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Generalizations of the Fermi-Segrè formula

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Phase-integral formulas obtained by Fröman, Fröman, and the present author for the limit of $u_N(l,E,r)/r^{l+1}$ as $r \rightarrow 0$, where $u_N(l,E,r)$ is a normalized nonrelativistic wave function for bound or unbound states, are compared with corresponding formulas obtained by Pratt and co-workers from analytical perturbation theory. It is demonstrated that the phase-integral formulas are practically always advantageous to the perturbation-theory formulas. If one substitutes the perturbation-theory approximation for the energy into the respective phase-integral formula for the limit of u_N/r^{l+1} as $r \rightarrow 0$ and performs approximations according to a well-defined scheme, the approximate perturbation-theory formulas for the limit of u_N/r^{l+1} as $r \rightarrow 0$ are obtained. For bound s states the phase-integral formula and the perturbation-theory formula coincide with the Fermi-Segrè formula in the nonrelativistic approximation.

I. INTRODUCTION

The nonrelativistic Fermi-Segrè formula[1–5] gives a remarkably simple expression for the value of a normalized bound-state radial wave function of an atomic or ionic s electron at the origin. This formula is of importance for the interpretation of hyperfine-structure splittings, isotope shifts of spectral lines, Knight-shift data, and chemical shifts of Mössbauer lines. A generalization, which removes the particularization to an s state but is restricted to highly excited states with small values of the angular momentum quantum number l, has been given by Bouchiat and Bouchiat [Eq. (AI.49) in Ref. 6]. Formulas related to the Bouchiat-Bouchiat formula but valid for high absolute values of the energy have been obtained by McEnnan, Kissel, and Pratt [Eqs. (36), (94), and (101) in Ref. 7, where the last-mentioned equation is to be corrected according to Ref. 8] and by Iwinksi, Kim, and Pratt [Eqs. (A8), (A9), and (A10) in Ref. 9; Ref. 10]. McEnnan, Kissel, and Pratt have also considered the normalization of unbound states [Eq. (94) in Ref. 7]. Fröman and Fröman[11] have derived a generalization of the Fermi-Segrè formula for which the above-mentioned restrictions are largely removed. References 6–11 have in common the use of certain special properties of the Coulomb wave functions, and the methods presented in these references are limited to cases where the deviation of the atomic potential from a Coulomb potential is in some sense or some region small. Thus, Fröman and Fröman[11] introduced the assumption that the physical potential is given by a Coulomb term plus a constant term in the whole of the classically forbidden region adjacent to the origin. The accuracy of the formula derived in Ref. 11 was investigated by application to a particular screened Coulomb potential for which the radial wave function can be expressed in terms of hypergeometric functions.[12–15] Instead of using this particular model as an illustrative example, the author together with Fröman and Fröman[16] exploited it in a more general way to obtain new formulas in which the screening is accounted for more accurately than in the results in Ref. 11.

In the present investigation we compare the perturbation-theory formulas obtained by Pratt and co-workers[7–10] with the phase-integral formulas in Ref. 16 expressed in terms of the energy E, the quantum number l, the charge number Z, and the coefficients in the power-series expansion of the regular part of the potential around $r=0$. For bound states it is demonstrated in Sec. III that the perturbation-theory formula[7–10] is obtained from the phase-integral formula[16] if in the latter formula the quantity c_l equal to the residue of the inverse square of the wave function at $r=0$ is approximated by its value for the perturbed energy in a consistent way. Since this quantity is energy independent for s states,[5] the phase-integral formula and the perturbation-theory formula coincide with one another for $l=0$, and hence according to Ref. 5 with the usual Fermi-Segrè formula.

For unbound states the perturbation theory formula (94) in Ref. 7 expresses the normalized wave function close to $r=0$ as a function of an (artificial) unperturbed Coulomb energy $\hbar^2 k_c^2/2m$, and the dependence on the actual energy $\hbar^2 k^2/2m$ is obtained by inverting a perturbation expansion for the continuum energy. Substituting this expansion into the phase-integral formula for unbound states and performing approximations according to a well-defined scheme the perturbation-theory formula given in Ref. 7 is obtained in Sec. IV.

In Sec. V, the particular model potential[12–15] mentioned above, which goes over into a Coulomb potential in the limit when the screening vanishes, is used to illustrate the accuracy of the perturbation-theory formulas.

Consider a nonrelativistic particle moving in a spherically symmetric potential, which behaves as $-Z\hbar^2/ma_0 r$ close to $r=0$, where a_0 is equal to the Bohr radius and where the atomic number Z is assumed to be positive. The state considered corresponds to the angular momentum quantum number l and the energy E. The radial Schrödinger equation is written

$$\frac{d^2u}{dr^2}+R(r,E)u=0\ , \tag{1}$$

where, with obvious notations,

$$R(r,E)=\frac{2m}{\hbar^2}\left[E-V(r)-\frac{\hbar^2 l(l+1)}{2mr^2}\right]$$
$$=-\frac{l(l+1)}{r^2}+\frac{2Z}{a_0 r}+a_0^{-2}\sum_{n=0}^{\infty} b_n(r/a_0)^n \ , \tag{2}$$

the last expression representing $R(r,E)$ close to $r=0$. Particularly for unbound states the notation

$$E=\hbar^2k^2/2m \tag{3}$$

is convenient.

