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Generalization of the Fermi-Segrè formula

N. Fröman and P. O. Fröman

Institute of Theoretical Physics, University of Uppsala, Thunbergsvägen 3, S-752 38 Uppsala, Sweden

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Résumé. — Par l'usage d'une méthode d'intégrale de phase nous obtenons une généralisation de la formule non-relativiste de Fermi-Segrè en une formule qui est valable aussi pour des valeurs du nombre quantique l du moment cinétique orbital différentes de zéro. La formule ainsi obtenue, qui exprime la limite de $u(r)/r^{l+1}$ quand $r \rightarrow 0$, où $u(r)$ est la fonction d'onde radiale normalisée d'un état lié, par la dérivée du niveau d'énergie E_n par rapport au nombre quantique radial n' , est une amélioration et une généralisation d'une formule obtenue par M. A. Bouchiat et C. Bouchiat. Elle se réduit à leur formule pour une classe particulière de potentiels et d'états très excités correspondant à des valeurs de l pas trop grandes, et elle se réduit à la formule de Fermi-Segrè quand, pour un système atomique ou ionique, $l = 0$. Nous examinons la précision de notre formule, ainsi que celle de la formule de Bouchiat-Bouchiat, par l'application à un modèle exactement soluble.

On peut aussi écrire notre formule sous une autre forme en remplaçant dE_n/dn' par une certaine intégrale le long d'une courbe fermée (autour des points limites généralisés du mouvement classique) dans le plan complexe r . Cette intégrale dépend du potentiel physique $V(r)$ dans lequel la particule se déplace, ainsi que des dérivées de ce potentiel par rapport à r .

Nous montrons aussi que l'on peut exprimer la valeur exacte de la limite de $u(r)/r^{l+1}$ quand $r \rightarrow 0$ comme la valeur moyenne d'une certaine fonction dépendant du potentiel physique $V(r)$ et r ainsi que de l et E_n .

Abstract. — A generalization of the non-relativistic Fermi-Segrè formula into a formula which is valid also for angular momentum quantum numbers l different from zero, is derived by means of a phase-integral method. The formula thus obtained, which gives an expression for the limit of $u(r)/r^{l+1}$ as $r \rightarrow 0$, where $u(r)$ is a normalized bound-state radial wavefunction, in terms of the derivative of the energy level E_n with respect to the radial quantum number n' , is an improvement and generalization of a formula which has been obtained by M. A. Bouchiat and C. Bouchiat. It reduces to their formula for a particular class of potentials and highly excited states with not too large values of l , and it reduces to the Fermi-Segrè formula when $l = 0$. The accuracy of our formula, as well as that of the Bouchiat-Bouchiat formula, is investigated by application to an exactly soluble model.

The formula obtained can also be written in another form by replacing dE_n/dn' by an expression involving a closed-loop integral in the complex r -plane (around the generalized classical turning points), the integrand being a phase-integral quantity expressed in terms of the potential in which the particle moves.

It is also shown that the exact value of the limit of $u(r)/r^{l+1}$ as $r \rightarrow 0$ can be expressed as an expectation value of a certain function depending on the physical potential $V(r)$ and r as well as on l and E_n .

1. Introduction. — The non-relativistic Fermi-Segrè formula [1-5] gives a remarkably simple expression for the value of the normalized wavefunction of an atomic or ionic s-electron at the position of the nucleus. A generalization, which removes the restriction of an s-electron, has been given by M. A. Bouchiat and C. Bouchiat [6] ⁽¹⁾. Their treatment is, however,

restricted to highly excited states with comparatively small values of the angular momentum quantum number l of a valence electron in an atom. The purpose of the present paper is to derive, in a simple and straightforward way, a more accurate and more general generalization of the Fermi-Segrè formula for which these restrictions are largely removed. A generalization to $l \neq 0$ of our previously published procedure for deriving the Fermi-Segrè formula [5] seems to be useful only for small values of the angular momentum quantum number l , and therefore we shall use another procedure in the present paper.

2. Derivation of the generalized Fermi-Segrè formula. — Consider a non-relativistic electron which

⁽¹⁾ When the manuscript of the present paper was ready for publication, we noticed that formulas related to the Bouchiat-Bouchiat formula have also been obtained by McEnnan, Kissel and Pratt [Eqs. (36) and (101) in *Phys. Rev.* **A13** (1976) 532-559, where the last mentioned equation is to be corrected according to *Phys. Rev.* **A13** (1976) 2325] and by Iwinski, Kim and Pratt [Eqs. (A. 8), (A. 9) and (A. 10) in *Phys. Rev.* **C19** (1979) 1924-1937; *Phys. Rev.* **A22** (1980) 1358-1360].

moves in a local, spherically symmetric physical potential $V(r)$ and has the orbital angular momentum quantum number l . The corresponding radial Schrödinger equation can be written

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

where

$$Q^2(r, E) = \frac{2m}{\hbar^2} (E - V^{\text{eff}}(r)) \quad (2)$$

with the effective potential $V^{\text{eff}}(r)$ defined by

$$V^{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \quad (3)$$

the notations being obvious.

Let $u_1(r, E)$ and $u_2(r, E)$ be two real solutions of (1), fulfilling the conditions that $u_1 \rightarrow 0$ as $r \rightarrow +0$ and $u_2 \rightarrow 0$ as $r \rightarrow +\infty$. Furthermore, it is assumed that

$$u_1(r, E_n) = u_2(r, E_n) = u(r, E_n), \quad (4)$$

where E_n is an eigenvalue of (1) with the radial quantum number n , and $u(r, E_n)$ is the corresponding (unnormalized) eigenfunction. By means of a method, which has been devised by Furry [7], the integral (in our case from $r = +0$ to $r = +\infty$) of the square of the eigenfunction $u(r, E_n)$ can be expressed in terms of the energy derivatives of the functions $u_1(r, E)$ and $u_2(r, E)$ evaluated for $E = E_n$ at an arbitrary point r in the interval of integration. Furry's general result has been simplified in a very convenient way by Yngve [8], who noticed that Furry's expression for the above-mentioned normalization integral (obtained by summing equations (43) and (44) in [7]) can, apart from a constant factor, be written as the derivative with respect to the energy of the Wronskian of u_1 and u_2 ; cf. equations (6) and (2) in [8]. The formula for the normalization integral, written in this simplified way, and adapted to the present situation of a radial Schrödinger equation, is

$$\int_0^\infty u^2(r, E_n) dr = \frac{\hbar^2}{2m} \left\{ \frac{\partial}{\partial E} \left(u_1 \frac{\partial u_2}{\partial r} - u_2 \frac{\partial u_1}{\partial r} \right) \right\}_{E=E_n}. \quad (5)$$

It should be noted that the expression in the right-hand member of (5) is independent of r , since the Wronskian of u_1 and u_2 is known to be independent of r .

When the potential is smooth, except for isolated singularities, the radial Schrödinger equation (1) can be solved by means of the arbitrary-order phase-integral approximations described in [9-11] and on p. 126-131 in [12], where the notations to be used are also defined. We shall assume $V(r)$ to have at the most a Coulomb singularity at the origin. The phase-

integral approximations are then, for all values of l , valid also at the origin, if we choose $Q_{\text{mod}}^2(r, E)$ such that (cf. [11] and p. 126-131 in [12])

$$\lim_{r \rightarrow 0} r^2 [Q^2(r, E) - Q_{\text{mod}}^2(r, E)] = 1/4. \quad (6)$$

In particular one can fulfil (6) by choosing

$$Q_{\text{mod}}^2(r, E) = Q^2(r, E) - \frac{1}{4r^2}, \quad (7)$$

but it is not necessary to specify a particular choice of $Q_{\text{mod}}^2(r)$ here.

It is convenient to introduce the modified effective potential $V_{\text{mod}}^{\text{eff}}(r)$, which by definition shall fulfil the formula (cf. (2))

$$Q_{\text{mod}}^2(r, E) = \frac{2m}{\hbar^2} (E - V_{\text{mod}}^{\text{eff}}(r)). \quad (8)$$

According to (2), (3) and (8) the choice (7) of $Q_{\text{mod}}^2(r, E)$ is equivalent to choosing

$$V_{\text{mod}}^{\text{eff}}(r) = V(r) + \frac{\hbar^2(l+1/2)^2}{2mr^2}, \quad (7')$$

but, as already mentioned, it is not necessary to specify a particular choice of $V_{\text{mod}}^{\text{eff}}(r)$ here.

