g_\lambda^0(r) = [-\pi(\lambda+\tfrac{1}{2})]^{-1}f_{-\lambda-1}^0(r). \tag{B9}$$

Recalling Eq. (B2), we see that this definition leads to the appropriate Wronskian

$$W(f_\lambda^0, g_\lambda^0) = 2/\pi. \tag{B10}$$

When $\lambda=\lambda_R+i\alpha$ is complex in (3.1), the analog of f_λ^0 is its real part and the analog of $f_{-\lambda-1}^0$ is

$$\mathrm{Im}f^0_\lambda=\frac{1}{2i}(f^0_\lambda-f^0_{\lambda*})\ . \tag{B11}$$

This function serves then as g^0_λ, with the additional normalization factor required to fit (B10). Equation (B8) remains a valid definition of $\mathscr{G}_\lambda$ with the values of $\mathscr{B}_\lambda$ and δ_λ drawn from Appendix A and appropriate to the treatment of complex λ. No complex values of λ belong to the special set λ_c, but numerical difficulties may arise for $\lambda=-\frac{1}{2}+i\alpha$ and $\alpha\ll 1$.

(b) $\lambda=\lambda_c$. The limiting form of (B5) for $\lambda\to\lambda_c$ is

$$g_{\lambda_c}(r)=\frac{(-1)^m[\partial f_{-\lambda-1}(r)/\partial\lambda]_{\lambda_c}-[\partial f_\lambda(r)/\partial\lambda]_{\lambda_c}}{[\partial(\delta_\lambda-\delta_{-\lambda-1})/\partial\lambda]_{\lambda_c}} \tag{B12}$$

with

$$m=(\delta_{\lambda_c}-\delta_{-\lambda_c-1})/\pi\ . \tag{B13}$$

[The denominator of (B12) would reduce to -2π for $\epsilon<0$, according to (B4), but its general expression is preserved in the following.] The definition of $g^0_{\lambda_c}$ from the g_{λ_c} in (B12) must identify and separate out the parts of (B12) that depend on ϵ sensitively at threshold. At $\epsilon>0$ such parts include $\delta_\lambda-\delta_{-\lambda-1}$. Our procedure will be simplified by defining $g^0_{\lambda_c}$ at $\epsilon<0$, with a smooth dependence on ϵ, extrapolating the result to $\epsilon>0$, and obtaining separate expressions of $\mathscr{G}_\lambda$ in the two energy ranges.

To this end we return to the initial expression (B5) of g_λ and transcribe it, using Eqs. (B2) and (B3) at $\epsilon<0$, into

$$g_\lambda(r)=\frac{A_\lambda^{-1/2}\bar{f}^0_{-\lambda-1}(r)-A_\lambda^{1/2}\cos(\beta_\lambda-\beta_{-\lambda-1})f^0_\lambda(r)}{\sin(\beta_\lambda-\beta_{-\lambda-1})} \qquad \epsilon<0 \tag{B14}$$

where

$$\bar{f}^0_{-\lambda-1}(r)=-\frac{\sin(\beta_\lambda-\beta_{-\lambda-1})}{\pi(\lambda+\frac{1}{2})}f^0_{-\lambda-1} \underset{\lambda\to\lambda_c}{\to} A_{\lambda_c}\cos(\beta_{\lambda_c}-\beta_{-\lambda_c-1})f^0_{\lambda_c} \tag{B15}$$

remains finite as $\lambda\to\lambda_c$ unlike $f^0_{-\lambda-1}$ and g^0_λ itself in (B9). The limiting form of (B14) at λ_c, which will replace (B12), is

$$g_{\lambda_c}(r)=\frac{(-1)^m A_{\lambda_c}^{-1/2}(\partial\bar{f}^0_{-\lambda-1}/\partial\lambda)_{\lambda_c}-A_{\lambda_c}^{1/2}(\partial f^0_\lambda/\partial\lambda)_{\lambda_c}-A_{\lambda_c}^{-1/2}(\partial A_\lambda/\partial\lambda)_{\lambda_c}f^0_{\lambda_c}}{[\partial(\beta_\lambda-\beta_{-\lambda-1})/\partial\lambda]_{\lambda_c}}\ ,\quad \epsilon<0\ . \tag{B16}$$

The factor $(\partial A/\partial\lambda)_{\lambda_c}$ in the numerator of (B16) is now identified as the only one that depends sensitively on ϵ near threshold and hence is to be incorporated in $\mathscr{G}_{\lambda_c}$. Indeed $\partial f^0_\lambda/\partial\lambda$ and $\partial\bar{f}^0_{-\lambda-1}/\partial\lambda$ are smooth functions of energy by definition. The same hold for A_{λ_c} itself which equals $(-1)^m\bar{f}^0_{-\lambda_c-1}/f^0_{\lambda_c}$ according to (B15) and for $\beta_\lambda-\beta_{-\lambda-1}$ which is energy independent. Hence we define

$$\mathscr{G}_{\lambda_c}=-\frac{(\partial A_\lambda/\partial\lambda)_{\lambda_c}}{[\partial(\beta_\lambda-\beta_{-\lambda-1})/\partial\lambda]_{\lambda_c}}\ ,\quad \epsilon<0\ . \tag{B17}$$