The results obtained at the end of Chap. 7 in Ref. 17 as well as the final formulas in Ref. 16 contain the quantity

$$c_l=\operatorname*{Res}_{r=0}\left[\frac{1}{u^2}\right] , \tag{4}$$

where u is the particular solution of (1) with (2) for which (in Ref. 16)

$$\lim_{r\to 0}(u/r^{l+1})=1 \ . \tag{5}$$

The index in the notation c_l indicates explicitly that c_l depends on the angular momentum quantum number l, where $2l+1$ is a non-negative integer.

For the details of the derivation of c_l, we refer to Appendix A in Ref. 16. In short, we proceed as follows. Assuming that the regular part of the potential [and hence of $R(r,E)$] is developed in a known power series of r as in (2), we derive the corresponding coefficients in the power-series expansion of the solution of (1), which fulfills (5). We then obtain the quantity c_l, pertaining to this solution, as a function of the energy, the quantum number l, the charge number Z, and the coefficients in the expansion of the regular part of the potential:

$$c_l=\frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2}\left\{\prod_{\substack{s=0\\ \text{or } 1/2}}^{l}\left[1+\left[\frac{b_0}{Z^2}-\frac{l(l+1)}{2}\frac{b_1}{Z^3}\right]s^2\right.\right.$$
$$\left.\left.+\frac{3}{2}\frac{b_1}{Z^3}s^4\right]+R_l\right\} ,$$
$$c_{-1/2}=1 \ , \tag{6}$$

where in the product s takes all non-negative integral or half-integral values, respectively, up to l, and where

$$R_l=0 \quad \text{for } l=0,\tfrac{1}{2},1 \ , \tag{7a}$$

$$R_l=\frac{9}{4}\left[\frac{b_2}{Z^4}+\frac{9}{16}\left[\frac{b_1}{Z^3}\right]^2\right] \quad \text{for } l=\tfrac{3}{2} \ , \tag{7b}$$

$$R_l=18\left[\frac{b_2}{Z^4}+\frac{b_3}{Z^5}+\left[\frac{b_1}{Z^3}\right]^2\right] \quad \text{for } l=2 \ , \tag{7c}$$

$$R_l=\frac{1989}{16}\left[\frac{b_1}{Z^3}\right]^2+81\frac{b_2}{Z^4}+180\frac{b_3}{Z^5}$$
$$+225\left[\frac{b_4}{Z^6}-\frac{5}{16}\left[\frac{b_1}{Z^3}\right]^3\right]$$
$$+\frac{225}{4}\frac{b_0}{Z^2}\left[\frac{b_2}{Z^4}+\frac{21}{16}\left[\frac{b_1}{Z^3}\right]^2\right] \quad \text{for } l=\tfrac{5}{2} \ , \tag{7d}$$

$$R_l=45\left[6\frac{b_2}{Z^4}+22\frac{b_3}{Z^5}+13\left[\frac{b_1}{Z^3}\right]^2\right]$$
$$+675\left[4\frac{b_4}{Z^6}+\frac{b_1}{Z^3}\frac{b_2}{Z^4}+6\frac{b_5}{Z^7}\right]$$
$$+45\frac{b_0}{Z^2}\left[14\frac{b_2}{Z^4}+18\frac{b_3}{Z^5}+27\left[\frac{b_1}{Z^3}\right]^2\right]$$
$$\text{for } l=3 \ . \tag{7e}$$

It should be noted that all formulas above are exact.

II. THE PHASE-INTEGRAL APPROXIMATIONS

To obtain a useful approximate expression for the radial wave function, we shall use the phase-integral method, involving phase-integral approximations of arbitrary order, devised by Fröman and Fröman (see Refs. 17—20 and pp. 126—131 in Ref. 21). For the higher orders these phase-integral approximations differ from the higher-order Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximations in a way which has been explained in some detail by Fröman[19] and by Dammert and Fröman.[22] It is also important to note that the above-mentioned approximations are more general than the JWKB approximations since they contain an unspecified function $Q^2(r,E)$, which can be chosen in a way appropriate for the problem under consideration. For the purpose of the present paper we shall choose this function such that

$$\lim_{r\to 0} r^2[Q^2(r,E)-R(r,E)]=l(l+1) \ , \tag{8a}$$

a possible choice being

$$Q^2(r,E)=R(r,E)+\frac{l(l+1)}{r^2}=\frac{2m}{\hbar^2}[E-V(r)] \ . \tag{8b}$$

For the phase-integral approximations of the order $2N+1$, we have

$$q(r,E)=Q(r,E)\sum_{n=0}^{N} Y_{2n} \ , \tag{9}$$

the first few quantities Y_{2n} being

$$Y_0=1 \ , \tag{10a}$$

$$Y_2=\tfrac{1}{2}\epsilon_0 \ , \tag{10b}$$

$$Y_4=-\frac{1}{8}\epsilon_0^2-\frac{1}{8}\left[\frac{1}{Q(r,E)}\frac{d}{dr}\right]^2\epsilon_0 \tag{10c}$$

with

$$\epsilon_0=\frac{R-Q^2}{Q^2}+\frac{1}{16Q^6}\left[5\left[\frac{dQ^2}{dr}\right]^2-4Q^2\frac{d^2Q^2}{dr^2}\right]. \tag{11}$$

Explicit expressions for Y_{2n} up to Y_8 are given in Refs. 23 and 24 and up to Y_{20} in Ref. 25.