The previously defined function $u_1(r, E)$, which, since $V(r)$ is assumed to have at the most a Coulomb singularity at the origin, for small values of r has the behaviour

$$u_1(r, E) = cr^{l+1} + \text{higher powers of } r, \quad (9)$$

where c is a so far unspecified constant factor, is, in the classically forbidden region (in the generalized sense) adjacent to the origin (cf. Fig. 1), represented by the phase-integral formula

$$u_1(r, E) = cC |q^{-1/2}(r, E)| \times \exp \left\{ - \left| \frac{i}{2} \int_{\Gamma_1'(r)} q(r, E) dr \right| \right\}, \quad 0 < r < r_1, \quad (10)$$

where $\Gamma_1'(r)$ is a contour shown in figure 1, and C is a certain r -independent positive factor. This formula is very accurate when r lies close to the origin, provided that the condition (6) is fulfilled and the factor C is chosen appropriately. We shall now assume that the physical potential $V(r)$ is approximately given by

$$V(r) = -\frac{Ze^2}{r} + V_0, \quad Z > 0, \quad (11)$$

in the region from the origin to the first generalized classical turning point r_1 (cf. Fig. 1) as well as in a small region around r_1 , which according to (2), (3) and (11) means that in these regions, unless cancella-

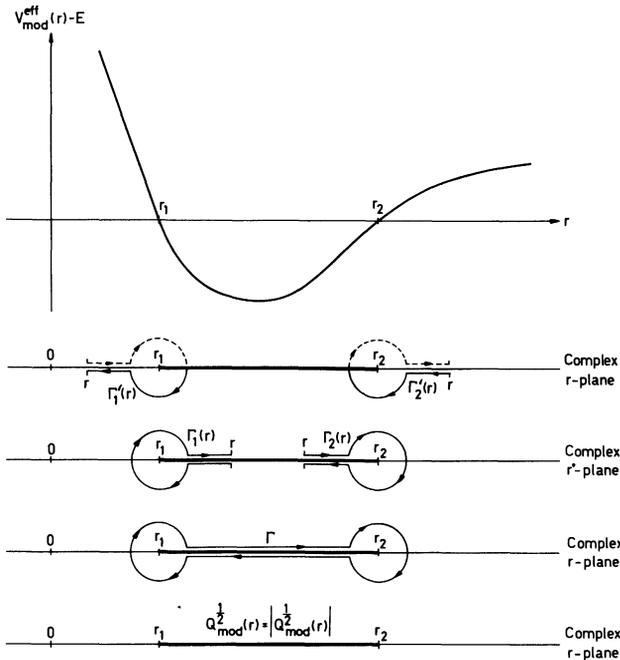


Fig. 1. — This figure shows $V_{\text{mod}}^{\text{eff}}(r) - E$ (cf. (8)) for the case of a bound-state with two generalized classical turning points, r_1 and r_2 . The contours of integration used in the paper are also shown. The heavy line between r_1 and r_2 in the complex r -plane is a cut. On the upper lip of this cut $Q_{\text{mod}}^{1/2}(r, E)$ is chosen to be positive, and hence $q^{1/2}(r, E)$ is also positive there. Note that by turning $\Gamma_1'(r)$ continuously one can make it coincide with $\Gamma_1(r)$, even as regards the direction of integration. The corresponding assertion is also true for the contours $\Gamma_2'(r)$ and $\Gamma_2(r)$.

tions occur, $Q^2(r, E)$ is approximately given by the formula

$$Q^2(r, E) = \frac{2m(E - V_0)}{\hbar^2} + \frac{2Z}{a_0 r} - \frac{l(l+1)}{r^2} \quad (12)$$

in which

$$a_0 = \hbar^2/(me^2) \quad (13)$$

is the Bohr radius. We emphasize that to derive our generalization of the Fermi-Segrè formula it is not necessary to assume (12) to be valid in the classically allowed region so far to the right of r_1 (cf. Fig. 1) that the phase-integral approximations are valid there. Since the radius of the circular part of the contour of integration $\Gamma_1'(r)$ shown in figure 1 can be made fairly small, while the integrand $q(r, E)$ remains smooth and depends smoothly on the parameters appearing in the problem, our assumption concerning the region of validity of (11) in the complex r -plane is sufficient for making, on the contour $\Gamma_1'(r)$, the actual expression for $q(r, E)$ approximately equal to that obtained by using for $Q^2(r, E)$ the expression (12) and for $Q_{\text{mod}}^2(r, E)$ an appropriate expression fulfilling (6). Recalling (1) and (12) and the expressions for the phase-integral approximations of arbitrary order, we therefore realize that, if, when r lies between 0 and r_1 and in a small region around r_1 , the difference

$Q^2(r, E) - Q_{\text{mod}}^2(r, E)$ depends only on r but not appreciably on any of the parameters appearing in $Q^2(r, E)$, the factor C in (10) depends essentially only on the quantities $2m(E - V_0)/\hbar^2$, $2Z/a_0$ and l . This fact is exploited in the determination of the explicit expression for C , carried out in Appendix A.

Although we shall not restrict our treatment to potentials associated with valence electrons in atoms or ions, we remark that for that particular class of potentials the energy levels E_n of the bound states are negative, and, since the screening of the core electrons makes V_0 positive, the inequality $E_n < V_0$ is valid. We also remark that for a heavy atom or ion the constant V_0 in (11) can be determined approximately by the use of a statistical model for the atom or ion. Using the Thomas-Fermi model without Amaldi's correction (cf. p. 116-122 in volume II of [13]), one obtains in the case of a neutral atom

$$V_0 = 1.79 Z^{4/3} e^2/a_0;$$

cf. p. 917 in [6].

We have assumed $V(r)$ to be approximately given by (11) in the interval $(0, r_1)$ and in a small region around r_1 . As the only further essential restriction on the smooth potential $V(r)$ we shall assume that the modified effective potential $V_{\text{mod}}^{\text{eff}}(r)$, which need not be chosen according to (7') but should be chosen such that (6) is fulfilled, has the shape of an unspecified single-well potential in the interval $0 < r < \infty$; cf. figure 1. Whether $V_{\text{mod}}^{\text{eff}}(r)$ remains finite or tends to $+\infty$ as $r \rightarrow +\infty$ is immaterial. Using a connection formula (cf. equations (21) and (22) in [10]) valid for a general smooth potential, when arbitrary-order phase-integral approximations are used, we obtain from (10) the phase-integral formula

$$u_1(r, E) = 2cCq^{-1/2}(r, E) \times \cos\left(\frac{1}{2} \int_{\Gamma_1(r)} q(r, E) dr - \frac{1}{4}\pi\right), \quad r_1 < r < r_2, \quad (14)$$

where $\Gamma_1(r)$ is a contour shown in figure 1, and the phase of $Q_{\text{mod}}^{1/2}(r)$, which determines that of $q^{1/2}(r, E)$, is chosen as indicated in the same figure.

For $r > r_2$ (cf. Fig. 1) the function $u_2(r, E)$ is given by the phase-integral formula

$$u_2(r, E) = (-1)^n cC |q^{-1/2}(r)| \times \exp\left\{-\left|\frac{1}{2} \int_{\Gamma_2'(r)} q(r, E) dr\right|\right\}, \quad r > r_2, \quad (15)$$

where $\Gamma_2'(r)$ is a contour shown in figure 1, and the constant factor in the right-hand member of (15) has been chosen such that (4) is fulfilled, as will be seen presently. Using the same connection formula for phase-integral approximations of arbitrary order as previously, i.e. equations (21) and (22) in [10], we obtain from (15) the phase-integral formula

$$\begin{aligned}
u_2(r, E) &= 2(-1)^{n'} c C q^{-1/2}(r, E) \cos\left(\frac{1}{2} \int_{\Gamma_2(r)} q(r, E) dr - \frac{1}{4} \pi\right) \\
&= 2(-1)^{n'} c C q^{-1/2}(r, E) \cos\left(\frac{1}{2} \int_{\Gamma_1(r)} q(r, E) dr + \frac{1}{4} \pi - \frac{1}{2} \int_{\Gamma} q(r, E) dr\right), \quad r_1 < r < r_2, \quad (16)
\end{aligned}$$

where $\Gamma_2(r)$ and Γ are contours shown in figure 1. Since the eigenvalues $E_{n'}$ fulfil the quantization condition (cf. [9] and [11])

$$\frac{1}{2} \int_{\Gamma} q(r, E_{n'}) dr = \left(n' + \frac{1}{2}\right) \pi, \quad (17)$$

it follows from (14) and (16) that (4) is fulfilled, as already anticipated above.

