

# Parametrized Slater Modified Hartree-Fock Method Applied to Actinide Ions\*

CARL J. LENANDER

Department of Physics, University of California, Los Angeles, California

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A Slater modified Hartree-Fock calculation is applied to several actinide ions. The coefficient of the Slater free electron exchange potential is treated as a parameter which is evaluated by matching a calculated  $4f$  orbital of  $\text{Pr}^{+3}$  to a Hartree-Fock  $4f$  orbital. The parameter is then used in the calculation of orbitals for  $\text{Th}^{+2}$ ,  $\text{U}^{+4}$ ,  $\text{Np}^{+4}$ , and the trivalent ions from  $\text{Pa}^{+3}$  to  $\text{Cf}^{+3}$ . The valence orbitals are used to calculate the matrix elements  $\langle r^2 \rangle$ ,  $\langle r^4 \rangle$ ,  $\langle r^6 \rangle$ ,  $\langle r^{-3} \rangle$ ,  $\zeta$ ,  $F^2$ ,  $F^4$ , and  $F^6$  which are presented in tabular form.

## INTRODUCTION

THE calculation of atomic radial wave functions, even with the development of modern high-speed digital computers, has been quite limited in the region of higher atomic number until the recent Hartree-Fock (HF) calculations on the trivalent rare earths by Freeman and Watson,<sup>1</sup> the conventional Slater modified Hartree-Fock (SHF) calculations on the un-ionized atoms of the entire periodic table reported by Herman and Skillman,<sup>2</sup> and the Hartree (H) calculations on the un-ionized atoms of the actinide series by Boyd, Larson, and Waber.<sup>3</sup>

The calculation of any actinide series atomic system according to the more accurate HF scheme, even with the fastest digital computer, would be a tremendous task.<sup>4</sup> The need for a slightly less accurate, but greatly more economic method of calculation is quite evident. Such a method is the SHF plane wave approximation to the exchange terms of the HF equations. The best known SHF calculation is Pratt's<sup>5</sup> on  $\text{Cu}^+$ . This calculation demonstrated that good approximations to the HF solutions could be obtained with an effort commensurate with an H calculation. An additional advantage of the SHF method is that inherent in the common central potential is the orthogonality of solutions, which is important in calculating matrix elements.

For the actinides, the question arises as to how accurate a HF solution would be if it were achieved. Freeman and Watson's<sup>1</sup> results tend to indicate that they would be, at best, reasonable approximations. This consideration and those mentioned above led to the adoption of the following scheme.

## PARAMETRIZED SLATER EXCHANGE AMPLITUDE

First, a conventional SHF calculation on  $\text{Pr}^{3+}$  and a comparison of the valence orbitals with the HF solution<sup>1</sup> was made. The relative shape of the orbitals as seen in

Pratt's SHF solution<sup>6</sup> and the HF solution<sup>7</sup> was preserved in the rare earths. This difference in shape is attributed to the overemphasis of the exchange potential by the SHF method.<sup>8</sup> It was suggested by Hartree<sup>8</sup> that a decrease of the amplitude of the SHF exchange potential by some empirical factor might improve the accuracy of the method. This suggestion was applied to the case of  $\text{Pr}^{3+}$  where the valence orbitals were fit consistent with a characteristic difference in numerical and analytical solutions observed by Watson.<sup>9</sup> The required multiplicative factor was  $\frac{4}{5}$ , which produced solutions whose matrix elements agreed with Freeman and Watson's<sup>1</sup> as shown in Table I. This agreement is precisely what is expected consistent with the characteristic difference pointed out in reference 9.<sup>9a</sup>

Strictly speaking, the SHF method is applicable only to systems that can be described by a single determinantal wavefunction and should have a different exchange potential for the electrons of different spins. However, it is felt that good results for an "average of configuration" can be obtained, because of the large atomic numbers involved, by the use of one exchange potential for all orbitals.