According to the results obtained on pp. 74—79 in Ref. 17, the particular solution u of (1), which fulfills (5), is given by the approximate formula (7.28) in Ref. 17, which is valid for the first-order approximation. Generalized to an arbitrary-order approximation (see for instance Sec. 10 in Ref. 26), this formula states that when r lies sufficiently far to the right of the origin in the classically allowed region containing $r=0^+$ and $Q(r,E)$ is chosen to be positive in the region under consideration, u is given by the (approximate) phase-integral formula

$$u\approx(\pi c_l)^{-1/2}q^{-1/2}(r,E)\times\cos\left[\tfrac{1}{2}\int_{\Gamma(r)}q(r,E)dr-(l+\tfrac{3}{4})\pi\right], \tag{12a}$$

where $\Gamma(r)$ is a contour encircling the origin as shown in Fig. 1, and where $2l+1$ is a non-negative but not too large integer.

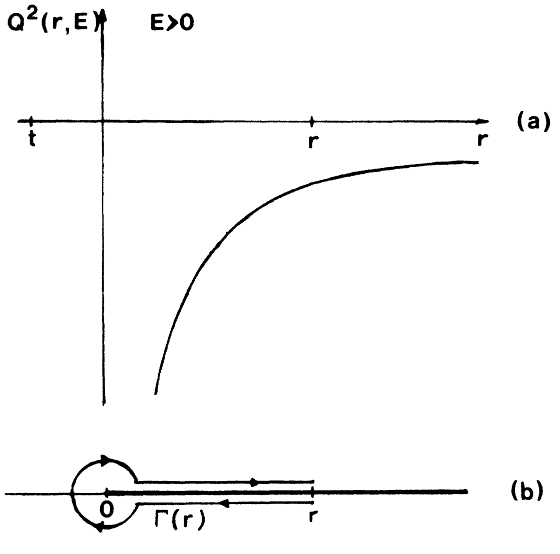

FIG. 1. (a) Qualitative behavior for real positive r of $-Q^2(r)$ for the case of unbound states. The position of the zero t of $Q^2(r)$ on the negative real r axis is also indicated. (b) Contour of integration for the integral appearing in the formulas (12a) and (12b) for phase-integral wave functions.

It is necessary for the validity of formula (12a) that there be no zero of $Q^2(r,E)$ in the immediate neighborhood of $r=0$. For too high unbound-state energies, when the zero t of $Q^2(r,E)$ on the negative real r axis indicated in Fig. 1 comes too close to the pole at $r=0$, the accuracy of formula (12a) is in general expected to be rather mediocre. The high-energy correction to formula (12a) is due to the small-distance properties of the wave function.[27] The formula for the wave function in the classically allowed region correct also for high energies reads[16]

$$u=\begin{cases}\{1+(-1)^{2l+1}\exp[-2\pi Z/(\tilde{k}a_0)]\}^{1/2}(\pi c_l)^{-1/2}q^{-1/2}(r,E) \\ \qquad\times\cos\left[\frac{1}{2}\int_{\Gamma(r)}q(r,E)dr-(l+\frac{3}{4})\pi+\phi_l\right], & \tilde{k}\text{ real and positive} \\ (\pi c_l)^{-1/2}q^{-1/2}(r,E)\cos\left[\frac{1}{2}\int_{\Gamma(r)}q(r,E)dr-(l+\frac{3}{4})\pi\right] & \tilde{k}^2\text{ not real and positive ,}\end{cases} \tag{12b}$$

where $\tilde{k}a_0/Z$ satisfies the equation

$$\frac{b_0}{Z^2}=\left[\frac{\tilde{k}a_0}{Z}\right]^2+\frac{1}{2}\frac{b_1}{Z^3}\left[3\left[\frac{\tilde{k}a_0}{Z}\right]^{-2}+l(l+1)\right], \tag{13}$$

and hence

$$\frac{\tilde{k}^2a_0^2}{Z^2}=\frac{1}{2}\frac{b_0}{Z^2}-\frac{l(l+1)}{4}\frac{b_1}{Z^3}+\left[\left[\frac{1}{2}\frac{b_0}{Z^2}-\frac{l(l+1)}{4}\frac{b_1}{Z^3}\right]^2-\frac{3}{2}\frac{b_1}{Z^3}\right]^{1/2}. \tag{14}$$

An explicit expression for ϕ_l can be obtained using a similar method as in Ref. 27 but adapted to the present modification (8a). For the purpose of the present paper, however, we do not need the high-energy correction to the phase.

A detailed derivation of a formula, from which (12b) is easily obtained, is presented elsewhere.[16] We shall here merely give a few strong arguments in support of the correction to the amplitude for high energies in (12b) as compared to (12a). Formula (12b) gives the correct amplitude for the case of the Coulomb potential, which can be easily shown, e.g., with the aid of Chap. 14 in Ref. 28. Moreover, for a general potential, which behaves as $-Z\hbar^2/ma_0r$ close to $r=0$, we note that for $\tilde{k}^2>0$ and $l=0$ the multiplicative factor in front of $q^{-1/2}(r,E)\cos(\cdots)$ on the right-hand side of (12b) is equal to the multiplicative factor in front of $q^{-1/2}(r,\frac{1}{2}\hbar^2\tilde{k}^2/m)\cos(\cdots)$ for the Coulomb wave function satisfying (5) of energy $\hbar^2\tilde{k}^2/2m$. This is in complete agreement (for low-order perturbation theory) with the conjecture made by Pratt and Tseng[29] based on empirical observations and used in our Appendix. It should in this context be noted that c_0 is independent of the energy according to (6) with (7a) and that $q(r,\frac{1}{2}\hbar^2k^2/m)\rightarrow k$ as

$r \to \infty$. The derivation of the formula in Ref. 16 corresponding to (12b) does not involve perturbative arguments such as the one above, but exploits the properties of the exactly soluble model in Sec. V, in particular the small-distance properties for high energies.

