PHYSICAL REVIEW VOLUME 111, NUMBER 4 AUGUST 15, 1958

Fermi-Segrè Formula*

L. L. FOLDY
Case Institute of Technology, Cleveland, Ohio
(Received April 14, 1958)

A derivation of the nonrelativistic Fermi-Segrè formula for the probability of finding a valence s-electron at the nucleus of an atom in terms of the energy eigenvalues of the electron is presented which makes use of the effective-range method drawn from scattering theory and a refinement of the JBWK method which avoids problems with the Coulomb singularity of the ion core potential.

FOR the interpretation of fine structure splittings, hyperfine structure splittings, and isotope shifts of spectral lines, and more recently for the interpretation of Knight shift[1] data, it is necessary to have information concerning the probability of finding an electron at the nucleus. In 1933 Fermi and Segrè[2] derived a remarkably simple formula for the square of the wave function of a valence s-electron at the nucleus which is a refinement of a formula due to Goudsmit.[3] The Fermi-Segrè formula was derived essentially by the application of the JBWK method to an s-electron moving in an ion core potential which is Coulombic in character both very close to the nucleus and at great distances. The remarkable feature of the formula is that it makes no explicit reference to the detailed nature of the ion core potential (which generally is unknown) but allows the calculation of the probability density for the electron at the nucleus in terms of the energy levels of the electron in the potential only, quantities which are directly determinable from spectroscopic observation. The simplicity and elegance of the Fermi-Segrè formula so impressed the present author that he decided to explore the problem with the object of improving the derivation and placing limits of error on the formula itself. Although he was able to give a more rigorous derivation of the formula, the problem of its accuracy appears to be an order of magnitude more difficult and no substantial progress was achieved in this direction. Because of recent interest in the formula[4] in connection with the Knight shift, it was decided to publish this new derivation in the present paper.

It should be remarked that there is some question concerning the applicability of the Fermi-Segrè formula to actual atoms because it neglects configuration interaction, which may be important in some cases, and also since it assumes the existence of a local potential for the valence electron, which in view of the effects of exchange is not necessarily justifiable. We shall not be concerned with these aspects of the problem but shall address ourselves simply to the purely mathematical problem of the validity of the formula in the idealized case where one does have an s-electron moving in a potential of the type described. Furthermore, in the case of heavy atoms relativistic effects can be important. While these relativistic effects can be taken into account (and Fermi and Segrè do give a relativistic correction factor in their formula) we shall deal with the entire problem nonrelativistically in the present paper.

The Fermi-Segrè formula with neglect of relativistic corrections can be written in the notation used in this paper as

$$\psi_n^2(0)=\frac{Zz^2}{\pi a_0^3\nu_n^3}\frac{d\nu_n}{dn}=\frac{Zz^2}{\pi a_0^3\nu_n^3}\left[1-\frac{d\Delta_n}{dn}\right]. \qquad (1)$$

Here $\psi_n^2(0)$ is the probability density for the s-electron at the nucleus in the nth stationary state, Z is the nuclear charge, z is the charge of the ion in the field of which the electron moves, $a_0=\hbar^2/me^2$ is the Bohr radius, ν_n is the effective quantum number of the nth stationary state defined by the fact that the term value in Rydberg units is given by z^2/ν_n^2, $\epsilon_n=1/\nu_n^2$, and $\Delta_n=n-\nu_n$ is the quantum defect of the nth state. The derivative $d\Delta_n/dn$ is presumed to be evaluated by smoothly interpolating the values of Δ_n as a function of n and evaluating the slope at n.

Equation (1) can be rewritten as

$$\psi_n^2(0)=\frac{Zz^2}{\pi a_0^3\nu_n^3[1-(2/\nu_n^3)(d\Delta_n/d\epsilon_n)]}, \qquad (2)$$

which is the form in which it is derived velow. As will be seen, the problem of deriving this formula breaks down naturally into two parts: (1) relating the value of the radial wave function at the nucleus to its value at large distances from the nucleus, and (2) evaluating the normalization integral for the radial wave function. In the derivation of Fermi and Segrè, both parts are treated by the ordinary JBWK method.[5] In our derivation, the first part of the problem is treated by a variant of the ordinary JBWK method which avoids in a simple and direct fashion the usual difficulties with the Cou-

---

* Work supported in part by the U. S. Atomic Energy Commission.