The irregular energy-smooth solution $g^0_{\lambda_c}$ is accordingly defined by

$$g^0_{\lambda_c}(r)=\frac{(-1)^m(\partial\bar{f}^0_{-\lambda-1}/\partial\lambda)_{\lambda_c}-A_{\lambda_c}(\partial f^0_\lambda/\partial\lambda)_{\lambda_c}}{[\partial(\beta_\lambda-\beta_{-\lambda-1})/\partial\lambda]_{\lambda_c}}\ , \tag{B18}$$

initially at $\epsilon<0$ and by extrapolation at all ϵ. This extrapolation does not extend to $\mathscr{G}_{\lambda_c}$, however, which is nonanalytic at $\epsilon=0$. The combination of Eq. (B1) with (B5) and (B18) yields instead

$$\mathscr{G}_{\lambda_c}=-\left[\frac{\partial[B_\lambda\sin(\beta_\lambda-\beta_{-\lambda-1})/\sin(\eta_\lambda-\eta_{-\lambda-1})]/\partial\lambda}{\partial(\beta_\lambda-\beta_{-\lambda-1})/\partial\lambda}\right]_{\lambda_c}\ ,\quad \epsilon>0\ . \tag{B19}$$

APPENDIX C: QDT PARAMETERS FOR FREE-PARTICLE WAVE FUNCTION

To illustrate the interplay of different elements of this paper, we identify here the QDT parameters for a trivially simple example. The wave equation $\frac{1}{2}y''+\epsilon y=0$ has the regular solution

$$f^0(r)=\begin{cases}k^{-1}\sin(kr)\ , & \epsilon>0\\ \kappa^{-1}\sinh(\kappa r)\ , & \epsilon<0\end{cases} \tag{C1}$$

normalized to $f^0\to r$ for $r\to 0$.

The parameters B and η are given by (3.12a) and (3.11a) for $\epsilon>0$ in terms of the Jost functions $J^{\pm}$, which are in turn read off the representation (2.5) of (C1). Thus one finds in our example,

$$B=2k/\pi\ ,\quad \eta=0\ . \tag{C2}$$

For $\epsilon<0$, we avoid here the possible ambiguity in separating D from β by applying procedures from Sec. IV B. In general $\alpha(r)$ must be calculated numerically from (4.26), but for the present example a real solution with the energy-independent small-r normalization $\alpha(r=0)=1$ is given in closed form by

$$\alpha(r)=\kappa^{-1}[\sinh^2(\kappa r)+\kappa^2\cosh^2(\kappa r)]^{1/2}\ . \tag{C3}$$

The corresponding phase function (4.34) is then

$$\phi(r)=\tan^{-1}[\kappa^{-1}\tanh(\kappa r)]\ , \tag{C4}$$

from which follows, by (4.35),

$$\beta=\tan^{-1}(1/\kappa)\ ,\quad \sin\beta=(1+\kappa^2)^{-1/2}\ . \tag{C5}$$

The energy-normalized base pair for $\epsilon<0$ is now given by (4.30) in terms of α and ϕ,

$$\begin{aligned}f(r)&=\left[\frac{2}{\pi\kappa^2}\right]^{1/2}[\sinh^2(\kappa r)+\kappa^2\cosh^2(\kappa r)]^{1/2}\\ &\quad\times\sin\left[\tan^{-1}\left[\frac{1}{\kappa}\tanh(\kappa r)\right]\right]\\ &=\left[\frac{2}{\pi\kappa^2}\right]^{1/2}\sinh(\kappa r)\ ,\\ g(r)&=-\left[\frac{2}{\pi}\right]^{1/2}\cosh(\kappa r)\ .\end{aligned} \tag{C6}$$

The final parameter D is generally obtained from (4.42), in terms of f, g, and β (previously found) and of f^+. In our case f^+ coincides with $e^{-\kappa r}$ at all r, removing any need of integrating it inward from $r=\infty$; Eq. (4.42) then gives

$$D=\left[\frac{2\kappa}{1+\kappa^2}\right]^{1/2}\ . \tag{C7}$$

The same Eq. (4.42) gives also the singular function

$$f^-(r)=e^{\kappa r}-\frac{1-\kappa^2}{1+\kappa^2}e^{-\kappa r}\ , \tag{C8}$$

which does include a decaying term of specified amplitude.

In accordance with Sec. IV B we set here $\mathcal{G}=0$ for $\epsilon<0$, whence

$$g^0(r)=A^{1/2}g(r)=-(2/\pi)\cosh(\kappa r)\ ,\quad \epsilon<0 \tag{C9}$$

where $A=2/\pi$ is obtained using Eq. (4.37). This function continues smoothly across the threshold into

$$g^0(r)=-(2/\pi)\cos(kr)\ ,\quad \epsilon>0\ . \tag{C10}$$

Section IV B regards (f,g) and (f^0,g^0) at $\epsilon>0$ as connected nontrivially by (2.5), with $\mathcal{G}$ given by (4.41); however, $\mathcal{G}$ vanishes in our example because $\eta^0=0$, too.

Some of the QDT parameters obtained by this procedure differ from those that result from Sec. III and Appendix A for the same example. The differences stem in part from alternative specifications of the singular function f^-.

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