III. BOUND STATES

Let us now consider the case, illustrated in Fig. 1 of Ref. 5, that there exists a turning point t on the positive real r axis, which separates the classically allowed region adjacent to the origin from the classically forbidden region extending to $+\infty$.

The bound-state wave function with radial quantum number n' is normalized according to

$$\int_0^\infty u_N^2(l,E_n,r)dr = 1, \quad n = n'+l+1, \quad n' = 0,1,2,\dots, \tag{15}$$

where E_n is an energy eigenvalue in general depending on n and l. For s states formula (12a) together with the appropriate quantization condition and normalization formula,[30,31] was used by Fröman and Fröman[5] to obtain the bound-state wave function at the origin. Since the same derivation holds for any non-negative integral value of $2l+1$, we give here directly the final result

$$\lim_{r\to 0}\left[\frac{u_N(l,E_n,r)}{r^{l+1}}\right] = \left[\frac{2m}{\hbar^2}c_l\right]^{1/2}\left[\frac{\partial}{\partial E}\frac{1}{2\pi}\int_\Gamma q(r,E)dr\right]_{E=E_n}^{-1/2}. \tag{16}$$

In (16) Γ is the closed contour of integration (see Fig. 1 in Ref. 5) encircling in the negative sense the pole at $r=0$ and the zero t of $Q^2(r,E)$ and occurring in the quantization condition[32]

$$\tfrac{1}{2}\int_\Gamma q(r,E_n)dr = n\pi, \quad n = n'+l+1, \quad n' = 0,1,2,\dots. \tag{17}$$

Since the function $Q^2(r,E)$, according to assumptions introduced above, has a first-order pole at $r=0$ and a first-order zero at $r=t$, the quantization condition (17) differs from the generalized Bohr-Sommerfeld quantization condition, which applies to the case of a smooth function $Q^2(r,E)$ with two zeros.

Following Fröman and Fröman,[5] in accordance with the quantization condition (17) we replace

$$\frac{\partial}{\partial E_n}\frac{1}{2\pi}\int_\Gamma q(r,E_n)dr$$

by dn/dE_n, i.e., by $1/(dE_n/dn)$. In this way we obtain from (16) the generalized Fermi-Segrè formula[16]

$$\lim_{r\to 0}\left[\frac{u_N(l,E_n,r)}{r^{l+1}}\right] = \left[\frac{2m}{\hbar^2}c_l\frac{dE_n}{dn}\right]^{1/2}. \tag{18}$$

The structure of formula (18) should be noted. The quantity c_l is determined entirely from the local properties of the potential close to $r=0$, whereas dE_n/dn is a global quantity which can be obtained, e.g., by means of spectroscopic data. For $l=0$ formula (18) with (6) and (7) is recognized as the usual Fermi-Segrè formula.[5]

Introducing the perturbation approximation (5) in Ref. 10 [(A1) in the Appendix] into the right-hand side of the exact formula (6) with Eqs. (7) and bringing along contributions up to order b_2/Z^4 [hence neglecting contributions of the order b_3/Z^5, $(b_1/Z^3)^2$, b_1b_2/Z^7, etc.] we obtain after some calculations

$$c_l \approx \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2}\left[1-\frac{1}{4}l(l+1)(2l+1)\left[\frac{b_1}{Z^3}n^2+\frac{5}{3}\frac{b_2}{Z^4}n^4\right]+\cdots\right]\prod_{\substack{s=0\\ \text{or } 1/2}}^{l}\left[1-\frac{s^2}{n^2}\right] \quad (\text{exact for } l=0). \tag{19}$$

Introducing (19) into (18) we obtain

$$\lim_{r\to 0}\left[\frac{u_N(l,E_n,r)}{r^{l+1}}\right] \approx \left[\frac{2m}{\hbar^2}\frac{dE_n}{dn}\right]^{1/2}\frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \times\left[1-\frac{1}{4}l(l+1)(2l+1)\left[\frac{b_1}{Z^3}n^2+\frac{5}{3}\frac{b_2}{Z^4}n^4\right]+\cdots\right]^{1/2}\prod_{\substack{s=0\\ \text{or } 1/2}}^{l}\left[1-\frac{s^2}{n^2}\right]^{1/2}. \tag{20}$$

Formula (20) coincides exactly with the corresponding formula obtained from analytical perturbation theory by Iwinski, Kim, and Pratt.[9,10] Hence, the perturbation-theory formula is obtained from the phase-integral formula as a particular case, when the perturbation approximation for the energy eigenvalue is introduced, except for $l=0$, when the phase-integral and perturbation-theory formulas coincide exactly with one another and with the usual Fermi-Segrè formula.

IV. UNBOUND STATES

According to (12b) with (5) and the fact that $q(r,\frac{1}{2}\hbar^2k^2/m)\to k$ as $r\to\infty$ the unbound-state ($k^2>0$) wave function, $u_N(l,k,r)$, normalized to $\sin[kr-\frac{1}{2}l\pi+\delta_l(k)]$ as $r\to\infty$, fulfills at the origin the approximate phase-integral formula

$$\lim_{r\to 0}\left[\frac{u_N(l,k,r)}{r^{l+1}}\right] = \begin{cases}\left[\dfrac{\pi k c_l}{1+(-1)^{2l+1}\exp(-2\pi Z/\tilde{k}a_0)}\right]^{1/2}, & \tilde{k} \text{ real and positive} \\ (\pi k c_l)^{1/2}, & \tilde{k}^2 \text{ not real and positive}, \end{cases} \tag{21}$$

where $\tilde{k}a_0/Z$ is obtained from (14) or (13).