From (14) and (16) we obtain

$$\begin{aligned}
u_1 \frac{\partial u_2}{\partial r} - u_2 \frac{\partial u_1}{\partial r} &= 4(-1)^{n'} c^2 C^2 \times \\
&\times \sin\left(\frac{1}{2} \int_{\Gamma} q(r, E) dr - \frac{1}{2} \pi\right). \quad (18)
\end{aligned}$$

Inserting (18) into (5) and using (17), we get the phase-integral formula

$$\begin{aligned}
\int_0^{\infty} u^2(r, E_{n'}) dr &= \\
&= \frac{2 \hbar^2 c^2 C^2}{m} \left(\frac{\partial}{\partial E} \frac{1}{2} \int_{\Gamma} q(r, E) dr\right)_{E=E_{n'}}. \quad (19)
\end{aligned}$$

Requiring that the eigenfunction $u(r, E_{n'})$ be normalized to unity, i.e., that

$$\int_0^{\infty} u^2(r, E_{n'}) dr = 1, \quad (20)$$

we obtain from (19) the formula

$$c = \frac{1}{C} \left(\frac{m}{2 \hbar^2}\right)^{1/2} \left(\frac{\partial}{\partial E} \frac{1}{2} \int_{\Gamma} q(r, E) dr\right)_{E=E_{n'}}^{-1/2}, \quad (21)$$

where the sign of c has been chosen conveniently. The energy derivative in (21) can be evaluated in two quite different ways, the usefulness of which depends on the information available. Either one can

use the approximate formula (cf. [14], Eq. (26) in [15], and our formula (2))

$$\begin{aligned}
\frac{\partial}{\partial E} \frac{1}{2} \int_{\Gamma} q(r, E) dr &= \frac{1}{2} \int_{\Gamma} \frac{1}{2} \frac{\partial Q^2(r, E)}{\partial E} \frac{dr}{q(r, E)} \\
&= \frac{m}{\hbar^2} \frac{1}{2} \int_{\Gamma} \frac{dr}{q(r, E)}, \quad (22)
\end{aligned}$$

getting

$$c = \frac{1}{C \sqrt{2}} \left(\frac{1}{2} \int_{\Gamma} \frac{dr}{q(r, E_{n'})}\right)^{-1/2}, \quad (23)$$

or one can use the approximate formula yielded by (17) :

$$\left(\frac{\partial}{\partial E} \frac{1}{2} \int_{\Gamma} q(r, E) dr\right)_{E=E_{n'}} = \pi dn'/dE_{n'}, \quad (24)$$

getting

$$c = \frac{1}{C} \left(\frac{m}{2 \pi \hbar^2} dE_{n'}/dn'\right)^{1/2}. \quad (25)$$

For the evaluation of c according to (23) one must know the analytic expression for the potential $V(r)$ on the contour Γ , while for the evaluation of c according to (25) one can use values of $dE_{n'}/dn'$ obtained from experimental data.

To determine the as yet unspecified expression for C , we consider the particular case of a hydrogen-like ion and utilize the properties of C , mentioned below (13), to extend the validity of the result to the more general assumptions introduced in the derivation of (23) and (25). The details of the derivation are, as already mentioned, given in Appendix A. The resulting expression for C is given by the formula (A.23), which is expected to be valid when, in addition to the assumptions introduced in connection with (11) and (12) and between (13) and (14), the condition (A.24) is fulfilled, but is expected to be invalid when the condition (A.25) is violated.

Using (4), (9) and (A.23), we now obtain from (23) and (25) the two alternative formulas

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \frac{(2\pi)^{1/2}}{\left(\frac{1}{2} \int_{\Gamma} \frac{dr}{q(r, E_{n'})}\right)^{1/2}} \frac{\prod_{s=0}^l \left\{ 1 + \left(\frac{a_0}{Z}\right)^2 \frac{2m(E_{n'} - V_0)}{\hbar^2} s^2 \right\}^{1/2}}{\left[1 - H(E_{n'} - V_0) \exp \left\{ -2\pi \frac{Z}{a_0} \left(\frac{\hbar^2}{2m(E_{n'} - V_0)}\right)^{1/2} \right\} \right]^{1/2}} \quad (26)$$

and

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \left(\frac{2m}{\hbar^2} dE_{n'}/dn' \right)^{1/2} \frac{\prod_{s=0}^l \left\{ 1 + \left(\frac{a_0}{Z} \right)^2 \frac{2m(E_{n'} - V_0)}{\hbar^2} s^2 \right\}^{1/2}}{\left[1 - H(E_{n'} - V_0) \exp \left\{ -2\pi \frac{Z}{a_0} \left(\frac{\hbar^2}{2m(E_{n'} - V_0)} \right)^{1/2} \right\} \right]^{1/2}} \quad (27)$$

where $H(E - V_0)$ is Heaviside's unit step function defined by (A.22). The condition (A.24), as well as the less restrictive condition (A.25), with $E = E_{n'}$, ensures that the product with respect to s occurring in (26) and (27) cannot assume imaginary values, and therefore these formulas give positive values for the limit of $u(r, E_{n'})/r^{l+1}$ when $r \rightarrow 0$, in agreement with our assumption at the beginning of this paper that the wavefunctions are chosen to be real.

It is now convenient to summarize the conditions for the validity of the formulas (26) and (27), which are the main results in the present paper. The expression (11) for the physical potential $V(r)$ shall be valid in the interval from the origin to the first generalized classical turning point r_1 as well as in a small region around r_1 . The modified effective potential $V_{\text{mod}}^{\text{eff}}(r)$ need not be chosen according to (7) but should be chosen such that (6) is fulfilled, which according to (2) and (8) means that the quantity $r^2[V_{\text{mod}}^{\text{eff}}(r) - V^{\text{eff}}(r)]$ should tend to $\hbar^2/(8m)$ as r tends to zero. Furthermore, when r lies in the interval $(0, r_1)$ and in a small region around r_1 , the difference $Q^2(r, E) - Q_{\text{mod}}^2(r, E)$ shall depend only on r and be approximately independent of the parameters appearing in $Q^2(r, E)$; cf. (12). Moreover, in the interval $0 < r < \infty$, $V_{\text{mod}}^{\text{eff}}(r)$ shall be a single-well potential. Finally, the condition (A.24) or at least the condition (A.25), with $E = E_{n'}$, should be fulfilled. These conditions are automatically fulfilled when $E_{n'} - V_0$ is positive, but when $E_{n'} - V_0$ is negative, they impose, for fixed $Z (> 0)$ and l , lower bounds on the values of $E_{n'} - V_0$.

Our generalization (27) of the Fermi-Segrè formula, as well as the investigation of its accuracy which will be described in section 3, was presented

at the Swedish National Physics Conference in Linköping 13-15 June 1978 (p. 35 in the conference proceedings). For the particular case that $E_{n'} > V_0$ an equivalent formula was later given in a report by Bell and Pasupathy (Ref. TH. 2649, CERN, 26 March 1979). However, their derivation requires unnecessarily restrictive assumptions. As we have already pointed out, it is not necessary to assume that the formula (11) in the present paper is valid up to those points in the classically allowed region, where the asymptotic (JWKB) expression for the wavefunction can be used. Furthermore, as we have also seen, the derivation of the formula need not be restricted to the use of the first-order JWKB approximation, but can be carried out with the aid of phase-integral approximations of arbitrary order. The derivation of the formula under these less restrictive assumptions shows that the formula is much more accurate and has a larger range of validity than one might expect from the derivation given by Bell and Pasupathy. Their numerical illustration of the accuracy of the formula for the charmonium potential

$$V(r) = -\alpha/r + fr,$$

i.e. for a model where $E_{n'} > V_0$, is a complement to our investigation of the accuracy of (27) for a model where $E_{n'} < V_0$, which will be described in section 3.

