(2) S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters **6**, 60 (1961).
(3) L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).
(4) J. H. Wood, Phys. Rev. **117**, 714 (1960).
(5) D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604 (1964).
(6) R. Ingalls, Phys. Rev. **155**, 157 (1967).
(7) R. Ingalls, H. G. Drickamer, and G. De Pasquali, Phys. Rev. **155**, 165 (1967).
(8) I. B. Bersuker, V. I. Gol'danskii, and E. F. Makarov, Zh. Eksperim. i Teor. Fiz. **49**, 699 (1965) [English transl.: Soviet Phys.—JETP **22**, 485 (1966)].
(9) J.-P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, Phys. Rev. Letters **17**, 809 (1966).
(10) H. S. Möller and R. L. Mössbauer, Phys. Letters **24A**, 416 (1967).

Relative to the author's formulation to the ionization equilibrium equation of state at high densities [C. A. Rouse, Astrophys. J. **139**, 339 (1964); Naval Research Laboratory Report No. NRL 6594 (unpublished)], the experimental results reported in above references (5), (7), and (10) are of particular interest.

ACKNOWLEDGMENTS

The hospitality and assistance of the E. O. Hulburt Center staff is gratefully acknowledged. In particular, I wish to express my appreciation to Dr. Herbert Friedman for providing an atmosphere that the author found very pleasant and productive for scientific research.

I also wish to thank Dr. Jerome Karle of NRL for helpful discussions and reviewing the manuscript.

Finally, I wish to acknowledge the cooperation and assistance of the staff of the NRL Research Computation Center. Here, the programming of Mrs. Doris E. Gossett was of great value.

This research was conducted while the author was an E. O. Hulburt Research Appointee supported by the U. S. Office of Naval Research and the National Science Foundation. I sincerely thank both organizations for the support that made this investigation possible.

PHYSICAL REVIEW VOLUME 163, NUMBER 1 5 NOVEMBER 1967

Relativistic Effects in Low-Energy Electron Scattering by Atoms*

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(Received 10 May 1967)

Low-energy electron-scattering phase shifts and bound-state energies of neutral atomic potentials are computed using the Fredholm method. The relativistic and nonrelativistic results are compared. It is concluded that relativistic corrections to the phase shifts are unimportant for the potentials considered here.

I. INTRODUCTION

RECENTLY,[1,2] it has been pointed out that relativistic effects in the scattering of low-energy electrons from heavy atoms can be significant. The reason for this seems to stem from the fact that for some atomic models the electron can penetrate far enough into the atom to be accelerated by the nuclear charge to a high speed. Under such circumstances, one might expect classically some modification of the elastic differential scattering cross section. That such reasoning also applies to a quantum-mechanical treatment has been demonstrated by Browne and Bauer,[1] who have numerically computed phase shifts and differential cross sections for several atomic-potential models, using Schrödinger's equation and the second-order relativistic wave equation.

It was later discovered[3] that for potentials representing singly charged atoms, the binding energy of the valence electron was different for the relativistic and nonrelativistic equations. Thus, when the potential was adjusted so as to obtain the same values of the binding energy, the relativistic corrections to the low-energy scattering phase shifts were found to be unimportant. Qualitative arguments[2] based on effective-range theory tend to support the view that for neutral atoms regions of strong interaction need not lead to significant relativistic effects, provided only that there exist an ionic bound state of small binding energy.

In the present work, scattering amplitudes are computed for the Schrödinger and Dirac equations for the case of a netural atomic potential, using the Fredholm method. These amplitudes are used to find both the phase shifts and bound states, and are of the form predicted by effective-range theory. The results (Sec. II) indicate that for a wide range of potentials, relativistic corrections to the phase shifts are unimportant for low-energy scattering; however, the binding energies, which were large compared to scattering kinetic energies, were significantly different in the relativistic and nonrelativistic treatments.

* Research supported by the U. S. Army Research Office (Durham).
[1] H. N. Browne and E. Bauer, Phys. Rev. Letters **16**, 495 (1966).
[2] L. Spruch, Phys. Rev. Letters **16**, 1137 (1966).
[3] M. Rotenberg, Phys. Rev. Letters **16**, 969 (1966).