[1] See W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

[2] E. Fermi and E. Segrè, Rend. accad. sci. fis. mat. e nat. soc. reale Napoli 4, 131 (1933); Z. Physik **82**, 729 (1933). For a discussion of this formula, see M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

[3] S. A. Goudsmit, Phys. Rev. **43**, 636 (1933).

[4] H. Brooks and F. S. Ham (to be published).

[5] See for example, L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), second edition p. 184 ff, and references contained therein.

lomb singularity of the potential at the origin. The second part is treated by a method analogous to the effective range method[6] in the theory of scattering, but is at the same time related to the so-called "quantum defect" method[7] which was developed independently of the effective range method for the treatment of solid-state problems. The connection between these two methods does not seem to have been noted before. Although we feel that our derivation is more satisfactory than that of Fermi and Segrè, we are still unable to ascertain the limits of error of the formula.

The two methods introduced for dealing with this problem would appear to have more general applications to atomic problems. It is hoped that study of such applications will be possible in the future. We now proceed to the presentation of our derivation.

I

Consider an s-electron moving in a spherically symmetric ion core potential $V(r)$. If the nucleus has a charge Ze and the ion core a charge ze, then

$$\begin{aligned} V(r) &\rightarrow ze^2/r \qquad (r\rightarrow\infty) \\ &\rightarrow Ze^2/r \qquad (r\rightarrow\infty). \end{aligned} \tag{3}$$

The potential $V(r)$ is close to its asymptotic value when r is substantially greater than a radius r_c which is of the order of a_0/z where $a_0=\hbar^2/me^2$ is the Bohr radius.

We designate the normalized wave function for the nth bound stationary eigenstate of the electron by $\psi_n(r)$ and introduce the radial wave function $u_n(r)$, with a normalization to be specified later, by the definition

$$u_n(r)=\left[4\pi\int_0^\infty u_n^2dr\right]^{\frac{1}{2}} r\psi_n(r). \tag{4}$$

Then u_n satisfies

$$d^2u_n/dr^2+(2m/\hbar^2)[E_n-V]u_n=0. \tag{5}$$

The quantity of interest to us, $\psi_n^2(0)$ can be written as

$$\psi_n^2(0)=\left(\frac{du_n}{dr}\right)^2_{r=0}\bigg/\left[4\pi\int_0^\infty u_n^2dr\right], \tag{6}$$

where use has been made of the fact that u_n vanishes linearly with r at $r=0$.

II

We first will obtain an expression for the normalization integral $\int_0^\infty u_n^2dr$ in terms of the energy levels for the electron in the ion core potential. It is convenient to convert Eq. (5) by the introduction of appropriate atomic units:

$$\begin{aligned} \rho&=zme^2r/\hbar^2=zr/a_0, \\ \epsilon_n&\equiv 1/\nu_n^2=-2\hbar^2E_n/z^2me^4, \\ v(\rho)&=-2\hbar^2V(r)/z^2me^4. \end{aligned} \tag{7}$$

It will be noted that ν_n is just the *effective quantum number* of the nth state as conventionally defined. The equation for u_n then becomes

$$d^2u_n/d\rho^2+[-\epsilon_n+v(\rho)]u_n=0, \tag{8}$$

while (6) becomes

$$\psi_n^2(0)=\frac{z^3}{4\pi a_0^3}\left(\frac{du_n}{d\rho}\right)^2_{\rho=0}\bigg/\int_0^\infty u_n^2d\rho. \tag{9}$$

We note that

$$\begin{aligned} v(\rho)&=2Z/z\rho \qquad (\rho\rightarrow 0), \\ v(\rho)&=2/\rho \qquad (\rho>\rho_c\sim 1). \end{aligned}$$

If one writes Eq. (8) for a second eigenfunction u_m, then one has immediately

$$\begin{aligned} \int_\rho^\infty \left[u_m\frac{d^2u_n}{d\rho^2}-u_n\frac{d^2u_m}{d\rho^2}\right]d\rho &= u_n(\rho)\frac{du_m(\rho)}{d\rho}-u_m(\rho)\frac{du_n(\rho)}{d\rho} \\ &=(\epsilon_n-\epsilon_m)\int_\rho^\infty u_nu_md\rho. \end{aligned} \tag{10}$$