To prepare for the discussion of the connection between our generalization (27) of the Fermi-Segrè formula and the generalization given by M. A. Bouchiat and C. Bouchiat [6], it is convenient to use the definition (13) of the Bohr radius to rewrite (27) in the form

$$\lim_{r \rightarrow 0} u(r, E_{n'})/r^{l+1} = \frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \left(\frac{2}{e^2 a_0} dE_{n'}/dn' \right)^{1/2} \times \frac{\prod_{s=0}^l \left\{ 1 + \frac{2(E_{n'} - V_0)}{(\alpha Z)^2 mc^2} s^2 \right\}^{1/2}}{\left[1 - H(E_{n'} - V_0) \exp \left\{ -2\pi \left(\frac{(\alpha Z)^2 mc^2}{2(E_{n'} - V_0)} \right)^{1/2} \right\} \right]^{1/2}} \quad (27')$$

where

$$\alpha = e^2/(\hbar c) \approx 1/137 \quad (28)$$

is the fine structure constant. The conditions for the

validity of (27') are summarized in the paragraph following that containing (26) and (27). Of these conditions the condition (A.25) with $E = E_{n'}$ is now

conveniently rewritten with the aid of the definitions (13) and (28) in the form

$$\frac{2(E_{n'} - V_0)}{(\alpha Z)^2 mc^2} (l + 1/2)^2 > -1. \quad (29)$$

When $E_{n'} > V_0$ this condition is automatically fulfilled for all values of l , but when $E_{n'} < V_0$ it gives, when $Z (> 0)$ and l are given, a lower bound for the values of $E_{n'} - V_0$.

In passing we remark that by putting $l = 0$ in (27') we obtain the formula

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r} = \frac{\left(4 \pi \frac{Z}{\pi a_0^2 e^2} dE_{n'}/dn' \right)^{1/2}}{\left[1 - H(E_{n'} - V_0) \exp \left\{ -2 \pi \left(\frac{(\alpha Z)^2 mc^2}{2(E_{n'} - V_0)} \right)^{1/2} \right\} \right]^{1/2}}, \quad (27'')$$

which reduces to the non-relativistic Fermi-Segrè formula (cf. Eq. (18) in [5]), when the term in the denominator, containing Heaviside's unit step function, can be neglected. We shall now verify that this is the case when the assumptions introduced in the derivation of the Fermi-Segrè formula in [5] are fulfilled. Recalling (12), we see that the quantity B in equation (7.14) in [16] is $B = 2Z/a_0$. In order that, for $l = 0$, the Coulomb term in (12) shall dominate (cf. p. 74 in [16] and p. 2065 in [5]), we require that $r \ll Ze^2/|E - V_0|$; cf. (13). According to p. 74 in [16] the appropriate μ -integral is therefore of the order

$$\begin{aligned} (Br)^{-1/2} &= [(2Z/a_0)r]^{-1/2} \\ &\gg [(2Z/a_0)Ze^2/|E - V_0|]^{-1/2} = \\ &= 1/2 [(\alpha Z)^2 mc^2 / (2|E - V_0|)]^{-1/2}; \end{aligned}$$

cf. (13) and (28). In order that $\mu \ll 1$ it is therefore necessary that $[(\alpha Z)^2 mc^2 / (2|E - V_0|)]^{1/2}$ is much larger than unity. Hence the term in the denominator of (27''), which contains Heaviside's unit step function, is negligible, when the conditions introduced in the derivation of the Fermi-Segrè formula in [5] are fulfilled.

We shall now return to (27') and introduce the approximations needed to arrive at the Bouchiat-Bouchiat formula. Assuming that $|E_{n'} - V_0|$ is sufficiently small and that l is not too large, we obtain the approximate formula

$$\begin{aligned} \prod_{s=0}^l \left\{ 1 + \frac{2(E_{n'} - V_0)}{(\alpha Z)^2 mc^2} s^2 \right\}^{1/2} &\approx \\ &\approx 1 + \frac{E_{n'} - V_0}{(\alpha Z)^2 mc^2} \sum_{s=0}^l s^2 = \\ &= 1 + \frac{E_{n'} - V_0}{(\alpha Z)^2 mc^2} \frac{l(l+1)(2l+1)}{6}, \quad (30) \end{aligned}$$

which (according to a somewhat more careful derivation) is valid if the condition

$$\frac{2|E_{n'} - V_0|}{(\alpha Z)^2 mc^2} l(l+1) \frac{l+1/2}{6} \ll 1 \quad (31)$$

is fulfilled. Inserting (30) into (27'), and restricting ourselves, for the sake of simplicity in the writing of the resulting formula, to considering only cases where $E_{n'} - V_0 < 0$, we obtain

$$\begin{aligned} \lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} &= \\ &= \frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \left(\frac{2}{e^2 a_0} dE_{n'}/dn' \right)^{1/2} \times \\ &\times \left(1 - \frac{V_0 - E_{n'}}{(\alpha Z)^2 mc^2} \frac{l(l+1)(2l+1)}{6} \right), \quad E_{n'} < V_0. \quad (32) \end{aligned}$$

This approximate formula is equivalent to equation (A1.50) in [6], which was, however, derived on the unnecessarily restrictive assumption that the physical potential is Coulombic for large values of r . In our derivation of the general formulas (26) and (27), and hence also in our derivation of (27') and (32), the only assumption concerning the potential in the region $r > r_1$ was that the modified effective potential has the shape of a smooth single-well potential, and we performed the derivation with the aid of phase-integral approximations of arbitrary order. The conditions for the validity of our generalization of the Fermi-Segrè formula are summarized in the paragraph following that containing (26) and (27). The condition (A.25) with $E = E_{n'}$ mentioned there, which is conveniently written in the form (29) when our generalization of the Fermi-Segrè formula is written in the form (27'), gives, for fixed $Z (> 0)$ and l , a lower bound for the values of $E_{n'} - V_0$. For the validity of (32), i.e. the Bouchiat-Bouchiat generalization of the Fermi-Segrè formula, one has the further condition (31), which gives, for fixed $Z (> 0)$ and l , an upper bound for the absolute value of $|E_{n'} - V_0|$.

3. Investigation of the accuracy of the generalized Fermi-Segrè formula by means of an exactly soluble model.

— The bound states in the effective potential

$$\begin{aligned} V^{\text{eff}}(r) &= -Ze^2 \frac{v}{e^{vr} - 1} + \frac{\hbar^2 l(l+1)}{2m} e^{vr} \left(\frac{v}{e^{vr} - 1} \right)^2 = \frac{e^2}{a_0} \left\{ -Z \frac{va_0}{\exp\{vr\} - 1} + \right. \\ &\quad \left. + \frac{l(l+1)}{2} \exp\{vr\} \left(\frac{va_0}{\exp\{vr\} - 1} \right)^2 \right\}, \quad Z > 0, \quad v > 0, \quad (33) \end{aligned}$$

which yields an exactly soluble Schrödinger equation, have been treated by Manning and Rosen [17] and by Infeld and Hull [18] and more recently in a paper by Myhrman [19], where also the behaviour at the origin of the normalized eigenfunctions has been determined. According to these investigations the energy levels are (in our notations)

$$E_{n'} = -\frac{\hbar^2}{2m} \left(\frac{Z}{a_0(n' + l + 1)} - \frac{1}{2} v(n' + l + 1) \right)^2 = -\frac{Z^2 e^2}{2 a_0(n' + l + 1)^2} \left(1 - (n' + l + 1)^2 \frac{va_0}{2Z} \right)^2, \quad (34)$$

where n' , which is the radial quantum number, i.e., the quantum number in the quantization condition (17), shall fulfil the condition

$$0 \leq n' < \left(\frac{2Z}{va_0} \right)^{1/2} - (l + 1), \quad (35)$$

and the normalized radial wavefunction corresponding to the radial quantum number n' has the following behaviour at the origin (in our notations)

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+3/2}}{(2l+1)! \sqrt{2} (n' + l + 1)^{3/2}} \left\{ 1 - \left(\frac{va_0}{2Z} \right)^2 (n' + l + 1)^4 \right\}^{1/2} \times \\ \times \prod_{s=0}^l \left\{ \left(1 - \frac{s^2}{(n' + l + 1)^2} \right) \left[1 - \left(\frac{va_0}{2Z} \right)^2 (n' + l + 1)^2 s^2 \right] \right\}^{1/2}. \quad (36)$$

Because of the condition (35), we realize that the quantity on the right-hand side of (36) is real, as it shall be, since we are considering real eigenfunctions.

