

## Fermi-Segrè Formula

Nanny Fröman and Per Olof Fröman

*Institute of Theoretical Physics, University of Uppsala, Uppsala, Sweden*

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For a nonrelativistic quantal particle moving with the angular momentum  $l=0$  in a spherically symmetric, smooth potential well, which in the neighborhood of the center of force gives rise to an attractive Coulomb force, a formula for the probability density of the particle at the center of force is derived by means of certain phase-integral approximations of an arbitrary order. From this formula, which is expected to be very accurate, the nonrelativistic approximation of the Fermi-Segrè formula for the probability density of finding an  $s$  electron at the nucleus of an atom or ion is obtained. The limits of validity of the Fermi-Segrè formula in the nonrelativistic approximation are clarified by this derivation.

### I. INTRODUCTION

The Fermi-Segrè formula,<sup>1-4</sup> which gives a remarkably simple expression for the probability density of finding an atomic or ionic  $s$  electron at the position of the nucleus, is of importance for the interpretation of hyperfine structure splittings, isotope shifts of spectral lines, Knight-shift data, and chemical shifts of Mössbauer lines. Impressed by the simplicity and elegance of the Fermi-Segrè formula, Foldy<sup>4</sup> undertook the task of improving the derivation of the Fermi-Segrè formula in the nonrelativistic approximation. He was able to give a more rigorous derivation of the formula, but as regards the question of the accuracy of the formula, no substantial progress was achieved. In the present paper we shall derive the Fermi-Segrè formula in the nonrelativistic approximation by means of the theory of certain phase-integral approximations, which has been developed previously by the present authors.<sup>5-7</sup> This derivation gives information on the accuracy of the Fermi-Segrè formula when relativistic effects, exchange effects, and configuration interactions are neglected.

As in Foldy's treatment,<sup>4</sup> we consider a nonrelativistic  $s$  electron which moves in a local potential. The normalized wave function of the electron can thus be written

$$\psi_n(r) = \frac{1}{r} \frac{u(r, E_n)}{(4\pi \int_0^\infty u^2(r, E_n) dr)^{1/2}}, \quad (1)$$

where  $u(r, E_n)$  is the real, unnormalized, bound-state solution corresponding to the eigenvalue  $E_n$  of the radial Schrödinger equation

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

with  $Q^2(r, E)$ , in obvious notations, defined by

$$Q^2(r, E) = \frac{2m}{\hbar^2} [E - V(r)]. \quad (3)$$

The integral appearing in (1) can be expressed

in a convenient form by means of an elegant method which has been devised by Furry.<sup>8</sup> Furry's general result for the normalization integral of the real wave function for a bound state in a one-dimensional potential well was recently formally simplified by Yngve,<sup>9</sup> who noticed that Furry's expression for the normalization integral [Eqs. (43) and (44) in Ref. 8] can, apart from a certain constant factor, be written as the derivative with respect to the energy of a certain Wronskian [see Eqs. (6) and (2) in Ref. 9]. The general formula given by Furry, written in this simplified way and adapted to the present situation, is

$$\int_0^\infty u^2(r, E_n) dr = \frac{1}{2} a_0 e^2 \left[ \frac{\partial}{\partial E} \left( u_1 \frac{\partial u_2}{\partial r} - u_2 \frac{\partial u_1}{\partial r} \right) \right]_{E=E_n}, \quad (4)$$

where  $a_0 = \hbar^2 / (me^2)$  is the Bohr radius and  $e$  is the electron charge. Formula (4) is an exact relation provided  $u_1$  and  $u_2$  are exact solutions of (2) which, for any value of  $E$ , have the properties that  $u_1 \rightarrow 0$  when  $r \rightarrow 0$  and  $u_2 \rightarrow 0$  when  $r \rightarrow \infty$ , and that, furthermore,  $u_1 = u_2 = u(r, E_n)$  when  $E = E_n$ . It should be noted that the right-hand member of (4) is independent of  $r$ , since the Wronskian of  $u_1$  and  $u_2$  is known to be independent of  $r$ .