We now turn our attention to the function $w_n(\rho)$ defined as that solution of the equation

$$d^2w_n/d\rho^2+[-\epsilon_n+2/\rho]w_n=0, \tag{11}$$

which vanishes as $\rho\rightarrow\infty$ and which is normalized to

$$w_n(0)=1. \tag{12}$$

We shall see shortly that except when ϵ_n is the reciprocal of the square of an integer, a solution with these properties exists. Again, from Eq. (11) and the corresponding equation for w_m, one can derive the relation analogous to (10):

$$w_n(\rho)\frac{dw_m(\rho)}{d\rho}-w_m\frac{dw_n(\rho)}{d\rho}=(\epsilon_n-\epsilon_m)\int_\rho^\infty w_nw_md\rho. \tag{13}$$

The normalization of u_n is now fixed such that

$$u_n(\rho)\rightarrow w_n(\rho), \qquad (\rho\rightarrow\infty), \tag{14}$$

which is possible since both functions satisfy the same equation and the same boundary condition at infinity for $\rho>\rho_c$. Subtracting Eq. (10) from Eq. (11) and

---

[6] This method is originally due to G. Breit. See, for example, G. Breit, Revs. Modern Phys. **23**, 238 (1951). Our treatment follows more closely H. A. Bethe, Phys. Rev. **76**, 38 (1949). Other treatments are contained in the following papers: F. C. Barker and R. E. Peierls, Phys. Rev. **75**, 312 (1949); J. M. Blatt and J. D. Jackson, Phys. Rev. **76**, 118 (1949); Revs. Modern Phys. **22**, 77 (1950); G. F. Chew and M. L. Goldberger, Phys. Rev. **75**, 1637 (1949).

[7] See, for example, F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, and references contained therein.

passing to the limit $\rho\to 0$, we obtain

$$\lim_{\rho\to 0}\left[\frac{dw_m}{d\rho}-\frac{dw_n}{d\rho}\right]=(\epsilon_n-\epsilon_m)\int_0^\infty [w_nw_m-u_nu_m]d\rho. \quad (15)$$

The limit on the left is required since $dw_n/d\rho$ has a logarithmic singularity at $\rho=0$. In writing the above we have used the fact that $u_n(0)=0$, $w_n(0)=1$. We now discuss the left and right sides, respectively, of this equation.

The change in variable $\rho=\nu_nx/2$ reduces Eq. (11) to Whittaker's equation[8] from which it follows that the solution having the specified boundary properties can be written

$$w_n(\rho)=\Gamma(1-\nu_n)W_{\nu_n,\frac{1}{2}}(2\rho/\nu_n), \quad (16)$$

where $W_{\nu_n,\frac{1}{2}}$ is the Whittaker function and Γ is the gamma function.[8] The known behavior of the Whittaker function in the neighborhood of the origin then leads to

$$w_n(\rho)\xrightarrow[\rho\to 0]{}1-2\rho\bigg[\ln 2\rho-\psi(\nu_n)+\pi\cot\pi\nu_n -\psi(1)-\psi(2)+\frac{1}{2\nu_n}-\ln\nu_n\bigg], \quad (17)$$

where ψ is the logarithmic derivative of the gamma function, Γ'/Γ. Hence

$$\frac{dw_n}{d\rho}\xrightarrow[\rho\to 0]{}-2\ln 2\rho-2\bigg[1+\psi(\nu_n)+\pi\cot\pi\nu_n -\psi(1)-\psi(2)+\frac{1}{2\nu_n}-\ln\nu_n\bigg], \quad (18)$$

and the left side of (15) can be written

$$\lim_{\rho\to 0}\left[\frac{dw_m}{d\rho}-\frac{dw_n}{d\rho}\right]=\tfrac{1}{2}[G(\nu_n)-G(\nu_m)], \quad (19)$$

where

$$G(\nu)=\pi\cot\pi\nu+\psi(\nu)-\ln\nu+1/2\nu. \quad (20)$$

It is convenient to write

$$G(\nu)=\pi\cot\pi\nu+g(\nu), \quad (21)$$

where

$$g(\nu)=\psi(\nu)-\ln\nu+1/2\nu. \quad (22)$$

We note that for numerical calculation, one can conveniently use the asymptotic expansion for the ψ function, valid when $\nu\gg 1$, namely

