

high-resistivity samples at temperatures below 550°K, data could not be taken with the current densities needed for accurate readings. Therefore, the Ettingshausen coefficient for these high-resistivity samples is reported only above this temperature.

The Bridgman relation permits one to calculate the thermal conductivity of a material from the measured

values of the Nernst and Ettingshausen coefficients. This was done for the samples used in our experiments and the results are shown in Fig. 3. These values for the thermal conductivity are seen to scatter around the straight line described by Eq. (2) on which the determination of the theoretical Ettingshausen coefficients was based.

## Statistical Potential for Actinide Metal Energy Band Calculations\*

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A simple analytic potential energy function,  $V$ , is developed from a Thomas-Fermi ion model for the actinide metals and is found to provide good agreement with wave functions derived from the Hartree self-consistent field approach by Ridley for the  $5f$ ,  $6d$ , and  $7s$  states of uranium. The estimated  $5f$ ,  $6d$ , and  $7s$  bandwidths are 1.1, 7.3, and 11.8 eV, respectively, in satisfactory agreement with those of Ridley.

Dirac's equations are solved for the  $5f$ ,  $6d$ , and  $7s$  states using this nonrelativistic potential energy function with the Wigner-Seitz boundary condition. The relativistic energy shift for the  $7s$  state is roughly 13 eV.

### I. INTRODUCTION

A ONE-ELECTRON statistical potential energy function is derived in this paper which is suitable for studying the electronic structure of the actinide metals, in particular, the cubic phases of thorium, uranium, and plutonium.

It was pointed out in a previous paper<sup>1</sup> that spin-orbit effects must be taken into account for an adequate description of the electronic structure of the actinide metals. A detailed approach was also presented which took spin-orbit coupling into account via an appropriate unitary transformation of the energy matrix,  $H_0$ , obtained by neglecting spin-orbit effects. The primary purpose of this paper is to derive a statistical potential energy function,  $V$ , which is currently being used to compute radial wave functions which are needed to determine the  $H_0$  matrix for gamma uranium using the 1937 version of Slater's augmented plane wave approach.<sup>2</sup>

Wave functions derived from this statistical potential approach are compared in Sec. III with the Hartree self-consistent (nonrelativistic) calculations carried out by Ridley for gamma uranium.<sup>3</sup>

Some numerical solutions of Dirac's equations using the statistical potential energy function derived in Sec. II are also presented in order to determine qualitative effects of relativistic forces on the  $5f$ ,  $6d$ , and  $7s$  orbitals in uranium. The numerical procedures for determining the relativistic as well as the nonrelativistic radial

wave functions used in this paper are outlined in an appendix.

### II. POTENTIAL FUNCTION

Each valence electron in the metallic actinides is considered to move in a potential field arising from three sources: (i) the nuclear charge for an ion whose atomic number is  $Z$  and the charge distribution due to the  $(1s)^2(2s)^2(2p)^6 \dots (5d)^{10}$  closed shell configuration of 78 electrons, (ii) the charge distribution due to the  $(6s)^2(6p)^6$  closed shell configuration of eight electrons, and (iii) the charge distribution due to the presence of the  $n_v - 1$  other valence electrons, where  $n_v$  is the total number of electrons outside closed shells. For thorium, uranium, and plutonium,  $n_v = 4, 6$ , and  $8$ , respectively.

#### A. Iron Core Potential Energy

In atomic units, the ion-core potential energy is given by

$$V_{\text{ion}}(r) = -\frac{2Z}{r} + 2 \int d\mathbf{r}' \frac{\rho_c(N, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where  $\rho_c(N, \mathbf{r})$  is the electron density at the point  $\mathbf{r}$  of the  $N$  core electrons contained inside a sphere of radius  $r_c$ . If the  $6s$ ,  $6p$ , and valence electrons were absent, one could take  $\rho_c$  to be the usual Thomas-Fermi electron density,  $\rho_{TF}(N, \mathbf{r})$  associated with the ion under consideration here.<sup>4</sup> In the model used in this paper, it is assumed that  $\rho_c = \lambda^3 \rho_{TF}(N, \lambda \mathbf{r})$  is a good approximation

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<sup>1</sup> G. W. Lehman, Phys. Rev. **116**, 846 (1959).

<sup>2</sup> J. C. Slater, Phys. Rev. **51**, 846 (1937).

<sup>3</sup> E. Cicley Ridley, Proc. Roy. Soc. (London) **A247**, 199 (1958).