II. CALCULATIONS AND RESULTS

A. Schrödinger's Equation

The Fredholm solution of the radial Schrödinger equation has been studied by many authors,[4] so we only give here a brief summary of the results. As is well known, phase shifts and bound-state energies may be computed from the Fredholm denominator function. This function may be given explicitly by a power-series expansion of the potential strength:

$$\mathfrak{D}_l(\lambda,k)=1+\sum_{n=1}^{\infty}\frac{\lambda^n}{n!}\int_0^\infty\cdots\int_0^\infty G_l\begin{pmatrix}\xi_1 & \cdots & \xi_n\\ \xi_1 & \cdots & \xi_n\end{pmatrix}\times V(\xi_1)\cdots V(\xi_n)d\xi_1\cdots d\xi_n, \quad (1)$$

where

$$G_l\begin{pmatrix}x_1 & \cdots & x_n\\ y_1 & \cdots & y_n\end{pmatrix}=\begin{vmatrix}G_l(x_1,y_1) & \cdots & G_l(x_1,y_n)\\ \vdots & & \vdots\\ G_l(x_n,y_1) & \cdots & G_l(x_n,y_n)\end{vmatrix}$$

and

$$G_l(x,y)=2ikxyj_l(kx_<)h_l(kx_>).$$

Here j and h are the usual spherical Bessel functions, and k is the particle momentum.

For k real and positive, the scattering phase shifts are obtained from the formula,[5]

$$e^{i\delta}\sin\delta=-[\mathrm{Im}\mathfrak{D}_l(\lambda,k)]/\mathfrak{D}_l(\lambda,k). \quad (2)$$

In addition, solutions of the equation

$$\mathfrak{D}_l(\lambda,i\chi)=0$$

for χ real and positive give the bound-state eigenvalues $E_B=-\frac{1}{2}\chi^2$.

In this example, a potential representing a neutral atom,

$$V(r)=-(Z\alpha e^{-\beta r}/r)(1+\tfrac{1}{2}\beta r), \quad (3)$$

was chosen because of its simplicity. Such a potential represents a positive point charge of magnitude Z at the origin and an equal negative charge distributed exponentially about it, with range $\sim 1/\beta$. Here α is the fine-structure constant. Substitution of Eq. (3) into Eq. (1) yields the first-order s-wave $\mathfrak{D}$ function

$$\mathfrak{D}_0(Z\alpha,k)=1-Z\alpha\left\{\frac{i\ln(1-2ik/\beta)}{k}+\frac{1}{\beta-2ik}\right\}. \quad (4)$$

For the case of hydrogen ($Z=1$, $\beta=2\alpha$), Eq. (4) agrees with the results of Nutt.[6]

[4] T. Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), p. 43; M. Baker, Ann. Phys. (N. Y.) 4, 271 (1958).

[5] R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill Book Company, Inc., New York, 1966), p. 343.

[6] G. L. Nutt, Phys. Rev. **135**, A345 (1964).

B. Dirac Equation

The Fredholm solution of Dirac's equation for potential scattering is a simple two-dimensional extension of the results of Sec. II A. For the Dirac case, we shall be interested in solutions of the coupled pair of equations[7]

$$\frac{d}{dr}\begin{pmatrix}u_1\\ u_2\end{pmatrix}=\begin{pmatrix}-\kappa/r & 1+W-\lambda V(r)\\ 1-W+\lambda V(r) & \kappa/r\end{pmatrix}\begin{pmatrix}u_1\\ u_2\end{pmatrix}, \quad (5)$$

which are regular at the origin and have the asymptotic form

$$\begin{pmatrix}u_1\\ u_2\end{pmatrix}\simeq N\begin{pmatrix}\sin(kr-l\pi/2+\delta)\\ [(W-1)/(W+1)]^{1/2}\cos(kr-l\pi/2+\delta)\end{pmatrix}$$

at infinity. Here

$$\kappa=l \quad \text{for} \quad j=l-\tfrac{1}{2},$$
$$=-l-1 \quad \text{for} \quad j=l+\tfrac{1}{2},$$

and $k=(W^2-1)^{1/2}$, ($m_e=c=\hbar=1$).

These wave functions (which we shall call the "physical" solutions) are given by the solutions of

$$\mathbf{u}(r)=\mathbf{v}(r)-\lambda\int_0^\infty \mathbf{G}^{(\kappa)}(r,r')V(r')\mathbf{u}(r')dr', \quad (6)$$

where

$$\mathbf{u}(r)=\begin{pmatrix}u_1\\ u_2\end{pmatrix},$$

$$\mathbf{v}(r)=\begin{pmatrix}krj_l(kr)\\ S_\kappa[(W-1)/(W+1)]^{1/2}krj_{\bar{l}}(kr)\end{pmatrix}, \quad (7)$$

$$\mathbf{n}(r)=\begin{pmatrix}krn_l(kr)\\ S_\kappa[(W-1)/(W+1)]^{1/2}krn_{\bar{l}}(kr)\end{pmatrix},$$

and $\mathbf{w}(r)=\mathbf{v}(r)+i_i(\mathbf{n}r)$. The Green's function is given by

$$G_{ij}{}^{(\kappa)}(r,r')=i\left(\frac{W+1}{W-1}\right)^{1/2}\begin{cases}v_i(r)w_j(r') & \text{for } r<r'\\ w_i(r)v_j(r') & \text{for } r>r'.\end{cases} \quad (8)$$