## NUMERICAL PROCEDURES

The set of integrodifferential equations to be solved is

$$\frac{d^2 P_i(r)}{dr^2} + \left\{ E_i + \frac{2}{r} [Z_p(r) + \lambda Z_x(r)] - \frac{l_i(l_i+1)}{r^2} \right\} P_i(r) = 0, \quad (1)$$

$i = 1s, 2s, \dots$

where

$$Z_p(r) = Z - \sum_i N_i \left[ \int_0^r P_i^2(q) dq + r \int_r^\infty P_i^2(q) \frac{dq}{q} \right] \quad (2)$$

and

$$Z_x(r) = 3[(3r/32\pi^2) \sum_i N_i P_i^2(r)]^{1/3}. \quad (3)$$

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<sup>1</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

<sup>2</sup> F. Herman and S. Skillman, Bull. Am. Phys. Soc. **7**, 214 (1962).

<sup>3</sup> R. G. Boyd, A. C. Larson, and J. T. Waber, Phys. Rev. (to be published).

<sup>4</sup> The author estimates  $\text{U}^{4+}$  ( $5f^2$ ) would require on the order of 100 h on an IBM 7090.

<sup>5</sup> J. C. Slater, Phys. Rev. **81**, 385 (1951).

<sup>6</sup> J. W. Pratt, Phys. Rev. **88**, 1217 (1952).

<sup>7</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

<sup>8</sup> D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 60.

<sup>9</sup> R. E. Watson, MIT Solid State and Molecular Theory Group, Tech. Report No. 12, p. 28.

<sup>9a</sup> Note added in proof. It has been suggested to the author that comparison with a light element should be reported to establish the constancy of  $\lambda$ . For  $\text{Cu}^+$ ,  $F^2$  and  $F^4$  values agree with Watson's (reference 9) values to within 0.85 and 1.12%, respectively.

TABLE I. Comparison of matrix elements (in atomic units) with those of Freeman and Watson.

	$\langle r^2 \rangle$ (a.u.)	$\langle r^4 \rangle$ (a.u.)	$\langle r^6 \rangle$ (a.u.)	$F^2$ (a.u.)	$F^4$ (a.u.)	$F^6$ (a.u.)
$\lambda = \frac{4}{5}$	1.096	2.802	14.033	0.471	0.296	0.213
Freeman and Watson <sup>a</sup>	1.086	2.822	15.726	0.477	0.300	0.216

<sup>a</sup> See reference 1.

$Z$  is the nuclear charge,  $N_i$  is the number of electrons with orbital  $P_i(r)$ , and  $\lambda$  is the factor  $\frac{4}{5}$ . The normalization,

$$\langle P_i | P_i \rangle = 1, \quad (4)$$

is required.

The integration technique was the Numerov<sup>10</sup> method. For a given potential, the solutions were integrated following the method described by Cooley<sup>11</sup> for matching inward and outward solutions. This match was required to less than 0.01% variation in the eigenvalue. And all quadratures were affected by the trapezoidal method.

Four ranges of radial increment were used: 0.001,  $R=0.001$  to 0.100; 0.005,  $R=0.105$  to 1.100; 0.01,  $R=1.110$  to 7.000; and 0.03,  $R=7.030$  to 10.300. The total number of points used was 1000.

Latter's approximate Thomas-Fermi function for free atoms<sup>12</sup> was used as a starting potential for  $U^{4+}$ . In calculating succeeding systems, the next nearest solution's orbitals were used to calculate the starting potential. Also, Latter's ionization potentials<sup>12</sup> for free atoms were used to establish ranges for the eigenvalue estimates.

### CONVERGENCE OF THE EQUATIONS

The convergence problem for the entire system of equations encountered by Pratt<sup>6</sup> was avoided by use of a different iteration technique.