As the modified effective potential $V_{\text{mod}}^{\text{eff}}(r)$ fulfilling (6) it is, in the present particular application, most natural to choose the potential obtained by replacing $l(l + 1)$ by $(l + 1/2)^2$ in the right-hand member of (33).

The potential $V_{\text{mod}}^{\text{eff}}(r)$ thus obtained is a potential well if $\frac{1}{2} (l + 1/2)^2 va_0/Z < 1$, and then the minimum of $V_{\text{mod}}^{\text{eff}}(r)$ lies at a point r satisfying

$$e^{vr} = 1 + \frac{(l + 1/2)^2 va_0/Z}{1 - \frac{1}{2} (l + 1/2)^2 va_0/Z},$$

and as $E \rightarrow 0$ the generalized classical turning point lying closest to the origin approaches a point r satisfying

$$e^{vr} = 1 + \frac{\frac{1}{2} (l + 1/2)^2 va_0/Z}{1 - \frac{1}{2} (l + 1/2)^2 va_0/Z}.$$

When $E < 0$, the value of $\exp \{ vr_1 \}$, where r_1 is the left generalized classical turning point, lies somewhere between the limits given by the right-hand members of the above two formulas for $\exp \{ vr \}$. Therefore, in order that we shall be able to make a power series expansion of (33), valid at least in the interval $(0, r_1)$, so that we shall be able to obtain from (3) and (33), by keeping in the power series expansion only the first few terms, an approximate formula for $V(r)$ of the form (11), which is valid from the origin to a point at least slightly to the right of r_1 , it is clear that we should require that

$$(l + 1/2)^2 va_0/Z \ll 1. \quad (37)$$

When $r \lesssim r_1$ we then have $vr \lesssim vr_1 \lesssim (l + 1/2)^2 va_0/Z \ll 1$, and therefore we obtain by means of (3), (33) and (13) the expansion

$$V(r) = -\frac{Ze^2}{r} + \frac{vZe^2}{2} \left(1 - \frac{1}{12} l(l + 1) va_0/Z \right) + \dots \\ = -\frac{Ze^2}{r} + \frac{Z^2 e^2}{2 a_0} \frac{va_0}{Z} \left(1 - \frac{1}{12} l(l + 1) va_0/Z \right) + \dots, \quad r \lesssim r_1, \quad (38)$$

which means that, unless cancellations occur, the relation (11) should be approximately valid in an interval extending from the origin to a point to the right of the left generalized classical turning point r_1 (cf. Fig. 1), V_0 being given by

$$V_0 = \frac{vZe^2}{2} \left(1 - \frac{1}{12} l(l + 1) va_0/Z \right) = \frac{Z^2 e^2}{2 a_0} \frac{va_0}{Z} \left(1 - \frac{1}{12} l(l + 1) va_0/Z \right). \quad (39)$$

Because of the condition (37) it follows from (39) that $V_0 \approx vZe^2/2 = [Z^2 e^2/(2 a_0)] [va_0/Z]$ and from (34) and (39) that $0 < V_0 \ll |E_0|$.

When $r \lesssim r_1$ and the condition (37) is fulfilled, we easily realize (cf. above) that, unless cancellations occur, $Q^2(r, E) - Q_{\text{mod}}^2(r, E)$ should be approximately equal to $1/(4r^2)$ and hence independent of the parameters appearing in $Q^2(r, E)$.

From (34) we obtain

$$\frac{2}{e^2 a_0} dE_{n'}/dn' = \frac{2Z^2}{a_0^2(n'+l+1)^3} \left\{ 1 - \left(\frac{va_0}{2Z} \right)^2 (n'+l+1)^4 \right\}, \quad (40)$$

and with $E_{n'}$ and V_0 given by (34) and (39), respectively, we have [cf. (13) and (28)]

$$\frac{2(V_0 - E_{n'})}{(\alpha Z)^2 mc^2} = \frac{1}{(n'+l+1)^2} + ((n'+l+1)^2 - l(l+1)/3) \left(\frac{va_0}{2Z} \right)^2. \quad (41)$$

Inserting (40) and (41) into our generalization (27') of the Fermi-Segrè formula, and noting that in the present application Heaviside's unit step function $H(E_{n'} - V_0)$ is equal to zero since $E_{n'} - V_0 < 0$, we obtain

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+3/2}}{(2l+1)! \sqrt{2}(n'+l+1)^{3/2}} \left\{ 1 - \left(\frac{va_0}{2Z} \right)^2 (n'+l+1)^4 \right\}^{1/2} \times \\ \times \prod_{s=0}^l \left\{ 1 - \left[\frac{1}{(n'+l+1)^2} + ((n'+l+1)^2 - l(l+1)/3) \left(\frac{va_0}{2Z} \right)^2 \right] s^2 \right\}^{1/2}. \quad (42)$$

Comparing this approximate result with the exact result (36), we easily find

$$\frac{\lim_{r \rightarrow 0} u(r, E_{n'})/r^{l+1}}{\lim_{r \rightarrow 0} u(r, E_{n'})/r^{l+1}} \text{ approx} = \prod_{s=0}^l \left\{ 1 + \frac{\left(\frac{va_0}{2Z} \right)^2 \left(\frac{1}{3} l(l+1) - s^2 \right) s^2}{\left(1 - \frac{s^2}{(n'+l+1)^2} \right) \left[1 - \left(\frac{va_0}{2Z} \right)^2 (n'+l+1)^2 s^2 \right]} \right\}^{1/2}. \quad (43)$$

Inserting (40) and (41) into the more approximate Bouchiat-Bouchiat generalization (32) of the Fermi-Segrè formula, we get

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+3/2}}{(2l+1)! \sqrt{2}(n'+l+1)^{3/2}} \left\{ 1 - \left(\frac{va_0}{2Z} \right)^2 (n'+l+1)^4 \right\}^{1/2} \times \\ \times \left\{ 1 - \frac{l(l+1)(2l+1)}{12} \left[\frac{1}{(n'+l+1)^2} + \left((n'+l+1)^2 - \frac{1}{3} l(l+1) \right) \left(\frac{va_0}{2Z} \right)^2 \right] \right\}. \quad (44)$$

Comparing this approximate result with the exact result (36), we find that

$$\frac{\lim_{r \rightarrow 0} u(r, E_{n'})/r^{l+1}}{\lim_{r \rightarrow 0} u(r, E_{n'})/r^{l+1}} \text{ approx} = \frac{1 - \frac{l(l+1)(2l+1)}{12} \left\{ \frac{1}{(n'+l+1)^2} + \left((n'+l+1)^2 - \frac{1}{3} l(l+1) \right) \left(\frac{va_0}{2Z} \right)^2 \right\}}{\prod_{s=0}^l \left\{ \left(1 - \frac{s^2}{(n'+l+1)^2} \right) \left[1 - \left(\frac{va_0}{2Z} \right)^2 (n'+l+1)^2 s^2 \right] \right\}^{1/2}}. \quad (45)$$

In table I we give numerical values of the relative error in our generalization of the Fermi-Segrè formula and in the Bouchiat-Bouchiat generalization of the same formula for $va_0/Z = 1/10$ and the possible values of l and n' , and in figure 2 we show a graphical representation of the absolute values of the corresponding relative errors for $va_0/Z = 1/100$ and $l = 1$ as well as $l = 6$ with the possible values of n' . It is seen that our formula is more accurate than the Bouchiat-Bouchiat formula, but both formulas break down when l becomes too large. It is possible that the high accuracy obtained for the particular potential and the parameter values used here is fortuitous and that the accuracy for more realistic atomic or ionic potentials may be less, but it is not the purpose of the present paper to settle this question.

Table I. — For the effective potential (33) with $va_0/Z = 1/10$ we give in this table numerical values of the relative error in our generalization of the Fermi-*Segrè* formula (the upper figures) and in the Bouchiat-Bouchiat generalization of the same formula (the lower figures). These relative errors are obtained by subtracting unity from the expressions (43) and (45), respectively. For a given value of l , the radial quantum number n' is restricted by the condition (35), which for $va_0/Z = 1/10$ means that $0 \leq n' \leq 3 - l$.