To obtain useful approximate expressions for the radial wave functions  $u_1$ ,  $u_2$ , and  $u$  which appear in (4) and (1), we shall use the previously mentioned phase-integral approximations of an arbitrary order  $2N+1$ . For the first order, i.e., for  $N=0$ , these approximations reduce to the first-order JWKB approximation. For the higher orders, i.e., for  $N>0$ , they are closely related to, but not identical with, the higher-order JWKB approximations. The difference has been explained in detail in Ref. 7. According to Ref. 7 and the references given in that paper, one can, under certain conditions, which are in general fulfilled in physical applications, to a very high degree of accuracy, write the solutions of the radial Schrödinger equation (2) as linear combinations of the

phase-integral functions

$$q^{-1/2}(r, E) \exp[\pm i \int^r q(r, E) dr], \quad (5)$$

where  $q(r, E)$  is a truncated series and hence depends on the order  $2N+1$  of the phase-integral approximation used. Our choice of phase of  $q^{1/2}$ , which agrees with that of  $Q^{1/2}$ , is shown in Fig. 1. Denoting the contributions to  $q(r, E)$  pertaining to the successive orders of the phase-integral approximations by  $q^{(2n+1)}(r, E)$ ,  $n=0, 1, 2, \dots$ , we may write, for the  $(2N+1)$ -order approximation,

$$q(r, E) = \sum_{n=0}^N q^{(2n+1)}(r, E). \quad (6)$$

We remark that  $q^{(1)}(r, E) = Q(r, E)$ . As regards the higher-order contributions to  $q(r, E)$ , up to the 9th-order approximation, we refer to Ref. 7 and to references given in that paper. We also mention that Campbell,<sup>10</sup> using a symbolic manipulation computer program, has calculated the expressions for  $q^{(2n+1)}$  up to the 21st-order phase-integral approximation.

For the sake of simplicity we shall, in Sec. II, perform the derivation of an approximate formula for  $\psi_n^2(0)$  using only the first-order phase-integral functions, i. e., the usual JWKB functions. This means that we can write the occurring integrals over  $q(r, E)$  as definite integrals along the real axis, while, in the general case of arbitrary order phase-integral approximations, certain contour integrals in the complex  $r$  plane will occur. We emphasize, however, that apart from such minor changes, the formula for  $\psi_n^2(0)$  which will be derived in Sec. II is valid for an arbitrary order of the phase-integral approximations.<sup>6</sup> Thus, by a simple generalization we shall, in Sec. III, obtain a formula for  $\psi_n^2(0)$  which is valid for any order  $2N+1$  of the phase-integral approximations. If the order of the phase-integral approximations used is chosen conveniently, one may in general expect this formula to be much more accurate than that corresponding to the first-order approximation. In Sec. IV we finally arrive at the Fermi-Segrè formula by introducing certain approximations in the formula for  $\psi_n^2(0)$  given in Sec. III.

## II. APPROXIMATE FORMULA FOR THE PROBABILITY DENSITY AT THE CENTER OF FORCE

We assume that the potential  $V(r)$  is attractive and reasonably smooth. The only detailed assumption to be made about the analytic form of  $V(r)$  is that, in the neighborhood of  $r=0$ ,  $V(r)$  is approximately equal to the potential of a point charge situated at  $r=0$  and having the charge number  $Z$ . As  $r$  tends to zero, the potential  $V(r)$  thus behaves as  $-Ze^2/r$ , and hence  $Q^2(r)$  behaves as  $2mZe^2/(\hbar^2 r) = 2Z/(a_0 r)$ . According to the results obtained on pp. 74-79 in Ref. 5, particularized to the case