<sup>4</sup> For a discussion of the Thomas-Fermi ion model see P. Gombas, *Die Statistische Theorie des Atoms* (Springer-Verlag, Wein, 1949).

to the true core density with the scaling parameter,  $\lambda$ , chosen to give the best fit to the self-consistent calculations of Ridley for uranium.

Equation (1) for the ion-core potential energy can be written in terms of the Thomas-Fermi function,  $\varphi$ ;

$$\begin{aligned} V_{\text{ion}} &= -(2/r)Z[\varphi(x) - x\varphi'(x_c)], & x \leq x_c \\ V_{\text{ion}} &= -(2/r)(Z-N), & x \geq x_c. \end{aligned} \quad (2)$$

The function,  $\varphi$ , satisfies the usual Thomas-Fermi differential equation  $\varphi'' = x(\varphi/x)^{3/2}$  with the boundary conditions  $\varphi(0) = 1$ ,  $\varphi(x_c) = 0$ , and  $-x_c\varphi'(x_c) = q$ , where the degree of ionization,  $q$ , is  $q = 1 - (N/Z)$ . In these expressions,  $r = \mu x/\lambda$  and  $\mu = 0.88534Z^{-1/2}$ .

Analytic approximations to  $\varphi$  have been obtained for  $0.1 \leq q \leq 0.2$  which have an overall accuracy of about one percent when compared to the numerical calculations of Miranda<sup>5</sup> for  $q = 0.122$ . The forms chosen to approximate  $\varphi$  are similar to those used by Latter.<sup>6</sup>

$$\begin{aligned} \varphi^{-1} &= 1 + 1.5882t^2 - 1.1355t^3, & 0 \leq x_1 \leq 0.04; \\ \varphi^{-1} &= 1 + 0.02747t + 1.243t^2 - 0.1486t^3 + 0.2302t^4 \\ &\quad + 0.007298t^5 + 0.011573t^6, & 0.04 \leq x_1 \leq 4; \quad (3) \\ 1000\varphi &= -0.88375X_4 + 3.11542X_5 - 4.4125X_6 + 3.03X_7 \\ &\quad - 0.92583X_8 + 0.07850X_9, & 4 \leq x_1 \leq 9.7558. \end{aligned}$$

In the above equations,

$$t^2 = x_1 = x + ax^2 + bx^3, \quad ax_c = (8.24674)q - 1,$$

$$3bx_c = -a, \quad x_c = 29.2674/(1 + 16.49348q),$$

and

$$X_n = (x_1 - 4)(x_1 - 5) \cdots (x_1 - 9)/(x_1 - n).$$

### B. Potential Energy Due to the $(6s)^2(6p)^6$ Configuration

The electron density of the  $(6s)^2(6p)^6$  closed shell configuration used in these calculations was obtained from solutions of the Schrödinger wave equation using the Mayer potential energy appropriate to uranium.<sup>7</sup> The potential energy,  $V_{sp}$ , associated with the electron density computed in this manner can be written as  $(2/r)Z_{sp}$ . To an accuracy of a few percent,

$$\begin{aligned} \frac{1}{8}Z_{sp} &= 1 - \exp(-0.4007r - 0.3963r^2), & 0 \leq r \leq 2; \\ &= 1 - 6.808 \exp(-2.1444r), & r \geq 2. \end{aligned} \quad (4)$$

It is assumed that this approximation is also suitable for thorium and plutonium.

### C. Total Potential Energy for a Valence Electron

The total potential energy,  $V(r)$ , for a valence electron in this model is a sum of  $V_{\text{ion}}$ ,  $V_{sp}$ , and the potential,  $V_{\text{val}}$ , associated with the  $n_v - 1$  other valence electrons. Here,  $V_{\text{val}}$  is constructed by distributing the

valence electrons uniformly over the Wigner-Seitz sphere whose radius is  $r_s$ . Using the integral expression in Eq. (1), one readily finds that  $V_{\text{val}} = (n_v - 1) \times [(3/r_s) - (r^2/r_s^3)]$  is appropriate for the actinide metals. The expression in the bracket is the potential energy associated with a single electron uniformly distributed over the Wigner-Seitz sphere.

## III. NUMERICAL RESULTS FOR METALLIC URANIUM

A numerical procedure for solving Dirac's radial wave equations (described in the Appendix) has been programmed for the IBM-709 digital computer. The radial wave functions reported in this section have been normalized for  $r_i = 2.8835$  which is the inscribed sphere radius associated with the body-centered cubic atomic polyhedron for gamma uranium. This normalization is convenient for the augmented plane wave calculations to be described in a later paper.