$l \backslash n'$	0	1	2	3
0	0 0	0 0	0 0	0 0
1	-6×10^{-4} 1×10^{-2}	-5×10^{-4} 2×10^{-3}	-5×10^{-4} 9×10^{-4}	
2	-2×10^{-2} 2×10^{-2}	-1×10^{-2} 4×10^{-3}		
3	-2×10^{-1} -1×10^{-1}			

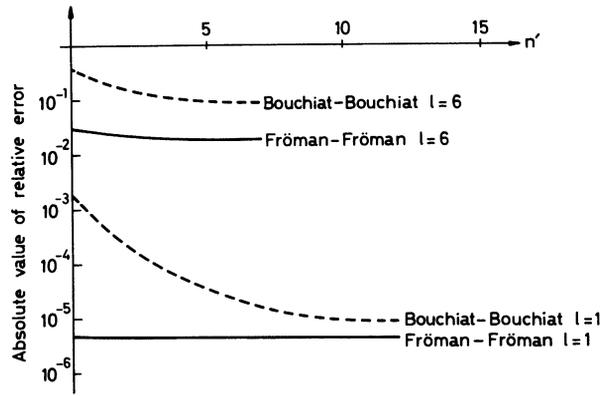


Fig. 2. — For the effective potential (33) we show in this figure a graphical representation of the absolute values of the relative error in our generalization of the Fermi-*Segrè* formula (the full-drawn curves) and in the Bouchiat-Bouchiat generalization of the same formula (the dashed curves) for $va_0/Z = 1/100$ and $l = 1$ as well as $l = 6$. The plotted quantities are obtained by first subtracting unity from the expressions (43) and (45), respectively, and then taking the absolute values. For a given value of l , the radial quantum number n' is restricted by the condition (35), which for $va_0/Z = 1/100$ means that $0 \leq n' \leq 13 - l$. Although the plotted quantities have physical meaning only when n' is an integer, they are represented by continuous curves.

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APPENDIX A

In this appendix we shall derive an expression for the quantity C defined by (9) and (10), when $V(r)$ is approximately given by (11) in the interval $(0, r_1)$ and in a small region around r_1 . Since formula (12) is then approximately valid in these regions and hence on the contour $\Gamma'_1(r)$, when this contour is chosen to lie close to the interval (r, r_1) , we know that C depends essentially only on the quantities $2m(E - V_0)/\hbar^2$, $2Z/a_0$ and l (as has already been stated below (13) in section 2). The general expression for C can therefore simply be obtained by considering the particular case of a bound or unbound state of a hydrogen-like ion. Since the cases $E < V_0$ and $E > V_0$ require different treatments, with differing resulting expressions for C , we shall treat these two cases separately.

a) FORMULA FOR C WHEN $E < V_0$: — We consider the particular case of a bound state for a hydrogen-like ion, which means that in the whole interval $0 < r < \infty$ the potential $V(r)$ is given by (11) with $V_0 = 0$, and we let $E = E_n (< 0)$ be an eigenvalue. We start by calculating in a straightforward way the value of $u(r, E_n)/r^{l+1}$ in the limit $r \rightarrow 0$, $u(r, E_n)$ being normalized according to (20). In this calculation we use some results which can be found in [20]. Introducing instead of the radial quantum number n' the total quantum number n defined by (cf. Eq. (18-39) in [20])

$$n = n' + l + 1, \tag{A.1}$$

and using equations (21-4) and (21-5) in [20], we get

$$\lim_{r \rightarrow 0} \frac{u(r, E_n)}{r^{l+1}} = \lim_{r \rightarrow 0} \frac{R_n(r)}{r^l} = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} \left(\frac{2Z}{na_0} \right)^l L_{n+l}^{2l+1}(0), \tag{A.2}$$

where L_{n+l}^{2l+1} is the associated Laguerre polynomial of degree $(n+l) - (2l+1) = n-l-1$ and of order

$2l + 1$ (with the notations in [20]). From equation (20-9) in [20] it follows that

$$L_{n+l}^{2l+1}(0) = - \frac{[(n+l)!]^2}{(n-l-1)!(2l+1)!}, \quad (\text{A.3})$$

which, when inserted into (A.2) with n replaced by $n' + l + 1$, yields

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+3/2}}{(2l+1)!} \left(\frac{(n'+2l+1)!}{2n'!(n'+l+1)^{2l+4}} \right)^{1/2}. \quad (\text{A.4})$$

Since the explicit expression for $E_{n'}$ is

$$E_{n'} = - \frac{mZ^2 e^4}{2\hbar^2 n'^2} = - \frac{\hbar^2(Z/a_0)^2}{2m(n'+l+1)^2}, \quad (\text{A.5})$$

we have

$$dE_{n'}/dn' = \frac{\hbar^2(Z/a_0)^2}{m(n'+l+1)^3}, \quad (\text{A.6})$$

and hence we can write (A.4) as follows

$$\lim_{r \rightarrow 0} \frac{u(r, E_{n'})}{r^{l+1}} = \frac{(2Z/a_0)^{l+1/2}}{(2l+1)!} \left(\frac{(n'+2l+1)!}{n'!(n'+l+1)^{2l+1}} \frac{2m}{\hbar^2} dE_{n'}/dn' \right)^{1/2}. \quad (\text{A.7})$$

Noting that according to (4) and (9) the left-hand side of (A.7) is by definition equal to c , we can put the right-hand member of (A.7) equal to the right-hand member of (25), getting

$$\begin{aligned} C &= \frac{(2l+1)!}{2\sqrt{\pi}} \left(\frac{a_0}{2Z} \right)^{l+1/2} \left(\frac{n'!(n'+l+1)^{2l+1}}{(n'+2l+1)!} \right)^{1/2} = \\ &= \frac{(2l+1)! [a_0/(2Z)]^{l+1/2} (n'+l+1)^{(2l+1)/2}}{2\sqrt{\pi} \prod_{s=-l}^{+l} (n'+l+1+s)^{1/2}} = \frac{(2l+1)! [a_0/(2Z)]^{l+1/2}}{2\sqrt{\pi} \prod_{s=-l}^{+l} \left(1 + \frac{s}{(n'+l+1)} \right)^{1/2}} \\ &= \frac{(2l+1)! [a_0/(2Z)]^{l+1/2}}{2\sqrt{\pi} \prod_{s=0}^l \left(1 - \frac{s^2}{(n'+l+1)^2} \right)^{1/2}}. \end{aligned} \quad (\text{A.8})$$

In view of the fact that, in the present particular case of a hydrogen-like ion, V_0 is equal to zero (cf. (11)), it follows from (A.5) that

$$\frac{1}{(n'+l+1)^2} = - \left(\frac{a_0}{Z} \right)^2 \frac{2m}{\hbar^2} (E_{n'} - V_0), \quad (\text{A.9})$$

which, when inserted into (A.8) and with the index n' on E omitted, yields

$$C = \frac{(2l+1)! \left(\frac{a_0}{2Z} \right)^{l+1/2}}{2\sqrt{\pi} \prod_{s=0}^l \left\{ 1 + \left(\frac{a_0}{Z} \right)^2 \frac{2m(E - V_0)}{\hbar^2} s^2 \right\}^{1/2}}, \quad E < V_0. \quad (\text{A.10})$$