$$\psi(\nu)=\ln\nu-\frac{1}{2\nu}-\frac{1}{12\nu^2}+\frac{1}{120\nu^4}-\frac{1}{252\nu^6}\cdots, \quad (23)$$

whence

$$g(\nu)\sim\frac{1}{12\nu^2}+\frac{1}{120\nu^4}-\frac{1}{252\nu^6}\cdots, \quad (24)$$

which is of adequate accuracy for our purposes for $\nu\gtrsim 1.5$.

Thus Eq. (15) is reduced to the form

$$G(\nu_n)-G(\nu_m)=\left(\frac{1}{{\nu_n}^2}-\frac{1}{{\nu_m}^2}\right)R_{nm}=(\epsilon_n-\epsilon_m)R_{nm}, \quad (25)$$

where the integral

$$R_{nm}=2\int_0^\infty [w_nw_m-u_nu_m]d\rho \quad (26)$$

will be recognized as closely related to the *effective range* of scattering theory.[6] We now turn to an analysis of the properties of this integral.

III

The integral R_{nm} can be regarded as a function of the two discrete variables ϵ_n and ϵ_m. We remark first that the integrand essentially vanishes for $r>r_c$ since the functions u_n and w_n are practically equal there, so that the principal contribution to the integral comes from the range $r<r_c$. It will be noted, however, that in this range the functions u_n and w_n are relatively insensitive to the values of ϵ_n provided the changes in the latter are relatively small compared to unity. This is a consequence of the fact that the potential functions appearing in the respective equations for these functions are both of the order of or larger than unity in this range and that the normalization of the functions at one point in the range is fixed by the defining conditions on these functions. Hence we conclude that for fixed ϵ_n, R_{nm} is a relatively insensitive function of ϵ_m for $|\epsilon_n-\epsilon_m|\ll 1$, and that the same is true for R_{nm} for fixed ϵ_m when regarded as a function of ϵ_n.

If the energy eigenvalues of the electron in the potential V are known, then the values of ϵ_n are likewise known through (7). Thus from these values one can compute the left side of Eq. (25) and obtain a matrix of R_{nm} values with the exception of diagonal values. The smooth variation of R_{nm} with ϵ_n and ϵ_m would then allow one to interpolate to obtain the diagonal values R_{nn}. If the latter are known, then as we shall see, we have the information required to obtain the normalization integral which we are seeking. An alternative procedure which is adequate for our purposes and simpler in practice is the following.

It is known empirically that in many cases, the effective quantum numbers ν_n can be represented by a formula of the form

$$\nu_n=n-\Delta_n=n-\alpha+\delta_n, \quad (\delta_n\ll 1,\ \delta_n\xrightarrow[n\to\infty]{}0), \quad (27)$$

where α is independent of n and represents the quantum

---

[8] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, 1940); H. Buchholz, *Die Konfluente Hypergeometrische Funktion* (Springer-Verlag, Berlin, 1953).

defect for asymptotically large quantum number. Furthermore the residuals δ_n do not vary erratically with n but can be represented quite accurately by a polynomial expression of the form

$$\delta_n=\beta_1\epsilon_n+\beta_2\epsilon_n^2+\cdots=\frac{\beta_1}{\nu_n^2}+\frac{\beta_2}{\nu_n^4}+\cdots. \tag{28}$$

If one substitutes this result into Eq. (25), one has

$$-\pi[\cot(\alpha-\delta_n)\pi-\cot(\alpha-\delta_m)\pi]+g(\nu_n)-g(\nu_m)=(\epsilon_n-\epsilon_m)R_{nm}. \tag{29}$$

Now both sides of this equation can be considered smoothly varying functions of the variable $\epsilon_n-\epsilon_m$ and hence one can divide both sides of this equation by this quantity and pass to the limit $\epsilon_m\rightarrow\epsilon_n$. The result is

$$\begin{aligned}R_{nn}&=-\pi^2\csc^2\nu_n\pi\left(\frac{d\delta_n}{d\epsilon_n}\right)-\frac{\nu_n^3}{4}\left(\frac{dg(\nu_n)}{d\nu_n}\right)\\&=-\frac{\pi^2\nu_n^3}{2}\csc^2\nu_n\pi\left[1+\frac{2}{\nu_n^3}\left(\frac{d\delta_n}{d\epsilon_n}\right)\right]-\frac{\nu_n^3}{4}\frac{dG(\nu_n)}{d\nu_n}.\end{aligned} \tag{30}$$