Here $S_\kappa=\kappa/|\kappa|$ and $\bar{l}=l-S_\kappa$. The scattering amplitude is given by

$$f=-e^{i\delta}\sin\delta=\lambda\left(\frac{W+1}{W-1}\right)^{1/2}\sum_{i=1}^{2}\int_0^\infty v_i(r)V(r)u_i(r)dr. \quad (9)$$

Application of the Fredholm theory[8] to Eq. (6) leads to the solution

$$\mathbf{u}(r)=\mathbf{v}(r)-\frac{\lambda}{\mathfrak{D}_\kappa(\lambda,W)}\int_0^\infty \mathbf{D}^{(\kappa)}(r,r';\lambda,W)\times V(r')\mathbf{v}(r')dr', \quad (10)$$

[7] M. E. Rose, *Relativistic Electron Theory* (John Wiley & Sons, Inc., New York, 1961), p. 159.

[8] F. G. Tricomi, *Integral Equations* (Interscience Publishers, Inc., New York, 1957), p. 49.

where

$$\mathfrak{D}_\kappa(\lambda,W) = 1+\sum_{n=1}^{\infty}\frac{\lambda^n}{n!}\sum_{k_1\cdots k_n=1}^{2}\int_0^\infty\cdots\int_0^\infty G_\kappa\begin{bmatrix}\xi_1 & \cdots & \xi_n\\ k_1 & \cdots & k_n\\ \xi_1 & \cdots & \xi_n\\ k_1 & \cdots & k_n\end{bmatrix} \times V(\xi_1)\cdots V(\xi_n)d\xi_1\cdots d\xi_n, \quad (11)$$

$$D_{ij}^{(\kappa)}(x,y;\lambda,W) = G_{ij}^{(\kappa)}(x,y)+\sum_{n=1}^{\infty}\frac{\lambda^n}{n!} \times\sum_{k_1\cdots k_n=1}^{2}\int_0^\infty\cdots\int_0^\infty G_\kappa\begin{bmatrix}x & \xi_1 & \cdots & \xi_n\\ i & k_1 & \cdots & k_n\\ y & \xi_1 & \cdots & \xi_n\\ j & k_1 & \cdots & k_n\end{bmatrix} \times V(\xi_1)\cdots V(\xi_n)d\xi_1\cdots d\xi_n, \quad (12)$$

and

$$G_\kappa\begin{bmatrix}x_1 & \cdots & x_n\\ i_1 & \cdots & i_n\\ y_1 & \cdots & y_n\\ j_1 & \cdots & j_n\end{bmatrix} = \begin{vmatrix} G_{i_1j_1}^{(\kappa)}(x_1,y_1) & \cdots & G_{i_1j_n}^{(\kappa)}(x_1,y_n)\\ \vdots & & \vdots\\ G_{i_nj_1}^{(\kappa)}(x_n,y_1) & \cdots & G_{i_nj_n}^{(\kappa)}(x_n,y_n)\end{vmatrix}. \quad (13)$$

It is shown in the Appendix that, for $W>1$ and real,

$$f=[\mathrm{Im}\mathfrak{D}_\kappa(\lambda,W)]/\mathfrak{D}_\kappa(\lambda,W), \quad (14)$$

and that solutions of the equation

$$\mathfrak{D}_\kappa(\lambda,W)=0 \quad (15)$$

for $-1<W<1$ give the bound-state eigenvalues of Eq. (5).

Using the potential given by Eq. (3), the first-order $\kappa=-1$ relativistic $\mathfrak{D}$ function may easily be computed from Eq. (11). The result is

$$\mathfrak{D}_{-1}(Z\alpha,W)=1-Z\alpha\left\{\frac{iW\ln(1-2ik/\beta)}{k}+\frac{1}{\beta-2ik}\right\}. \quad (16)$$

Note that the only difference between the relativistic and nonrelativistic $\mathfrak{D}$ functions is the energy factor multiplying the logarithmic term in the above expression.