This formula has been derived by the use of the properties of the bound states in the particular physical potential which, in the whole interval $0 < r < \infty$, is given by (11) with $V_0 = 0$. The corresponding eigenvalues $E_{n'}$ fulfil the inequality $-(Z/a_0)^2/(l+1)^2 \leq 2m(E_{n'} - V_0)/\hbar^2 < 0$ because of (A.5) and the fact that $V_0 = 0$. Although (A.10) has thus been derived by letting E be an eigenvalue in a particular potential, it is obvious from the comments below (13) and from the inequality for $E_{n'} - V_0$ just given, that the expression (A.10) for C is not res-

stricted to the pure Coulomb potential, but is approximately valid on the more general assumptions introduced in connection with (11) and (12) and between (13) and (14), provided that the further condition

$$- (Z/a_0)^2/(l + 1)^2 \leq 2 m(E - V_0)/\hbar^2 < 0 \tag{A.11}$$

is fulfilled. The approximate expression (A.10) for C may be valid for lower values of E than those fulfilling (A.11), but one of the essential assumptions used in the derivation of (A.10) cannot be fulfilled when E is so low that the generalized classical turning point r_1 no longer exists when the physical potential is given by (11). To estimate this ultimate limit for the expected validity of (A.10) we shall use the particular modification (7'). Since the minimum value $(V_{\text{mod}}^{\text{eff}})_{\text{min}}$ of the modified effective potential (7'), when $V(r)$ is given by (11), satisfies the formula $2 m[(V_{\text{mod}}^{\text{eff}})_{\text{min}} - V_0]/\hbar^2 = - (Z/a_0)^2/(l + 1/2)^2$, it is necessary for the existence of the generalized classical turning point r_1 , when the particular but very natural modification (7') is used, that the condition

$$- \frac{(Z/a_0)^2}{(l + 1/2)^2} < \frac{2 m(E - V_0)}{\hbar^2} \tag{A.12}$$

shall be fulfilled. Thus, we cannot expect (A.10) to be valid unless the condition (A.12) is fulfilled.

b) FORMULA FOR C WHEN $E > V_0$. — We consider, as in the derivation of (A.10), the case of a hydrogen-like ion. Assuming that $E > 0$, we can then write the radial Schrödinger equation (cf. (1), (2), (3) and (11) with $V_0 = 0$) as follows

$$\frac{d^2 u}{d(kr)^2} + \left(1 - \frac{2 \eta}{kr} - \frac{l(l + 1)}{(kr)^2} \right) u = 0 \tag{A.13}$$

where

$$k = (2 mE/\hbar^2)^{1/2} \tag{A.14}$$

and (cf. (13))

$$\eta = - \frac{mZe^2}{\hbar^2 k} = - \frac{Z}{ka_0} < 0. \tag{A.15}$$

The physically acceptable solution of (A.13), i.e., the solution which vanishes at $r = 0$, is proportional to the Coulomb wavefunction $F_l(\eta, kr)$, which, according to 14.1.4-7, 6.1.15 and 6.1.29 in [21] and the fact that $\eta < 0$, behaves as follows for small values of kr

$$\begin{aligned} F_l(\eta, kr) &= \frac{2^l |\Gamma(l + 1 + i\eta)|}{(2l + 1)! \exp\{\pi\eta/2\}} (kr)^{l+1} + \text{higher powers of } (kr) \\ &= \frac{(\pi k)^{1/2} (2k|\eta|)^{l+1/2} \prod_{s=0}^l (1 + s^2/\eta^2)^{1/2}}{(2l + 1)! [1 - \exp\{-2\pi|\eta|\}]^{1/2}} r^{l+1} + \text{higher powers of } r. \end{aligned} \tag{A.16}$$

According to (A.16) the Coulomb wavefunction $F_l(\eta, kr)$ is positive in the neighbourhood of the origin. Therefore, and because $F_l(\eta, kr)$ is a solution of (A.13), it must be possible to represent $F_l(\eta, kr)$, in the classically forbidden region adjacent to the origin, by a phase-integral expression equal to a positive constant factor

times $|q^{-1/2}(r, E)| \exp\left\{-\left|\frac{1}{2} \int_{r_1(r)} q(r, E) dr\right|\right\}$ where $q(r, E)$ is the same phase-integral quantity as pre-

viously in the present paper but pertaining to the particular case now under consideration (with only one generalized classical turning point, r_1 ; cf. Fig. 1). According to the connection formula (21) with (22) in [10] the Coulomb wavefunction $F_l(\eta, kr)$ must therefore, in the classically allowed region to the right of r_1 , be represented by a phase-integral expression equal to a positive constant factor times

$$q^{-1/2}(r, E) \cos\left(\frac{1}{2} \int_{r_1(r)} q(r, E) dr - \frac{1}{4} \pi\right),$$

the quantity $q(r, E)$ being positive in the classically allowed region; cf. figure 1. Since, furthermore, according to 14.5.1, 14.5.5, 14.5.6 and 14.5.9 in [21], the Coulomb wavefunction $F_l(\eta, kr)$ is a cosine-function with unit amplitude in the limit when $r \rightarrow +\infty$, and $q(r, E)$ tends to k as $r \rightarrow +\infty$, the last mentioned positive constant factor must be equal to $k^{1/2}$. We have thus arrived at the phase-integral formula

$$F_l(\eta, kr) = k^{1/2} q^{-1/2}(r, E) \cos\left(\frac{1}{2} \int_{r_1(r)} q(r, E) dr - \frac{1}{4} \pi\right), \quad r > r_1, \tag{A.17}$$

where $\Gamma_1(r)$ is defined analogously as in figure 1 but adapted to the case now under consideration (with only one generalized classical turning point, r_1). To be consistent with (A.17) and the connection formula (21) with (22) in [10], the Coulomb wavefunction under consideration must, in the interval $0 < r < r_1$, be given by the approximate phase-integral formula

$$F_l(\eta, kr) = \frac{1}{2} k^{1/2} |q^{-1/2}(r, E)| \exp \left\{ - \left| \frac{1}{2} \int_{\Gamma_1(r)} q(r, E) dr \right| \right\}, \quad 0 < r < r_1, \quad (\text{A.18})$$

where $\Gamma_1(r)$ is a contour shown in figure 1, which should now be adapted to the present case of only one generalized classical turning point.

In the particular case of a hydrogen-like ion now under consideration, the function $u_1(r, E)$, defined in the beginning of the present paper, is proportional to $F_l(\eta, kr)$. Since, furthermore, $u_1(r, E)$ shall fulfil (9) for small values of r , it follows from (A.16) and (A.18) that in the interval $0 < r < r_1$ the function $u_1(r, E)$ is given by the phase-integral formula

$$u_1(r, E) = c \frac{(2l+1)! [1 - \exp\{-2\pi|\eta|\}]^{1/2}}{2\sqrt{\pi} (2k|\eta|)^{l+1/2} \prod_{s=0}^l (1 + s^2/\eta^2)^{1/2}} \times |q^{-1/2}(r, E)| \exp \left\{ - \left| \frac{1}{2} \int_{\Gamma_1(r)} q(r, E) dr \right| \right\}, \quad 0 < r < r_1. \quad (\text{A.19})$$

Using (A.14), (A.15) and (13) to rewrite (A.19), and comparing the resulting formula with (10), and noting that E can be replaced by $E - V_0$, since $V_0 = 0$ for the particular potential now under consideration, we get

$$C = \frac{(2l+1)! \left(\frac{a_0}{2Z}\right)^{l+1/2} \left[1 - \exp \left\{ - 2\pi \frac{Z}{a_0} \left(\frac{\hbar^2}{2m(E - V_0)} \right)^{1/2} \right\} \right]^{1/2}}{2\sqrt{\pi} \prod_{s=0}^l \left\{ 1 + \left(\frac{a_0}{Z}\right)^2 \frac{2m(E - V_0)}{\hbar^2} s^2 \right\}^{1/2}}, \quad E > V_0. \quad (\text{A.20})$$

From the comments below (13) it is obvious that (A.20) is not restricted to the pure Coulomb potential now discussed but is also valid on the more general assumptions introduced in connection with (11) and (12) and between (13) and (14). In particular it is not necessary that energies $E > V_0$ shall correspond to non-bound states, which one might at first sight think from the derivation of (A.20); see also our remark at the very end of this appendix.

c) FORMULA FOR C COVERING BOTH CASES $E < V_0$ AND $E > V_0$. — To summarize the results obtained in this appendix we note that the solution of (1), which behaves according to (9) for small values of r , is, in the classically forbidden region (in the generalized sense) adjacent to the origin, represented by the phase-integral formula (10), where, on the assumptions introduced in connection with (11) and (12) and between (13) and (14), the factor C is given by (A.10) when $E < V_0$ (provided that (A.11), or possibly (A.12), is also fulfilled) and by (A.20) when $E > V_0$. The mathematical reason why the expression for C is not the same when $E > V_0$ as when $E < V_0$ can be understood if one derives the above-mentioned result by evaluating, by means of the method of steepest descents, a convenient contour integral representation of the appropriate solution of (1), when $Q^2(r, E)$ is given by (12); it then turns out that, as $E - V_0$ passes through the value zero, the two saddle-points change their analytical character, after having moved to infinity when $E - V_0 = 0$. Note, however, that by keeping $Z (> 0)$ and l fixed, and letting $E \rightarrow V_0$, we obtain from (A.10) as well as from (A.20) the limit

$$\lim_{E \rightarrow V_0} C = \frac{(2l+1)!}{2\sqrt{\pi}} \left(\frac{a_0}{2Z}\right)^{l+1/2} \quad (\text{A.21})$$