According to (13) and (A2) in the Appendix, for the order of approximation, when contributions of order b_2/Z^4 (and smaller) are neglected, $\tilde{k}$ is equal to k_c, where $\hbar^2 k_c^2/2m$ is the "unperturbed" unbound-state Coulomb energy in analytical perturbation theory.[7] The following relation is therefore valid:

$$1+(-1)^{2l+1}\exp(-2\pi Z/\tilde{k}a_0)$$
$$\approx 1+(-1)^{2l+1}\exp(-2\pi Z/k_c a_0)\,, \qquad (22)$$

exactly in the order of perturbation theory, when contributions of order b_2/Z^4 and smaller are neglected and to a high degree of accuracy for higher-order perturbation theory. We emphasize that in unbound-state perturbation theory[7] the unperturbed energy $\hbar^2 k_c^2/2m$ is calculated in terms of the actual energy $\hbar^2 k^2/2m$ from the perturbation series (A2) in the Appendix.

Introducing the perturbation approximation (A2) in the Appendix into the right-hand side of the exact formula (6) with Eqs. (7), and including contributions up to order b_2/Z^4 [hence neglecting contributions of order b_3/Z^5, $(b_1/Z^3)^2$, $b_1 b_2/Z^7$, etc.], we obtain after some calculations

$$c_l \approx \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2}\left[1+\frac{1}{4}l(l+1)(2l+1)\left[\frac{b_1}{Z^3}\frac{Z^2}{k_c^2 a_0^2}-\frac{5}{3}\frac{b_2}{Z^4}\frac{Z^4}{k_c^4 a_0^4}\right]+\cdots\right]\prod_{\substack{s=0\\ \text{or } 1/2}}^{l}(1+s^2 k_c^2 a_0^2/Z^2)$$
$$(\text{exact for } l=0)\,. \qquad (23)$$

It should be noted that (23) is formally obtained by replacing $-1/n^2$ by $(k_c a_0/Z)^2$ in the right-hand side of (10). In order to obtain an approximate value of c_l expressed in terms of k, one has to calculate k_c as a function of k from (A2) in the Appendix and introduce the resulting expression into (23).

Substituting (23) into the version of (12b) with (6) and (7) valid for $\tilde{k}>0$, and introducing into the resulting formula the approximation (22), we obtain the approximate perturbation-theory formula (94) in Ref. 7 [(A5) in the Appendix]. For the particular case $l=0$, the phase-integral formula and the perturbation-theory formula agree within the accuracy of the relation (22) for $\tilde{k}>0$, since (23) then involves no approximation. For integral values of $2l+1>1$ the perturbation-theory formula for $\tilde{k}>0$ is obtained from the phase-integral formula as a particular case, when the perturbation approximation [together with (22)] is introduced. For all non-negative integral values of $2l+1$, the perturbation-theory formulas break down for sufficiently small values of k, for which $\tilde{k}^2$ becomes nonpositive (and possibly complex), as is pointed out in footnote 21 of Ref. 7.

The formula for the normalized unbound-state wave function close to $r=0$ obtained from perturbation theory by McEnnan, Kissel, and Pratt[7] is according to the above analysis directly obtainable from the phase-integral formula (21) with (6) and (7), if the perturbation-theory approximation for c_l is carried through in a consistent way and the approximation (22) is introduced. The phase-integral formula (21) with (6) and (7) should be particularly satisfactory for small values of k, for which the perturbation-theory formula eventually breaks down. Hence, also for unbound states the perturbation-theory formula is obtained from the phase-integral formula as a particular case, when the perturbation approximation [together with (22) for unbound states] is introduced.

V. APPLICATION TO AN EXACTLY SOLUBLE MODEL

Considering as an illustration the l-dependent physical potential

$$V(r)=-\frac{\hbar^2 Z}{m a_0}\frac{\nu}{e^{\nu r}-1}+\frac{l(l+1)\hbar^2}{2m}e^{\nu r}\left[\frac{\nu}{e^{\nu r}-1}\right]^2$$
$$-\frac{l(l+1)\hbar^2}{2mr^2}\,,\quad \nu>0 \qquad (24)$$

we obtain from (2) with (3)

$$R(r,E)=k^2+\frac{2Z}{a_0}\frac{\nu}{e^{\nu r}-1}-l(l+1)e^{\nu r}\left[\frac{\nu}{e^{\nu r}-1}\right]^2,$$
$$\nu>0\,. \qquad (25)$$

With this expression for $R(r,E)$ the radial Schrödinger equation (1) is exactly soluble. It has been treated by Manning and Rosen,[12] by Infeld and Hull,[13] and more recently by Myhrman.[14,15]