If one uses the asymptotic expansion for g given in Eq. (24) one can also write

$$R_{nn}=-\pi^2\csc^2\nu_n\pi\left(\frac{d\delta_n}{d\epsilon_n}\right)-\frac{1}{12}+\frac{1}{60\nu_n^2}\cdots. \tag{31}$$

The quantity $d\delta_n/d\nu_n$ can be evaluated by a polynomial fit of the form (28) to the empirical data if desired.

IV

We will now assume that the values of R_{nn} have been determined by one of the empirical schemes already mentioned. The desired normalization integral can be expressed as

$$\int_0^\infty u_n^2d\rho=-\tfrac{1}{2}R_{nn}+\int_0^\infty w_n^2d\rho. \tag{32}$$

The integral on the right can be evaluated in a manner analogous to that which we have just employed for R_{nn}. Equation (13) is valid for all values of ϵ_n and ϵ_m and not simply the eigenvalues of the original problem. Hence in this equation we can divide by $\epsilon_n-\epsilon_m$ and pass to the limit $\rho\rightarrow0$, followed by $\epsilon_m\rightarrow\epsilon_n$, with the result

$$\int_0^\infty w_n^2d\rho=-\frac{\nu_n^3}{2}\frac{dG(\nu_n)}{d\nu_n}. \tag{33}$$

Hence if we use the particular result (30), we have

$$\int_0^\infty u_n^3d\rho=\pi^2\nu_n^3\csc^2\nu_n\pi\left[1+\frac{2}{\nu_n^3}\left(\frac{d\delta_n}{d\epsilon_n}\right)\right]. \tag{34}$$

Thus a knowledge of the eigenvalues of the electron in the potential V allows us to calculate the normalization integral quite precisely. In fact, since u_n is identical with w_n for $r>r_c$, w_n is a known function, and the normalization integral for u_n is now determined, one knows completely the wave function u_n for $r>r_c$.

It would be of interest to explore the degree of accuracy of Eq. (24). While this is a fascinating mathematical problem, it will not be gone into here. Exploratory investigation would suggest that it is of considerably higher accuracy than we shall be able to achieve in the calculation of $(du_n/d\rho)_{\rho=0}$.

V

The remainder of the problem at hand consists in evaluating $(du_n/d\rho)_{\rho=0}$. This cannot be done at all precisely without knowledge of the potential $V(r)$ and even with this knowledge would require integration of Eq. (5) and hence would negate any value of the Fermi-Segrè formula itself. It is therefore necessary to resort to an approximation method and some form of the JBWK method is indicated. The usual JBWK method is not too satisfactory here because of the difficulties with the Coulomb singularity at the origin. The following variant of the usual method would appear to be most appropriate to this problem. Unfortunately it becomes rather cumbersome unless restricted to terms of relative order ϵ_n. This is not too unsatisfactory a restriction and hence it will be adhered to below.

One begins with the function $j(\rho)$ defined by

$$j(\rho)=\sigma J_1(\sigma),\quad \sigma=(8\rho)^{\frac{1}{2}}, \tag{35}$$

where J_1 is the Bessel function of unit order. One can readily verify that $j(\rho)$ satisfies the equation

$$\frac{d^2j}{d\rho^2}+\frac{2}{\rho}j=0. \tag{36}$$

We now let

$$u_n(\rho)=AK_n'^{-\frac{1}{2}}j(K_n), \tag{37}$$

where

$$K_n=K_n(\rho),\quad K_n'=dK_n/d\rho. \tag{38}$$

Then u_n satisfies the differential equation

$$\frac{d^2u_n}{d\rho^2}+\left[\frac{2K_n'^2}{K_n}+\frac{K_n'''}{2K_n'}-\frac{3K_n''^2}{4K_n'^2}\right]u_n=0. \tag{39}$$