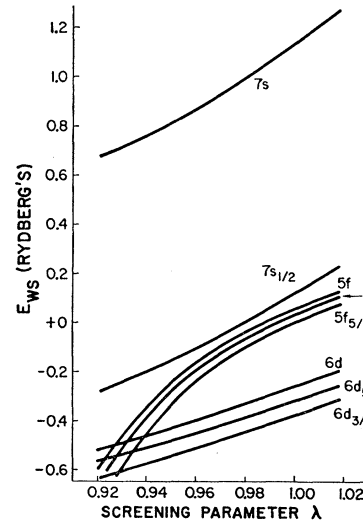


FIG. 1. Energy,  $E_{ws}$ , as a function of the screening parameter for uranium using the Wigner-Seitz boundary condition.

Numerous comparisons between the work of Ridley and results derived from the statistical potential approach used here are possible. In this paper, the comparisons will be restricted to results derived from an application of the well-known Wigner-Seitz boundary condition.

### A. Level Spacing for the $7s$ - $6d$ - $5f$ States as a Function of the Screening Parameter

The vanishing of the gradient of the radial wave function,  $u_l(E, r)$ , at the sphere edge,  $r = r_i$ , specifies the energy,  $E_{ws}$ , which satisfies the Wigner-Seitz boundary condition for the angular momentum quantum number,  $l$ . A plot of  $E_{ws}$  as a function of the screening parameter,  $\lambda$ , for the  $5f$ ,  $7s$ , and  $6d$  states is shown in Fig. 1. The effects of relativistic forces are also shown in this figure by the curves labeled  $7s_{1/2}$ ,  $6d_{3/2}$ ,  $6d_{5/2}$ ,  $5f_{5/2}$ , and  $5f_{7/2}$ , where the subscripts refer to the quantum number  $j$ .

<sup>5</sup> Reference 4, p. 360, Table 55.

<sup>6</sup> R. Latter, Phys. Rev. **99**, 510 (1955).

<sup>7</sup> M. Goppert-Mayer, Phys. Rev. **60**, 184 (1941).

Figure 1 shows that the variation in  $E_{ws}$  with  $\lambda$  is much more rapid for  $f$  than  $d$  states. The spin-orbit splittings of the  $5f$ ,  $7s$ , and  $6d$  states are roughly independent of  $\lambda$  since this splitting is essentially determined by the form of the potential energy near the nucleus.

The relativistic shift in  $E_{ws}$  for the  $7s$  state derived from our nonrelativistic potential is quite large, being roughly 13 ev. This shift might be exaggerated and might be reduced considerably if a suitable relativistic potential had been used.

### B. Comparison of $5f$ , $6d$ , and $7s$ Wave Functions Derived from Statistical and Self-Consistent Potentials for Uranium

Radial wave functions for the  $6d$  and  $5f$  states are plotted in Figs. 2 and 3 for  $\lambda=0.94$  which is the value

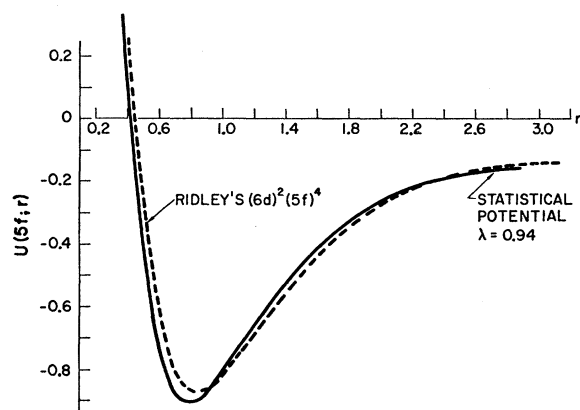


FIG. 2. Normalized  $5f$  radial wave functions as a function of the radius,  $r$ , for uranium derived from statistical and self-consistent potentials using the Wigner-Seitz boundary condition. Hartree units are used in this and subsequent figures.

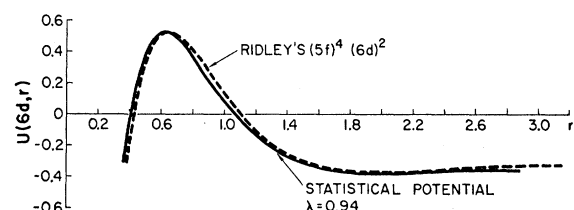


FIG. 3. Variation of the normalized  $6d$  radial wave functions with  $r$  for Wigner-Seitz boundary condition for uranium.

of the screening parameter which gives the best fit to Ridley's self-consistent wave functions associated with the  $(5f)^4(6d)^2$  configuration. It should be noted that the agreement between the  $d$  and  $f$  wave functions derived from the statistical and self-consistent models is quite good considering the approximations involved in the former.