Expanding the right-hand side of (25) in powers of r/a_0 and using (2) we obtain for the particular potential (24)

$$\frac{b_0}{Z^2}=\frac{k^2 a_0^2}{Z^2}-\frac{\nu a_0}{Z}+\frac{l(l+1)}{3}\left[\frac{\nu a_0}{2Z}\right]^2, \qquad (26a)$$

$$\frac{b_1}{Z^3}=\frac{2}{3}\left[\frac{\nu a_0}{2Z}\right]^2, \qquad (26b)$$

$$\frac{b_2}{Z^4}=-\frac{3l(l+1)}{20}\left[\frac{b_1}{Z^3}\right]^2, \qquad (26c)$$

$$\frac{b_3}{Z^5}=-\frac{1}{10}\left[\frac{b_1}{Z^3}\right]^2, \qquad (26d)$$

$$\frac{b_4}{Z^6}=\frac{l(l+1)}{28}\left[\frac{b_1}{Z^3}\right]^3, \qquad (26e)$$

$$\frac{b_5}{Z^7}=\frac{1}{70}\left[\frac{b_1}{Z^3}\right]^3. \qquad (26f)$$

Introducing Eqs. (26) into Eqs. (7), we obtain for the potential (24)

$$R_l=0,\quad 0<2l+1\leq 7 \tag{27}$$

which strongly indicates that $R_l=0$ for all values of l for the present potential. From (3), (6), (13), (26a), (26b), and (27) we obtain for positive integral values of $(2l+1)$ for the regular solution of (1) with (25)

$$\begin{aligned} c_l &= \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2} \prod_{\substack{s=0 \\ \text{or } 1/2}}^{l} \left[1+s^2\left[\frac{k^2a_0^2}{Z^2}-\frac{\nu a_0}{Z}\right]+s^4\left[\frac{\nu a_0}{2Z}\right]^2\right] \\ &= \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2} \prod_{\substack{s=0 \\ \text{or } 1/2}}^{l} \left[1+\frac{3}{2}\frac{b_1}{Z^3}\frac{Z^2s^2}{\tilde{k}^2a_0^2}\right]\left[1+\frac{\tilde{k}^2a_0^2s^2}{Z^2}\right], \end{aligned} \tag{28}$$

where

$$Z/\tilde{k}a_0=k/\nu-(k^2/\nu^2-2Z/a_0\nu)^{1/2}, \tag{29a}$$

and hence

$$2\tilde{k}/\nu=k/\nu+(k^2/\nu^2-2Z/a_0\nu)^{1/2}. \tag{29b}$$

For bound-state energies $E_n=\hbar^2k^2/2m$ the following relation is obtained from (10), (12) in Ref. 5, and (29a) if $Z>0$:

$$\tilde{k}^2a_0^2/Z^2=-1/n^2,\quad Z>0,\quad \text{for bound states}, \tag{30}$$

where

$$l+1\leq n<\left[\frac{2Z}{a_0\nu}\right]^{1/2}. \tag{31}$$

For the particular potential (24) the phase-integral formula (18) with (28) is exact according to Ref. 16 (cf. also Fig. 2).

For the comparison with perturbation-theory formulas we rewrite the exact formula (28) as

$$\begin{aligned} c_l &= \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2}\left[1+\frac{3}{2}\frac{b_1}{Z^3}\frac{Z^2}{\tilde{k}^2a_0^2}\sum_{\substack{s=0 \\ \text{or } 1/2}}^{l}s^2+\frac{9}{4}\frac{b_1^2}{Z^6}\frac{Z^4}{\tilde{k}^4a_0^4}\sum_{\substack{s',s \\ (s'<s)}}s'^2s^2+\cdots\right]\prod_{\substack{s=0 \\ \text{or } 1/2}}^{l}\left[1+\frac{\tilde{k}^2a_0^2}{Z^2}s^2\right] \\ &= \frac{(2Z/a_0)^{2l+1}}{[(2l+1)!]^2}\left[1+\frac{1}{4}l(l+1)(2l+1)\left[\frac{b_1}{Z^3}\frac{Z^2}{\tilde{k}^2a_0^2}\right.\right. \\ &\qquad \left.\left.+\frac{1}{40}(l-1)(2l-1)(5l+6)\frac{b_1^2}{Z^6}\frac{Z^4}{\tilde{k}^4a_0^4}\right]+\cdots\right]\prod_{\substack{s=0 \\ \text{or } 1/2}}^{l}\left[1+\frac{\tilde{k}^2a_0^2}{Z^2}s^2\right]. \end{aligned} \tag{32}$$

For $l=0$, $\frac{1}{2}$, and 1 the accidentally exact phase-integral formula (18) with (28) for bound states and the perturbation-theory formula (20) coincide exactly provided we truncate the perturbation series properly, i.e., we do not include the term $5b_2n^4/3Z^4$ in (20). Hence, for $l=\frac{1}{2}$ and 1 one deteriorates the accuracy of the perturbation formula by including the last-mentioned term in (20), whereas for $2l+1>3$ this term gives an insignificant contribution. This is due to the fact that the terms omitted in (20) contain b_3/Z^5 and $(b_1/Z^3)^2$, which according to (26c) and (26d) are of the same order of magnitude as b_2/Z^4 (if l is small). In other words, for the particular potential (24) one should either omit b_2/Z^4 contributions to the perturbation formulas or calculate further terms in the perturbation expansion. The last-mentioned alternative is, however, beyond the scope of the present investigation.