This coincides with Eq. (8) provided

$$\frac{2K_n'^2}{K_n}+\frac{K_n'''}{2K_n'}-\frac{3K_n''^2}{4K_n'^2}=v(\rho)-\epsilon_n, \tag{40}$$

while the boundary condition $u_n(0)=0$ is satisfied if $K_n(0)=0$. This equation cannot be solved exactly for K_n, but if in the spirit of the JBWK approximation the terms in K_n''' and $K_n''^2$ are neglected, integration is possible:

$$(8K_n)^{\frac{1}{2}}=\int_0^\rho (v-\epsilon_n)^{\frac{1}{2}}d\rho. \tag{41}$$

Since, as $\rho\rightarrow 0$, K_n as determined from this equation approaches $Z\rho/z$, the boundary condition at $\rho=0$ is satisfied.

We now consider the form of the solution (41) when $\rho>\rho_c$; there

$$(8K_n)^{\frac{1}{2}}=\int_0^\rho \left[(v-\epsilon_n)^{\frac{1}{2}}-\left(\frac{2}{\rho}-\epsilon_n\right)^{\frac{1}{2}}\right]d\rho$$

$$+\int_0^\rho \left(\frac{2}{\rho}-\epsilon_n\right)^{\frac{1}{2}}d\rho=\Lambda_n+\sigma\left[1-\frac{1}{12}\epsilon_n\rho\right], \tag{42}$$

to terms of first order in ϵ_n. Here

$$\Lambda_n=\int_0^\infty \left[(v-\epsilon_n)^{\frac{1}{2}}-\left(\frac{2}{\rho}-\epsilon_n\right)^{\frac{1}{2}}\right]d\rho, \tag{43}$$

where the upper limit has been made infinite since $v=2/\rho$ for $\rho>\rho_c$, and the integrand therefore vanishes in this range. To terms of first order in ϵ_n,

$$\Lambda_n=\Lambda+\epsilon_n\Omega, \tag{44}$$

where

$$\begin{aligned}\Lambda&=\int_0^\infty\left[v^{\frac{1}{2}}-\left(\frac{2}{\rho}\right)^{\frac{1}{2}}\right]d\rho,\\ \Omega&=\tfrac{1}{2}\int_0^\infty\left[\left(\frac{\rho}{2}\right)^{\frac{1}{2}}-\left(\frac{1}{v}\right)^{\frac{1}{2}}\right]d\rho.\end{aligned} \tag{45}$$

Substituting these results into Eq. (37) and retaining terms of first order in ϵ_n, we then have for $\rho>\rho_c$:

$$\begin{aligned}u_n(\rho)=A\sigma^{\frac{1}{2}}(1+\tfrac{1}{8}\epsilon_n\rho)[\sigma+\Lambda_n-\tfrac{1}{12}\epsilon_n\rho\sigma]^{\frac{1}{2}}&\\ \times J_1(\sigma+\Lambda_n-\tfrac{1}{12}\epsilon_n\rho\sigma).&\end{aligned} \tag{46}$$

In the appendix it is shown that to terms of order ϵ_n, and for $\rho\ll 2/\epsilon_n$,

$$\begin{aligned}w_n(\rho)=-\tfrac{1}{2}\pi\sigma^{\frac{1}{2}}(1+\tfrac{1}{8}\epsilon_n\rho)[\sigma-\tfrac{1}{12}\epsilon_n\rho\sigma]^{\frac{1}{2}}&\\ \times[\cot\pi\nu_n J_1(\sigma-\tfrac{1}{12}\epsilon_n\rho\sigma)+N_1(\sigma-\tfrac{1}{12}\epsilon_n\rho\sigma)].&\end{aligned} \tag{47}$$

By a proper choice of Λ_n and A, these expressions should agree in the range $\rho>\rho_c$. They do not, but the reason is that (46) suffers from the JBWK approximation. However, for $\rho>\rho_c$ the arguments of the Bessel functions are sufficiently large that only a moderate error is entailed in replacing the functions by the first term in their asymptotic expansions. In this case, Eq. (46) becomes

$$\begin{aligned}u_n(\rho)=-A(2\sigma/\pi)^{\frac{1}{2}}&\\ \times[1+\tfrac{1}{8}\epsilon_n\rho]\cos(\sigma+\Lambda_n-\tfrac{1}{12}\epsilon_n\rho\sigma+\tfrac{1}{4}\pi),&\end{aligned} \tag{48}$$

while (47) becomes

$$\begin{aligned}w_n(\rho)=(\tfrac{1}{2}\pi\sigma)^{\frac{1}{2}}[1+\tfrac{1}{8}\epsilon_n\rho]&\\ \times\csc\pi\nu_n\cos(\sigma-\pi\nu_n-\tfrac{1}{12}\epsilon_n\rho\sigma+\tfrac{1}{4}\pi).&\end{aligned} \tag{49}$$