Phase shifts for incident kinetic energies of 2, 20, and 200 eV, and binding energies, computed from Eqs. (4), (14)–(16), are shown as a function of β in Figs. 1 and 2 for the case of Cs ($Z=55$). The relativistic phase shifts, at these low values of incident energy, were within 0.1% of the nonrelativistic values for the range of β investigated; however, substantial relativistic energy shifts in the binding energy were obtained. This is not inconsistent with the results of Spruch[2] and Rotenberg,[3] since the binding energies are large compared to the scattering kinetic energies. For large β (small binding energy), the relativistic and nonrelativistic results are in approximate agreement, as they must be, according to effective-range theory.

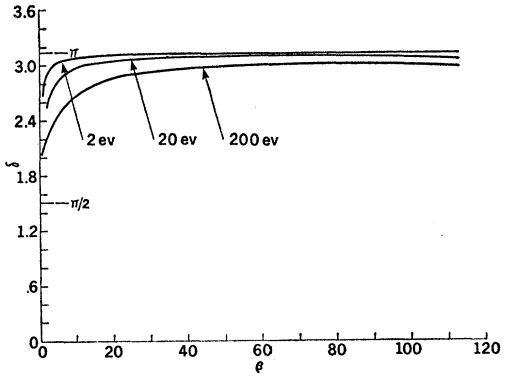

FIG. 1. S-wave phase shifts in radians as a function of β in units of $m\alpha$ for kinetic energies of 2, 20, and 200 eV. Relativistic and nonrelativistic results were identical.

Note that naive application of Fredholm theory to the second-order relativistic wave equation will not work because of the singular nature of the (energy-dependent) "potential" at the origin. (In this connection, see Ref. 1.) If a cutoff radius on the order of the nuclear size is employed, then the associated $\mathfrak{D}$ function *may* not be well represented by the first few terms in a power-series expansion. Numerical calculations found this to be, in fact, the case for the potential used here. Thus, working with the coupled Dirac equation proved to be a more reliable method of analysis.

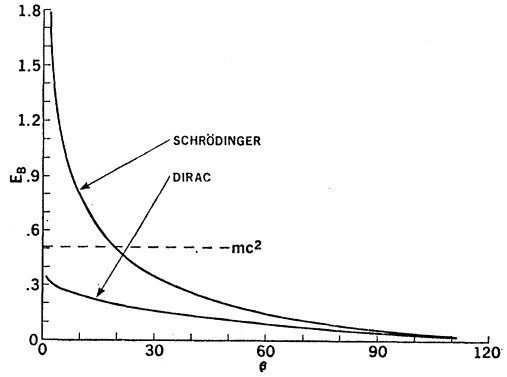

FIG. 2. Ionic binding energy E_B in MeV as a function of β for the relativistic and nonrelativistic equations.

ACKNOWLEDGMENT

The author is indebted to Z. Fried for suggesting this problem and for several helpful discussions.

APPENDIX

We show here that the Dirac partial-wave scattering amplitude is given by

$$f=[\mathrm{Im}\mathfrak{D}_\kappa(\lambda,W)]/\mathfrak{D}_\kappa(\lambda,W). \tag{14}$$

The proof essentially follows that given by Newton[5] for the Schrödinger equation.

In addition to the "physical" wave functions **u**, given by the solutions of Eq. (6), we introduce two auxiliary wave functions which are solutions of Volterra integral equations:

$$\mathbf{\Phi}(r)=\mathbf{v}(r)+\lambda\int_0^r \mathbf{g}(r,r')V(r')\mathbf{\Phi}(r')dr', \tag{17}$$

$$\mathbf{F}(r)=i\mathbf{w}(r)-\lambda\int_r^\infty \mathbf{g}(r,r')V(r')\mathbf{F}(r')dr', \tag{18}$$

where

$$\begin{aligned} g_{ij}(r,r')&=-i[(W+1)/(W-1)]^{1/2}[w_i(r)v_j(r')\\ &\qquad -w_j(r')v_i(r)]\\ &=[(W+1)/(W-1)]^{1/2}[n_i(r)v_j(r')\\ &\qquad -n_j(r')v_i(r)], \end{aligned} \tag{19}$$

and **v**, **n**, and **w** are given by Eq. (7). Here, **Φ** are the real and regular solutions of the inhomogeneous Dirac equation, and **F** are the irregular (Jost) solutions. It is easily shown that

$$\mathbf{u}(r)=\mathbf{\Phi}(r)/\mathcal{J} \tag{20}$$

$$=[\mathcal{J}^*\mathbf{F}(r)-\mathcal{J}\mathbf{F}^*(r)]/2i\mathcal{J}, \tag{21}$$

where the Jost function $\mathcal{J}$ is

$$\mathcal{J}(\lambda,W)=1+i\lambda\left(\frac{W+1}{W-1}\right)^{1/2}\sum_{i=1}^{2}\int_0^\infty w_i(r)V(r)\Phi_i(r)dr \tag{22}$$

$$=1+\lambda\left(\frac{W+1}{W-1}\right)^{1/2}\sum_{i=1}^{2}\int_0^\infty v_i(r)V(r)F_i(r)dr. \tag{23}$$