We shall now consider unbound states in the particular potential (24), i.e., states with $2mE/\hbar^2=k^2>0$. The exact expression for the limit of $u_N(l,k,r)$ when $r\to 0$ is, according to Ref. 16,

$$\begin{aligned} &\lim_{r\to 0}\left[\frac{u_N(l,k,r)}{r^{l+1}}\right] \\ &\quad=\left[\frac{k}{\pi}\right]^{1/2}\frac{\nu^{l+1/2}}{\Gamma(2l+2)}\left[\sinh(2\pi k/\nu)\Gamma\left[l+1+2i\frac{\tilde{k}}{\nu}\right]\Gamma\left[l+1-2i\frac{\tilde{k}}{\nu}\right]\Gamma\left[l+1+i\frac{Z}{a_0\tilde{k}}\right]\Gamma\left[l+1-i\frac{Z}{a_0\tilde{k}}\right]\right]^{1/2} \\ &\quad=\left[\frac{\pi k c_l}{1+(-1)^{2l+1}\exp(-2\pi Z/\tilde{k}a_0)}\right]^{1/2}\left[\frac{1-\exp(-4\pi k/\nu)}{1+(-1)^{2l+1}\exp(-4\pi\tilde{k}/\nu)}\right]^{1/2}. \end{aligned} \tag{33}$$

As was pointed out in Sec. III the perturbation-theory formula (94) in Ref. 7 [(A5) in the Appendix] for unbound states breaks down for sufficiently small values of the energy, for which $\tilde{k}^2$ becomes nonpositive (possibly complex). According to (29) this breakdown occurs for $k^2 < 2Zv/a_0$. Outside the breakdown region for the unbound-state perturbation theory, i.e., for $k^2 \geq 2Zv/a_0$, the ratio between the right-hand side of the exact formula (33) and the corresponding member of the phase-integral formula (21) becomes

$$[1-\exp(-4\pi k/v)]^{1/2}/[1+(-1)^{2l+1}\exp(-4\pi\tilde{k}/v)]^{1/2} ,$$

and inside the breakdown region for perturbation theory, i.e., for $0 < k^2 < 2Zv/a_0$, the ratio between these members becomes

$$\left\{\frac{1-\exp(-4\pi k/v)}{[1+(-1)^{2l+1}\exp(-4\pi\tilde{k}/v)][1+(-1)^{2l+1}\exp(-2\pi Z/\tilde{k}a_0)]}\right\}^{1/2}$$

$$=\left\{\frac{1-e^{-4\pi k/v}}{1+e^{-4\pi k/v}+(-1)^{2l+1}e^{-2\pi k/v}2\cosh\left[2\pi\left[\frac{k^2}{v^2}-\frac{2Z}{a_0v}\right]^{1/2}\right]}\right\}^{1/2} ,$$

the last equality being obtained with the aid of (29a) and (29b).

According to the analysis in connection with bound states above, for the particular potential (24) we shall henceforth omit b_2/Z^4 contributions to the perturbation formulas, which for unbound states corresponds to putting $k_c = \tilde{k}$ according to (13) and (A2) in the Appendix. For $l = 0$, $\frac{1}{2}$, and 1, the right-hand side of (33) with (32) is equal to the right-hand member of (A5) in the Appendix with the b_2/Z^4 term and higher terms omitted (and hence with $k_c = \tilde{k}$) multiplied by

$$[1-\exp(-4\pi k/v)]^{1/2}/[1+(-1)^{2l+1}\exp(-4\pi\tilde{k}/v)]^{1/2} .$$

However, for $k \geq (2Zv/a_0)^{1/2}$ this factor is precisely the ratio between the right-hand side of the exact formula (33) and the corresponding term of the phase-integral formula (21). Hence, for $l = 0$, $\frac{1}{2}$, and 1 and $k \geq (2Zv/a_0)^{1/2}$ the properly truncated perturbation formula (A5) in the Appendix is as exact as our phase-integral formula (21) with (28). It should be noted that according to Sec. IV for *s* states this is true for any potential. For $2l+1 > 3$, however, the perturbation-theory formula (A5) in the Appendix gives, according to (33) with (32), a large error if $\tilde{k}^2a_0^2/Z^2$ is small enough. For $k^2 < 2Zv/a_0$ the perturbation-theory formulas, as mentioned above, break down completely.

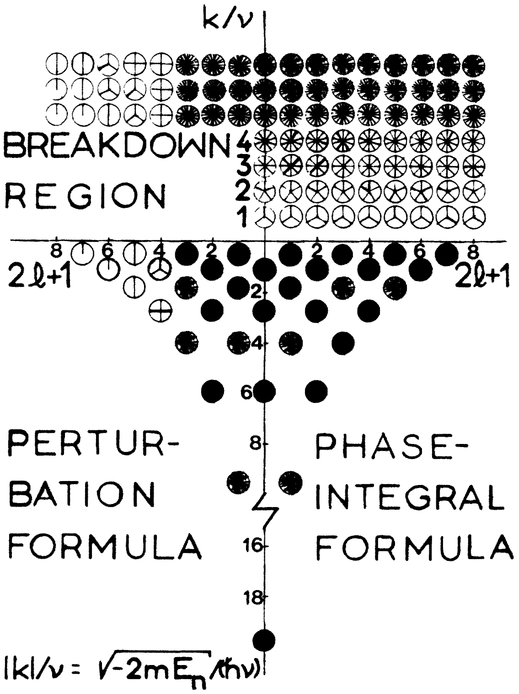

FIG. 2. Relative error of the perturbation-theory formulas (properly truncated) and the phase-integral formulas for the normalized wave function close to the origin for the potential (24) with $va_0/Z = \frac{1}{10}$. A "wheel" with *m* "spokes" indicates a point where the relative error is greater than or equal to 10^{-m-1} and less than 10^{-m}. Solid circles in the bound-state region indicate points where the formula is exact.