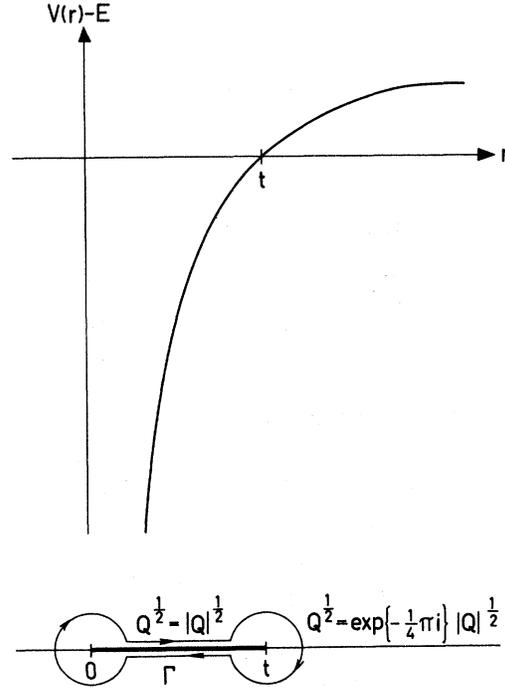


FIG. 1. Upper part of the figure shows the qualitative behavior of  $V(r)-E$  for an attractive potential  $V(r)$  with a Coulomb singularity at  $r=0$ . Lower part of the figure, which refers to the complex  $r$  plane, gives the phase of  $Q^{1/2}(r)$  on the part of the real axis to the right of the classical turning point  $t$  and on the upper lip of the cut (the heavy line) between 0 and  $t$ . The contour of integration  $\Gamma$  is also shown.

$l=0$ , the solution  $u_1(r, E)$  of the radial Schrödinger equation (2), which for any value of  $E$  is zero for  $r=0$  and normalized such that  $u_1(r, E)/r \rightarrow 1$  as  $r \rightarrow 0$ , is approximately [cf. in particular Eq. (7.28) with  $l=0$  in Ref. 5]

$$u_1(r, E) = \left(\frac{a_0}{2\pi Z}\right)^{1/2} Q^{-1/2}(r, E) \times \cos\left(\int_0^r Q(r, E) dr - \frac{3}{4}\pi\right), \quad (7)$$

when  $0 < r < t$ , where  $t$  is the classical turning point shown in Fig. 1. Using one of the well-known connection formulas of the JWKB approximation, namely Eq. (8.21) in Ref. 5, we find that the solution  $u_2(r, E)$  of the radial Schrödinger equation (2), which for any value  $E < V(\infty)$  tends to zero as  $r \rightarrow +\infty$ , is approximately (with a so far undetermined  $r$ -independent factor  $C$ )

$$u_2(r, E) = C Q^{-1/2}(r, E) \cos\left[\int_r^t Q(r, E) dr - \frac{1}{4}\pi\right], \quad (8)$$

when  $0 < r < t$ . The requirement that the functions  $u_1(r, E)$  and  $u_2(r, E)$  shall be equal for  $E = E_n$  gives, by means of (7) and (8), the quantization condition

$$\int_0^t Q(r, E_n) dr = n\pi, \quad n = 1, 2, 3, \dots, \quad (9)$$

and the condition that

$$C = (-1)^{n-1} (a_0/2\pi Z)^{1/2}, \quad (10)$$

when  $E = E_n$ . In the present paper we have a smooth function  $Q^2(r, E)$  with a first-order pole and a first-order zero, and therefore the quantization condition (9) differs from the Bohr-Sommerfeld (half-integer) quantization condition, which applies to the case of a smooth function  $Q^2(r, E)$  with two zeros.

The approximate solutions  $u_1$  and  $u_2$  given by (7) and (8) satisfy the conditions required for the approximate validity of (4) if the conditions (9) and (10) are fulfilled, and hence we can obtain an approximate expression for the normalization integral appearing in (1). In fact, from (7), (8), and (10) it follows that

$$u_1 \frac{\partial u_2}{\partial r} - u_2 \frac{\partial u_1}{\partial r} = (-1)^n \frac{a_0}{2\pi Z} \sin \left( \int_0^t Q(r, E) dr \right), \quad (11)$$

and when this expression is inserted in (4) and use is made of (9), we get

$$\int_0^\infty u^2(r, E_n) dr = \frac{a_0^2 e^2}{4\pi Z} \left( \frac{\partial}{\partial E} \int_0^t Q(r, E) dr \right)_{E=E_n}. \quad (12)$$

Inserting now (12) into (1), and recalling that  $u(r, E_n)/r = u_1(r, E_n)/r - 1$  as  $r \rightarrow 0$ , we arrive at the formula

$$\psi_n^2(0) = \frac{Z}{a_0^2 e^2} \left( \frac{\partial}{\partial E} \int_0^t Q(r, E) dr \right)_{E=E_n}^{-1}. \quad (13)$$