Using Heaviside's unit step function $H(E - V_0)$, defined by

$$H(E - V_0) = \begin{cases} 0 & \text{when } E - V_0 < 0 \\ 1 & \text{when } E - V_0 > 0, \end{cases} \quad (\text{A.22})$$

we can combine (A.10) and (A.20) into the formula

$$C = \frac{(2l+1)! \left(\frac{a_0}{2Z}\right)^{l+1/2} \left[1 - H(E - V_0) \exp \left\{ - 2\pi \frac{Z}{a_0} \left(\frac{\hbar^2}{2m(E - V_0)} \right)^{1/2} \right\} \right]^{1/2}}{2\sqrt{\pi} \prod_{s=0}^l \left\{ 1 + \left(\frac{a_0}{Z}\right)^2 \frac{2m(E - V_0)}{\hbar^2} s^2 \right\}^{1/2}}, \quad (\text{A.23})$$

which is thus derived on the assumptions introduced in connection with (11) and (12) and between (13) and (14), and which is expected to be valid if also the condition (cf. (A. 11))

$$2 m(E - V_0)/\hbar^2 \geq - (Z/a_0)^2/(l + 1)^2 \tag{A. 24}$$

is fulfilled, but should not be valid if the condition (A. 12), i.e.,

$$2 m(E - V_0)/\hbar^2 > - (Z/a_0)^2/(l + \frac{1}{2})^2 \tag{A. 25}$$

is violated. When $Z (> 0)$ and l are kept fixed, the limit of C is, as already mentioned, the same for $E - V_0 \rightarrow - 0$ as for $E - V_0 \rightarrow + 0$ and is given by (A. 21).

Formula (A. 23) gives different analytical expressions for C when $E < V_0$ and when $E > V_0$, but there is no discontinuity neither in C nor in $\partial^v C/\partial E^v$, $v = 1, 2, 3, \dots$, at $E = V_0$, since Heaviside's unit step function in (A. 23) is multiplied by an exponential factor which tends very rapidly to zero when $E - V_0$ tends to $+ 0$.

According to (9) and (10) the result (A. 23) concerns the phase-integral representation of a particular solution of (1) with (12) in the interval $0 \leq r < r_1$. We emphasize that the expression for $Q^2(r, E)$ shall be approximately given by (12) in the interval $0 \leq r \leq r_1$ and in a certain small region around r_1 but may differ considerably from (12) when r lies at some distance to the right of r_1 .

APPENDIX B

Exact formula for expressing the limit of $u(r, E_n)/r^{l+1}$ when $r \rightarrow 0$ as the expectation value of a quantity involving the physical potential. — From equation (IX) in [22], where we replace z by r and put $\psi_1 = \psi_2 = u$, $Q_1^2 = Q_2^2 = Q^2$ and $f = r^n$ (n being an unspecified exponent, not to be confused with the total quantum number n in Appendix A) and insert our expression (2) with (3) for Q^2 , it follows that

$$\begin{aligned} & \left\{ (n - 2l - 2)(n - 1)(n + 2l)r^{n-3} + 4n \frac{2m}{\hbar^2} [E - V(r)]r^{n-1} - 2 \frac{2m}{\hbar^2} V'(r)r^n \right\} u^2 = \\ & = \frac{d}{dr} \left\{ \left(2 \frac{2m}{\hbar^2} [E - V(r)]r^n + [n(n - 1) - 2l(l + 1)]r^{n-2} \right) u^2 - 2nr^{n-1} u \frac{du}{dr} + 2r^n \left(\frac{du}{dr} \right)^2 \right\}, \end{aligned} \tag{B. 1}$$

where $V'(r)$ denotes the derivative $dV(r)/dr$. We shall now assume that $V(r)$ has at the most a Coulomb singularity at the origin, which implies that the physically acceptable solution u is proportional to r^{l+1} for small values of r . The integral of the left-hand member of (B. 1) from $r = 0$ to $r = + \infty$ therefore converges at the origin if $n \geq - 2l$, and it converges at infinity if we consider a bound state. On these assumptions we obtain from (B. 1) the formula

$$\begin{aligned} & \int_0^\infty \left\{ (n - 2l - 2)(n - 1)(n + 2l)r^{n-3} + 4n \frac{2m}{\hbar^2} [E - V(r)]r^{n-1} - 2 \frac{2m}{\hbar^2} V'(r)r^n \right\} u^2 dr = \\ & = - \lim_{r \rightarrow 0} \left\{ \left(2 \frac{2m}{\hbar^2} [E - V(r)]r^n + [n(n - 1) - 2l(l + 1)]r^{n-2} \right) u^2 - 2nr^{n-1} u \frac{du}{dr} + 2r^n \left(\frac{du}{dr} \right)^2 \right\}, \\ & n \geq - 2l. \end{aligned} \tag{B. 2}$$

When $n > - 2l$ the limit in the right-hand member of (B. 2) is equal to zero, and thus formula (B. 2) gives

$$(n - 2l - 2)(n - 1)(n + 2l) \langle r^{n-3} \rangle + 4n \frac{2m}{\hbar^2} \langle [E - V(r)]r^{n-1} \rangle - 2 \frac{2m}{\hbar^2} \langle V'(r)r^n \rangle = 0, \quad n > - 2l, \tag{B. 3}$$

where the brackets denote expectation values with respect to the bound-state with energy E . For $l > 0$ and $n = 0$ this formula reduces to a formula equivalent to equation (40b) in [23].

When $n = - 2l$ formula (B. 2) yields

$$\begin{aligned} & \left\langle - 8l \frac{2m}{\hbar^2} [E - V(r)]/r^{2l+1} - 2 \frac{2m}{\hbar^2} V'(r)/r^{2l} \right\rangle = \\ & = - \lim_{r \rightarrow 0} \left\{ \left(2 \frac{2m}{\hbar^2} [E - V(r)]r^2 + 2l^2 \right) \left(\frac{u}{r^{l+1}} \right)^2 + 4l \frac{u}{r^{l+1}} \frac{du}{dr} + 2 \left(\frac{du}{dr} \right)^2 \right\}, \end{aligned} \tag{B. 4}$$

where u is assumed to be normalized according to (20), i.e.,

$$\int_0^{\infty} u^2 dr = 1. \quad (\text{B. 5})$$

Since u is proportional to r^{l+1} for small values of r , one easily realizes that

$$\lim_{r \rightarrow 0} \frac{du/dr}{r^l} = (l + 1) \lim_{r \rightarrow 0} \frac{u}{r^{l+1}}. \quad (\text{B. 6})$$

Inserting (B. 6) into (B. 4), we get

$$\left(\lim_{r \rightarrow 0} \frac{u}{r^{l+1}} \right)^2 = \frac{2m}{\hbar^2(2l+1)^2} \left\langle \frac{4l[E - V(r)]}{r^{2l+1}} + \frac{dV(r)/dr}{r^{2l}} \right\rangle. \quad (\text{B. 7})$$

For $l = 0$ this formula reduces to a formula equivalent to equation (40a) in [23], which in turn is equivalent to a relation ascribed to unpublished lecture notes of J. Schwinger; see equation (2.19) and the first footnote on p. 175 in a paper by Quigg and Rosner [24].

We remark that equation (2.30) in the just mentioned paper by Quigg and Rosner [24] is equivalent to our formulas (B.3) and (B.7), although of somewhat different form. The derivations are also somewhat different. Instead of the partial integrations used by Quigg and Rosner we use in our derivation a particularization of the general relation (IX) in [22] which, as pointed out in [22], is equivalent to formulas given by Moraal [25] already in 1973 and by Calogero [26, 27, 28] somewhat later.

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