Substitution of Eq. (20) into Eq. (9) gives

$$f=[\mathrm{Im}\mathcal{J}(\lambda,W)]/\mathcal{J}(\lambda,W). \tag{24}$$

Thus, we have only to show that the Jost function is identical to the Fredholm determinant for the Dirac equation.

Solve Eq. (17) for $v_i(r)$ and substitute this into Eq. (23). Then,

$$\begin{aligned} \mathcal{J}(\lambda,W)=1+\left(\frac{W+1}{W-1}\right)^{1/2}\Bigg\{&\lambda\sum_{i=1}^{2}\int_0^\infty F_i(r)V(r)\Phi_i(r)dr\\ &-\lambda^2\sum_{i,j=1}^{2}\int_0^\infty\Bigg[\int_0^r F_i(r)V(r)g_{ij}(r,r')\\ &\times V(r')\Phi_j(r')dr'\Bigg]dr\Bigg\}. \end{aligned} \tag{25}$$

Using Eqs. (17) and (18), we find after differentiation of Eq. (25) with respect to λ

$$\frac{\partial\mathcal{J}(\lambda,W)}{\partial\lambda}=\left(\frac{W+1}{W-1}\right)^{1/2}\sum_{i=1}^{2}\int_0^\infty F_i(r)V(r)\Phi_i(r)dr \tag{26}$$

or

$$\frac{\partial\ln\mathcal{J}(\lambda,W)}{\partial\lambda}=\int_0^\infty \mathrm{tr}\mathfrak{G}(r,r;\lambda,W)V(r)dr, \tag{27}$$

where

$$\begin{aligned} \mathfrak{G}_{ij}(r,r';\lambda,W)&\\ =\frac{1}{\mathcal{J}}\left(\frac{W+1}{W-1}\right)^{1/2}&\begin{cases}\Phi_i(r)F_j(r') & \text{for } r<r'\\ F_i(r)\Phi_j(r') & \text{for } r>r'.\end{cases} \end{aligned} \tag{28}$$

But $\mathfrak{G}(r,r';\lambda,W)$ is the exact Green's function for the physical wave functions, for if we write

$$\mathbf{u}(r)=\mathbf{v}(r)-\lambda\int_0^\infty \mathfrak{G}(r,r';\lambda,W)V(r')\mathbf{v}(r')dr', \tag{29}$$

then $\mathbf{u}(r)$ has the desired boundary values and satisfies the Dirac equation. Comparing Eq. (29) with the Fredholm solution [Eq. (10)], we find

$$\mathfrak{G}(r,r';\lambda,W)=\mathbf{D}(r,r';\lambda,W)/\mathfrak{D}(\lambda,W). \tag{30}$$

From the series expansions, Eqs. (11) and (12), it is easily shown that

$$\frac{\partial\mathfrak{D}(\lambda,W)}{\partial\lambda}=\int_0^\infty \mathrm{tr}\mathbf{D}(r,r;\lambda,W)V(r)dr. \tag{31}$$

Substitution of Eqs. (30) and (31) into Eq. (27) shows that $\mathcal{J}(\lambda,W)\equiv\mathfrak{D}(\lambda,W)$. The proof holds for all partial waves.

Finally, we note that from Eq. (18) the limiting values of the irregular solutions are

$$\begin{aligned} \mathbf{F}(r)&\simeq i\mathbf{w}(r) && \text{for } r\to\infty,\\ &\simeq i\mathcal{J}(\lambda,W)\mathbf{w}(r) && \text{for } r\to 0. \end{aligned}$$

Therefore, if we can find a value of W, $-1<W<1$, such that $\mathcal{J}(\lambda,W)=0$, then $k=(W^2-1)^{1/2}$ will be positive and imaginary on one of the Riemann surfaces of k. On this surface, $\mathbf{w}(r)$ is a decaying exponential and thus $\mathbf{F}(r)$ will be a regular (and real) bound-state solution of Dirac's equation.