### III. GENERALIZATION TO HIGHER-ORDER PHASE-INTEGRAL APPROXIMATIONS

In the derivation of formulas (9) and (13) given in Sec. II we can at every step use the phase-integral functions (5) of a convenient order instead of the first-order JWKB functions. The only complication is that, instead of integrals in which  $r=0$  or  $r=t$  appearing as constant limits of integration, there appear certain loop integrals.<sup>6</sup> The generalization of (7) has not been discussed previously, while the generalization of the connection formulas of the JWKB approximation, one of which was used to obtain (8), has been discussed in Ref. 7. In order to generalize the final formulas (9) and (13) given in Sec. II to apply to the phase-integral approximation of an arbitrary convenient order  $2N+1$ , we simply replace the integral  $\int_0^t Q(r, E) dr$  by a contour integral  $L(E)$  defined by

$$L(E) = \frac{1}{2} \int_{\Gamma} q(r, E) dr, \quad (14)$$

where  $q(r, E)$  is the truncated series (6) and  $\Gamma$ , as shown in Fig. 1, is a closed contour in the complex  $r$  plane encircling, in the negative sense, both the origin ( $r=0$ ) and the classical turning

point  $t$ . In this way we get as a generalization of (9) the quantization condition

$$L(E_n) = n\pi, \quad n = 1, 2, \dots, \quad (15)$$

and as a generalization of (13) the following formula for the probability density at the center of force is

$$\psi_n^2(0) = \frac{Z}{a_0^2 e^2} \left( \frac{\partial}{\partial E} L(E) \right)_{E=E_n}^{-1}. \quad (16)$$

This formula can be expected to possess the same accuracy as does the phase-integral approximation of the order  $2N+1$  at the optimal point, which we can choose to evaluate the Wronskian on the right-hand side of (4) by means of the phase-integral approximation of the actual order.

For a hydrogen atom or a hydrogenlike ion with the electron in an  $s$  state the formulas (15) and (16) are exact for any order of the phase-integral approximations.

We may get some further information on the accuracy of (15) and (16) by applying these formulas to the particular potential

$$V(r) = -\kappa Z e^2 / (e^{\kappa r} - 1), \quad (17)$$

where  $\kappa$  is a constant which can be given any positive value. This potential fulfills the condition that  $V(r)$  behaves as  $-Ze^2/r$  in the neighborhood of  $r=0$ , which was assumed in the derivation of formulas (15) and (16). The exact eigenvalues and eigenfunctions for the potential (17) were obtained in analytical form by Hulthén.<sup>11</sup> Utilizing his results, we can also obtain an exact expression for  $\psi_n^2(0)$ . Calculating, then, for the potential (17),  $E_n$  according to (15) and  $\psi_n^2(0)$  according to (16), we obtain exact agreement with the corresponding exact expressions for all orders of the phase-integral approximations.

Upper bounds for the errors of formulas (15) and (16) can be obtained from the results given in our previous papers.<sup>5-7</sup> Since, however, we may apply these formulas to situations in which the detailed shape of the potential is not assumed to be known, it is preferable to judge the accuracy of (15) and (16) in a more qualitative way. As mentioned above, formulas (15) and (16) are exact in all orders of approximation, both for the unscreened-Coulomb potential and for the potential (17), which has essentially the character of a screened-Coulomb potential. Hence, for the general case of an ion-core potential, which is smooth except for the Coulomb singularity at  $r=0$ , it is reasonable to expect that (15) and (16) are good already in the first-order approximation and that the higher-order approximations, in accordance with our general experience in working with the phase-integral approximations, yield considerable improvements. Thus, if we imagine the optimal

order of the phase-integral approximations to be used in the definition (14) of  $L(E)$ , we may expect formulas (15) and (16) to be very accurate.

#### IV. FERMI-SEGRE FORMULA

In accordance with the quantization condition (15) we now replace  $[(\partial/\partial E)L(E)]_{E=E_n}$  by  $\pi(dn/dE_n)$ , i. e., by  $\pi/(dE_n/dn)$ . In this way we obtain from (16) the nonrelativistic Fermi-Segrè formula

$$\psi_n^2(0) = \frac{Z}{\pi a_0^2 e^2} \frac{dE_n}{dn}, \quad (18)$$

where  $dE_n/dn$  is to be obtained by means of spectroscopic data.