We see that the two functions agree provided

$$\begin{aligned}\Lambda_n&=(n-\nu_n)\pi=\alpha-\beta_1\epsilon_n=\Lambda+\epsilon_n\Omega\\ A&=\pm\tfrac{1}{2}\pi\csc\pi\nu_n.\end{aligned} \tag{50}$$

These conditions are required simply in order that $V(r)$ should reproduce the energy eigenvalues of the electron in the approximation in which we are working.

Using these results we can now calculate $(du_n/d\rho)_{\rho=0}$ from (37) to obtain

$$\left(\frac{du_n}{d\rho}\right)^2_{\rho=0}=\frac{4\pi^2Z^2\csc^2\pi\nu_n}{z}. \tag{51}$$

Finally substituting this and the result for the normalization integral given in Eq. (34) into Eq. (9), we obtain

$$\psi_n^2(0)=\frac{Zz^2}{\pi a_0^3\nu_n^3[1+(2/\nu_n^3)(d\delta_n/d\epsilon_n)]}, \tag{52}$$

which is the result discussed in the introduction as being equivalent to the Fermi-Segrè formula.

ACKNOWLEDGMENT

The author is indebted to Dr. Lawrence Wilets for discussions concerning the Fermi-Segrè formula.

APPENDIX

For our development it was necessary to obtain the expansion of the function $w_n(\rho)$ in powers of ϵ_n correct to first order in ϵ_n. We were unable to find anything more than the zeroth order term in the literature.[†] To obtain the desired result we proceeded purely formally in the following way. We note that the function

$$y(\rho)=\sigma[AJ_1(\sigma)+BN_1(\sigma)],\quad \sigma=(8\rho)^{\frac{1}{2}} \tag{A-1}$$

satisfies Eq. (36), and in this case set

$$w_n(\rho)=K_n'^{-\frac{1}{2}}y(K_n), \tag{A-2}$$

where K_n is now a different function of ρ than in Eq. (37). Then K_n must satisfy Eq. (40) with v replaced by $2/\rho$. Again making the JBWK approximation, this may be solved to yield to terms of first order in ϵ_n,

$$K_n=\rho-\tfrac{1}{6}\epsilon_n\rho^2. \tag{A-3}$$

With this form for K_n, one finds that (A-2) above satisfies the following equation exactly:

$$\frac{d^2w_n}{d\rho^2}+\left[\frac{2}{\rho}-\epsilon_n+\frac{2\epsilon_n^2\rho}{9(1-\frac{1}{6}\epsilon_n\rho)}-\frac{\epsilon_n^2}{12(1-\frac{1}{3}\epsilon_n\rho)}\right]w_n=0. \tag{A-4}$$

[†] *Note added in proof.*—Dr. F. S. Ham has kindly informed us that such formulas have been derived and has quoted the following references: T. S. Kuhn, Quart. Appl. Math. **9**, 1 (1951); F. S. Ham, Quart. Appl. Math. **15**, 1 (1957).

Hence this is a solution to first order in ϵ_n and is a good approximation for $\rho \ll 2/\epsilon_n$. To determine A and B we make use of the fact that w_n given by (A-2) must approach the value given in Eq. (17) as $\rho \to 0$. Using the limiting forms of the Bessel functions as $\rho \to 0$, we find that for agreement it is necessary that $A = -(\pi/2)\cot\pi\nu_n$ and $B = -\pi/2$. Hence to first order in ϵ_n, $w_n(\rho)$ has the form given in Eq. (47).