Plots of the  $7s$  wave functions are shown in Fig. 4 for the relativistic as well as the nonrelativistic cases with  $\lambda=0.94$ . Ridley's  $7s$  wave function for the  $(5f)^2(6d)^2(7s)^2$

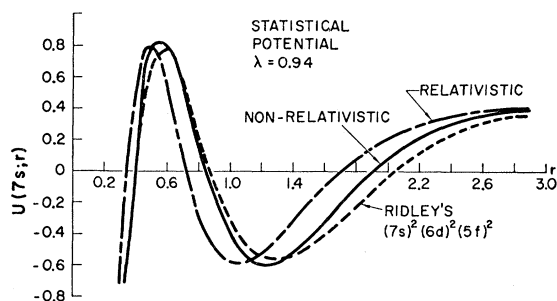


FIG. 4. Variation of normalized  $7s$  and  $7s_{1/2}$  radial wave functions for uranium with  $r$  using Wigner-Seitz boundary condition.

configuration is also shown for comparison purposes. The relativistic  $7s$  wave function is noticeably shifted toward the nucleus. Unfortunately, this effect might be exaggerated and might be reduced if the potential were derived from a proper relativistic scheme such as that used by Mayers for mercury.<sup>8</sup>

### C. Comparison of Estimated Bandwidths for $5f$ , $6d$ , and $7s$ States

Ridley<sup>3</sup> points out that the bandwidth can be measured roughly by  $(E_0 - E_{ws})/3$ , where  $E_0$  is obtained from  $u_i(E_0, r_s) = 0$ . The results of this investigation are compared with those of Ridley in Table I below.

Bandwidths estimated using the statistical potential are about 20% larger than those derived from the self-consistent approach owing to the fact that the inscribed sphere radius is smaller (about 15%) than the Wigner-Seitz radius used by Ridley.

## IV. SUMMARY

A statistical potential energy function for the actinide metals was developed in this paper using a parameterized Thomas-Fermi ion model to account for the  $(1s)^2(2s)^2 \dots (5d)^{10}$  closed shell configuration of 78 electrons. The potential energy associated with the  $(6s)^2(6p)^6$  closed shell configuration was computed from the charge density obtained from wave functions derived from the Mayer potential for uranium. Finally, the potential due to the  $n_v$  valence electrons was obtained from a uniform charge density of  $n_v - 1$  of these electrons.

For uranium, the best choice of  $\lambda$ , introduced into

TABLE I. Estimated bandwidths associated with  $5f$ ,  $6d$ , and  $7s$  levels in uranium.

| Level | Config.       | Ridley<br>Estimated<br>bandwidth | Statistical<br>estimated<br>bandwidth |
|-------|---------------|----------------------------------|---------------------------------------|
| $5f$  | $f^4 d^2$     | 0.9 ev                           | 1.1 ev                                |
| $6d$  | $f^4 d^2$     | 6.0 ev                           | 7.3 ev                                |
| $7s$  | $f^2 d^2 s^2$ | 13.0 ev                          | 16.8 ev                               |

<sup>8</sup> D. F. Mayers, Proc. Roy Soc. (London) A241, 1224 (1957).

the theory as a screening parameter to account for the interaction of the  $(6s)^2(6p)^6$  and valence electrons with the ion core, was found to be 0.94. The results derived in this paper were then found to agree quite well with those of Ridley for the case of the  $5f$  and  $6d$  wave functions.

It was pointed out that a very large and probably exaggerated relativistic energy shift of 13 eV was obtained for the  $7s_{1/2}$  state when Dirac's equations were solved for uranium using the nonrelativistic statistical potential. This point stresses the need for relativistic self-consistent field calculations for uranium.

The primary objective of the present work was to develop a simple analytic potential energy function which can be used to derive radial wave functions for thorium, uranium, and plutonium. These wave functions, in turn, are currently being used to construct the energy matrix,  $H_0$ , for gamma uranium using Slater's augmented plane wave approach.

The author believes that a strictly relativistic calculation will show that the  $7s$  states in the actinide metals probably lie above the Fermi level by a few volts. Consequently, the interaction of the  $s$  with  $d$  and  $f$  states would then be small for occupied states in the conduction band, thereby warranting detailed energy band calculations using the statistical potential energy presented in this paper.