Like formulas (15) and (16), also the nonrelativistic Fermi-Segrè formula (18) is exact in the particular cases of the attractive, pure-Coulomb potential and of the potential (17).

Recalling what was said at the end of Sec. III about the accuracy of formulas (15) and (16), we may draw the following conclusion as to the accuracy and applicability of the nonrelativistic Fermi-Segrè formula (18). If the idealized model used in the present paper were physically realistic, i. e., if it were completely justified to use the one-particle model with a nonrelativistic electron moving in a local potential, which in a certain region around  $r=0$  is approximately a Coulomb potential due to a point-shaped nucleus of charge number  $Z$ , then the essential limitation for the accuracy of the nonrelativistic Fermi-Segrè formula should be connected to the possibility of calculating  $de_n/dn$  by interpolation from the spectroscopic term values. For unperturbed terms this calculation has been discussed by Crawford and Schawlow on p. 1312 in Ref. 3.

<sup>1</sup>E. Fermi and E. Segrè, *Reale Accademia d'Italia, Memorie della classe di Scienze Fisiche, Matematiche e Naturali* (Reale Accademia d'Italia, Roma, 1933), Vol. IV, pp. 131-158.

<sup>2</sup>E. Fermi and E. Segrè, *Z. Physik* **82**, 729 (1933).

<sup>3</sup>M. F. Crawford and A. L. Schawlow, *Phys. Rev.* **76**, 1310 (1949).

<sup>4</sup>L. L. Foldy, *Phys. Rev.* **111**, 1093 (1958).

<sup>5</sup>N. Fröman and P. O. Fröman, *JWKB Approximation, Contributions to the Theory* (North-Holland, Amsterdam, 1965).

<sup>6</sup>N. Fröman, *Arkiv Fysik* **32**, 541 (1966).

<sup>7</sup>N. Fröman, *Ann. Phys. (N. Y.)* **61**, 451 (1970).

<sup>8</sup>W. H. Furry, *Phys. Rev.* **71**, 360 (1947).

<sup>9</sup>S. Yngve, *J. Math. Phys.* **13**, 324 (1972).

<sup>10</sup>Private communication from Dr. J. A. Campbell, Center for Particle Theory and Department of Computer Science, University of Texas at Austin, Austin, Texas 78712.

<sup>11</sup>L. Hulthén, *Arkiv Mat. Astron. Fysik* **28A**, No. 5 (1942).

## Determination of Mass-Attenuation Coefficients in Krypton and Xenon by Continuous Analysis between 8 and 0.8 keV

François Wulleumier

*Laboratoire de Chimie Physique de la Faculté des Sciences de Paris, Paris, France*

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The bremsstrahlung emitted from a tungsten anode in an x-ray tube has been used for continuous analysis of krypton and xenon absorption spectra between 8 and 0.8 keV (1.5 to 15 Å). Attenuation coefficients were determined every 0.05 Å between 1.5 and 8 Å (in steps of energy varying from 150 to 10 eV) and every 0.1 Å between 8 and 15 Å (20 to 5 eV). Results obtained are compared with previously determined experimental values and with semiempirical and theoretical determinations. Tabulated data of McMaster *et al.* and calculations of McGuire are shown to be in good agreement with the experimental results, generally within 10%. Multiply excited and ionized states have been observed in krypton, owing to simultaneous interaction of incident radiation with 2*p* and 4*p* (and 4*s*) electrons, and a nonhydrogenic behavior of the xenon 3*p*-subshell photoionization cross section has been revealed. Krypton and xenon  $L$  and xenon  $M_{III}$  absorption jump ratios have been determined. Finally, continuous oscillator strengths of krypton and xenon  $L$  shells and the xenon  $M$  shell have been evaluated.

### I. INTRODUCTION

Until about 1960 all x-ray attenuation-coefficient measurements were performed using x-ray characteristic lines as radiation sources. The various

semiempirical methods elaborated for attenuation-coefficient determinations (Jönsson,<sup>1</sup> Victoreen,<sup>2</sup> Henke *et al.*,<sup>3</sup> Leroux,<sup>4</sup> and Heinrich<sup>5</sup>) were thus based on a few discrete data points for each element. Using synchrotron radiation has made possi-