PHYSICAL REVIEW VOLUME 111, NUMBER 4 AUGUST 15, 1958

Variational Calculations of the 2 ^3S State of Helium*

J. Traub† and H. M. Foley
Columbia University, New York, New York

(Received March 13, 1958)

With a 12-parameter Hylleraas-type wave function containing only positive powers, a new calculation has been carried out for the 2 ^3S state of helium by the Ritz variational principle. The energy was minimized by a descent process. A nonrelativistic energy of -1.0876088 Hylleraas units was reached as compared with the best previously published value of -1.0876015 Hylleraas units from a 6-parameter function. When mass-polarization and $\alpha^2 R_y$ corrections are included, the 12-parameter function gives an ionization potential 2.52 cm^{-1} less than the experimental value of 38 454.64 cm^{-1}. The electron density at the nucleus is also calculated and compared with the experimental hyperfine-spectrum value. All numerical work was carried out on an I.B.M. 650 computer.

I. INTRODUCTION

A LONG series of calculations have been made of the energy of the ground state of helium,[1] culminating in the 38-parameter calculation of Kinoshita.[2] When relativistic and mass-polarization corrections are made, the resulting comparison with the experimental values of the ionization energy must be considered as very satisfactory.

The six-parameter variational calculations of Hylleraas[3] and Huang[4] represent the most accurate previously published wave functions of the 2 ^3S state.[5] They differ from the ground-state function with respect to symmetry and also in that two different exponential functions must be included, corresponding to 1*s* and 2*s* orbits. No calculation of the relativistic corrections has hitherto been made for the 2 ^3S state. The mass-polarization term was calculated by Stone[6] with a six-parameter function.

In this paper are presented the results of a twelve-parameter variational calculation of the 2 ^3S nonrelativistic energy together with relativistic and mass-polarization corrections. Compared with the elaborate character of the wave functions employed in some recent work,[2,7] the 12-parameter function employed here may be regarded as of intermediate complexity. In spite of this fact the total energy seems to converge very well, and indeed the agreement of our calculated value with experiment seems to be as good as was obtained by Chandrasekhar and Herzberg[8] for the ground state with an 18-parameter function. This is undoubtedly related to the fact that the independent-particle hydrogenic wave function, to which the Hylleraas trial function with few parameters reduces, is a much better approximation for a state with one electron excited than it is for the ground state with both electrons in the same orbit. (See also the discussion of mass polarization below.)

An additional quantity of interest which can be compared with experiment is the total charge density at the nucleus which enters as a factor in the hyperfine interaction.[9]

The rather lengthy calculations of the relativistic corrections have not previously been done for the excited states. It has appeared worthwhile to give an account of the methods employed in these calculations.

II. NONRELATIVISTIC INFINITE NUCLEAR MASS PROBLEM

A. Mathematical Preliminaries

The nonrelativistic Schrödinger equation for the helium atom is

$$\frac{\hbar^2}{2m}(\nabla_1{}^2+\nabla_2{}^2)\psi+\left(E+\frac{Ze^2}{r_1}+\frac{Ze^2}{r_2}-\frac{e^2}{r_{12}}\right)\psi=0, \qquad (1)$$

---

* Work supported by the National Science Foundation.

† Watson Laboratory Fellow, IBM.

[1] H. A. Bethe and E. E. Salpeter, *Handbook of Physics* (Academic Press, Inc., New York, 1957), Vol. 35, Atoms I, pp. 204–278.

[2] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[3] E. Hylleraas, Z. Physik **54**, 347 (1929); **65**, 209 (1930).

[4] Su-chu Huang, Astrophys. J. **108**, 354 (1948).

[5] Hylleraas gave $0.08761 \times 4R_{\mathrm{He}^4}hc$ for the nonrelativistic ionization potential of the 2 ^3S state of helium. This calculation was in error and was later corrected by Hylleraas[6] to $0.0876015 \times 4R_{\mathrm{He}^4}hc$. Huang employed a wave function which is formally identical with that of Hylleraas but obtained a value of $0.087600 \times 4R_{\mathrm{He}^4}hc$ due, it must be supposed, to incomplete minimization.

[6] A. P. Stone, Proc. Phys. Soc. (London) **A68**, 1152 (1955).

[7] Tycko, Thomas, and King, Phys. Rev. **109**, 369 (1958).

[8] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[9] W. B. Teutsch and V. W. Hughes, Phys. Rev. **103**, 1461 (1954).