#### APPENDIX. NUMERICAL PROCEDURE FOR SOLVING THE DIRAC EQUATIONS

The Dirac wave equations<sup>9</sup> for the radial components  $R_a$  and  $R_b$  are

$$\begin{pmatrix} D - (1/r)(k-1), & T_- \\ T_+, & D + (1/r)(k+1) \end{pmatrix} \begin{pmatrix} R_a \\ R_b \end{pmatrix} = 0,$$

where  $T_{\pm} = (\alpha/2)(E - V) \pm \alpha^{-1}$ ,  $\alpha^{-1} = 137$ , and  $D$  denotes differentiation. The quantum number  $k = -(l+1)$  or  $l$  for  $j = l + \frac{1}{2}$  or  $l - \frac{1}{2}$ , respectively. In our units,  $mc^2 = 2\alpha^{-2}$ , where  $m$  is the electron mass and  $c$  is the speed of light. When  $|V| \ll mc^2$  or  $r \gg \alpha^2 Z = 0.0049$  for uranium, one finds that the  $R_b$  component (referred to as  $u_l(E, r)$  in the text) satisfies the ordinary Schrödinger equation. Consequently, relativistic effects are confined to regions close to the nucleus.

Setting  $w = 2Zr$ ,  $R_a = \alpha Z p X$ , and  $R_b = p Y$ , where  $p = w^{|k|-1}$ , one can show that the Dirac radial wave equations can be transformed into

$$X = (1/A)[wY' + (|k| + k)Y], \quad (A1)$$

and

$$Y'' + BY' + CY = 0, \quad (A2)$$

with

$$B = [(2|k| + 1)/w] - (A'/A), \quad (A3)$$

and

$$C = (AG/w^2) - [(|k| + k)A'/wA]. \quad (A4)$$

Here,  $A = w + \tau G$ ,  $G = \frac{1}{4}w\epsilon Z^{-2} + \chi$ , and  $\tau = (\alpha Z)^2$ . The  $\chi$  function is defined in terms of the potential energy,  $V$ , by the equation  $V = (-2/r)Z\chi$  and  $\epsilon$  is the energy relative to  $mc^2$ .

#### A. Solution in Vicinity of Nucleus

When  $w < 1$ , one has  $G \cong 1$ , so that it is possible to obtain convenient power series expansions for  $X$  and  $Y$  given by the column vector expressions

$$\begin{pmatrix} X \\ Y \end{pmatrix} = w^\sigma \sum_{s=0}^{\infty} \begin{pmatrix} x_s \\ y_s \end{pmatrix} w^s.$$

Here,  $\sigma = -k + \eta$ ,  $\eta = (k^2 - \tau)^{\frac{1}{2}}$ ,  $y_0 = 1$ , and  $x_0 = 1/(\eta - k)$  or  $-(\eta + k)/\tau$  for  $k < 0$  or  $> 0$ , respectively. The higher order coefficients are connected by  $y_s = (\eta + s - k)x_s$  and  $s(s + 2\eta)x_s = -x_{s-1}$ . In the nonrelativistic case, one must take  $k = -(l + 1)$  with  $\tau = 0$ .

#### B. Numerical Procedure for Obtaining $X$ and $Y$

The differential equation for  $Y$  is solved for  $w > 1$  by solving an equivalent difference equation derived by a procedure similar to that used by Noumerov.<sup>10</sup>

Let  $w_{n+1} = w_n + h$ ,  $Y_n = Y(w_n)$ , and define a new variable  $Q = Y - (h^2/6)Y''$  to replace  $Y$ . Then, it is readily shown that

$$Q_{n+1} - Q_{n-1} = 2hY'_n - (7/180)h^5Y_n^{(v)} + \dots, \quad (A5)$$

and

$$Q_{n+1} - 2Q_n + Q_{n-1} = h^2Y_n'' - (h^4/12)Y_n^{(iv)} + \dots \quad (A6)$$

Hence, if terms of the order  $h^4$  and higher are dropped, one obtains

$$P_1Q_{n+1} = (2 - \frac{2}{3}h^2C_n)Q_n - P_2Q_{n-1}, \quad (A7)$$

where

$$P_i = 1 + (h^2/6)C_n - (-1)^i B_n(h/2), \quad \text{with } i = 1, 2. \quad (A8)$$

The quantities,  $Y_n$ , are obtained from

$$Y_n = [Q_n - (h^2/6)B_nY'_n][1 + (h^2/6)C_n]^{-1}, \quad (A9)$$

and the  $X_n$ 's from Eqs. (A1), (A5), and (A9).

<sup>9</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

<sup>10</sup> For an account of this procedure, see G. W. Pratt, Phys. Rev. 88, 1217 (1952).