For bound and unbound states a numerical illustration with b_2/Z^4 contributions to the respective perturbation formula omitted is given in Fig. 2. As mentioned in the Introduction, Fröman, Fröman, and the present author[16] exploited the particular model potential (24) in order to obtain the phase-integral formula (18) with (6) and (7) for bound states and formula (21) with (6) and (7) for unbound states. Therefore, one cannot draw too strong inferences from Fig. 2 as far as the respective phase-integral formula is concerned. It should be noted that for a problem with one classically allowed region and with only real turning points, which contribute, the respective phase-integral formula should give excellent results for small absolute values of *k*. The discrepancy between the phase-integral formula and the exact wave function for small positive values of k/v illustrated in Fig. 2 is due to the presence of extra complex zeros of $Q^2(r,E)$, the contributions of which cannot be neglected, if k/v is sufficiently small.[27]

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APPENDIX

The perturbation approximation (5) in Ref. 10 for the bound-state energy eigenvalue with quantum numbers $n = n' + l + 1$ and l is, in our notation

$$\frac{b_0}{Z^2} = \frac{2m}{\hbar^2}\frac{a_0^2}{Z^2}E_n - \frac{2m}{\hbar^2}\frac{a_0^2}{Z^2}\lim_{r\to 0}[V(r)+\hbar^2 Z/ma_0 r]$$

$$\approx -\frac{1}{n^2}+\frac{1}{2}\frac{b_1}{Z^3}[-3n^2+l(l+1)]+\frac{1}{2}\frac{b_2}{Z^4}n^2[-5n^2+3l(l+1)-1]+\cdots \,. \tag{A1}$$

For a derivation of (A1) see Sec. II of Ref. 7.

In Ref. 7 an unbound-state unperturbed Coulomb energy $\hbar^2 k_c^2/2m$ is introduced, and the continuum energy $\hbar^2 k^2/2m$ satisfies an equation, which is formally obtained by replacing $-1/n^2$ by $(k_c a_0/Z)^2$ in the right-hand side of (A1):

$$\frac{b_0}{Z^2} = \left[\frac{ka_0}{Z}\right]^2 - \frac{2m}{\hbar^2}\frac{a_0^2}{Z^2}\lim_{r\to 0}[V(r)+\hbar^2 Z/ma_0 r]$$

$$\approx \left[\frac{k_c a_0}{Z}\right]^2+\frac{1}{2}\frac{b_1}{Z^3}\left[3\left[\frac{k_c a_0}{Z}\right]^{-2}+l(l+1)\right]+\frac{1}{2}\frac{b_2}{Z^4}\left[\frac{k_c a_0}{Z}\right]^{-2}\left[-5\left[\frac{k_c a_0}{Z}\right]^{-2}-3l(l+1)+1\right]+\cdots \,. \tag{A2}$$

In other words, the unperturbed Coulomb energy is chosen such that the relation to the perturbed energy $\hbar^2 k^2/2m$ is the same as for bound states.

We denote by $F_l(-Z/a_0 k_c, k_c r)$ the regular Coulomb wave function normalized to be equal to $\sin[k_c r + (Z/a_0 k_c)\ln(2k_c r) - \frac{1}{2}l\pi + \sigma_l(-Z/a_0 k_c)]$ as $r\to\infty$. The following conjecture was made by Pratt and Tseng[29] based on empirical observations for unbound s states:

$$\lim_{r\to 0}\left[\frac{1}{k^{1/2}}\frac{u_N(0,k,r)}{r}\right] \approx \lim_{r\to 0}\left[\frac{1}{k_c^{1/2}}\frac{F_0(-Z/a_0 k_c, k_c r)}{r}\right], \tag{A3}$$

where $u_N(l,k,r)$ is normalized to be equal to $\sin[kr - \frac{1}{2}l\pi + \delta_l(k)]$ as $r\to\infty$. Calculating the right-hand side of (A3) with the aid of Chap. 14 (in particular Sec. 14.1) in Ref. 28, we obtain

$$\lim_{r\to 0}\left[\frac{u_N(0,k,r)}{r}\right] \approx (\pi k)^{1/2}(2Z/a_0)^{1/2}\left[1-\exp\left[-\frac{2\pi Z}{k_c a_0}\right]\right]^{-1/2}. \tag{A4}$$

Through rather lengthy calculations formula (A4) is generalized into the following approximate perturbation-theory formula [cf. Eq. (94) in Ref. 7]:

$$\lim_{r\to 0}\left[\frac{u_N(l,k,r)}{r^{l+1}}\right]$$

$$\approx (\pi k)^{1/2}\frac{(2Z/a_0)^{l+1/2}}{(2l+1)!}\left[1+(-1)^{2l+1}\exp\left[-\frac{2\pi Z}{k_c a_0}\right]\right]^{-1/2}$$

$$\times\left[1+\frac{1}{4}l(l+1)(2l+1)\left[\frac{b_1}{Z^3}\frac{Z^2}{k_c^2 a_0^2}-\frac{5}{3}\frac{b_2}{Z^4}\frac{Z^4}{k_c^4 a_0^4}\right]+\cdots\right]^{1/2}\prod_{\substack{s=0\\ \text{or } 1/2}}^{l}\left[1+\frac{s^2 k_c^2 a_0^2}{Z^2}\right]^{1/2}. \tag{A5}$$

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