For a given potential, the solutions to the eigenvalue problem will correspond to a minimum energy.<sup>13</sup> The self-consistent orbitals are the set of solutions whose self-consistent property in the system of equations is simultaneous with the minimum energy; however, for a particular potential, calculated from a given set of orbitals, the set of orbitals produced as solutions will correspond to a minimum energy for that potential, but need not be the self-consistent solutions. This variation of self-consistency with energy is important to predict the convergence of the system of equations.

Consider the potential produced when all of the orbitals are converged but the  $k$ th. Let  $(P_k, E_k)$  be the self-consistent solution in the potential  $V_0$  of the self-consistent field. If  $V_i$  is the potential produced by the  $(i-1)$ th approximation, then

$$[H_0 + V_0 + (V_i - V_0)]P_k^i = E_k^i P_k^i = (E_k + \delta E_k^i)P_k^i. \quad (5)$$

From perturbation theory, we have

$$\delta E_k^i \simeq \langle P_k | V_i - V_0 | P_k \rangle. \quad (6)$$

The Coulomb potential is by far the dominant term of  $V$ , so let

$$V_i - V_0 \simeq \frac{1}{r} \left[ \int_0^r (\rho_{i-1} - \rho_0) dq + r \int_r^\infty (\rho_{i-1} - \rho_0) \frac{dq}{q} \right], \quad (7)$$

where the  $\rho$ 's correspond to the sums in Eq. (2). Then, from (6) and (7) one obtains

$$\delta E_k^i \simeq 2 \left\langle P_k \left| \frac{1}{r} \int_0^r (\rho_{i-1} - \rho_0) dq \right| P_k \right\rangle. \quad (8)$$

An inward shift of the  $k$ th orbital in the  $(i-1)$ th approximation with respect to the self-consistent orbital causes

$$\int_0^r \rho_{i-1} dq < \int_0^r \rho_0 dq \quad (9)$$

and vice versa. Thus, an inward shift corresponds to  $\delta E_k^i < 0$  and an outward shift corresponds to  $\delta E_k^i > 0$ . If a Slater-type orbital<sup>14</sup> is used for an indicator, it is readily seen that the higher the "energy", the further out the principal maximum is and vice versa. Then  $|E_k^{i-1}| < |E_k|$  will lead to  $\delta E_k^i < 0$ , and  $|E_k^{i-1}| > |E_k|$  will lead to  $\delta E_k^i > 0$ .

For the more general case when more than one orbital is not converged, the  $\delta E_k^i$  of Eq. (8) will be a sum of terms like Slater integrals between different orbitals. However, the diagonal terms will be dominant.

The usual iteration schemes form some weighted combination of the  $i$ th and  $(i-1)$ th solution to produce the potential for the  $(i+1)$ th solution. A choice that utilizes the energy shift relations above and emphasizes the minimum energy function while promoting convergence is

$$\frac{E_k^i P_k^{i-1} + E_k^i P_k^{i-1}}{E_k^i + E_k^{i-1}}. \quad (10)$$

In the neighborhood of the self-consistent solution, we may write  $P_k^i = P_k + \delta P_k^i$  and  $E_k^i = E_k + \delta E_k^i$ , where  $(P_k, E_k)$  is the  $k$ th self-consistent solution. Let  $x = \delta P_k^i + \delta P_k^{i-1}$  and  $y = \delta E_k^i + \delta E_k^{i-1}$ ; then

<sup>10</sup> B. Numerov, Publ. Observ. Astrophys. Cent. Rusie 11 (Moscu, 1923); or reference 8, p. 71.

<sup>11</sup> J. W. Cooley, Math. Computation 15, 363 (1961).

<sup>12</sup> R. W. Latter, Phys. Rev. 99, 510 (1955).

<sup>13</sup> This is just a property of the Sturm-Liouville problem. See H. Margenau and G. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, New York, 1956), p. 270.

<sup>14</sup> J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1961), Vol. 1, p. 368.

$$\begin{aligned}
 & \frac{E_k^i P_k^i + E_k^{i-1} P_k^{i-1}}{E_k^i + E_k^{i-1}} \\
 &= \frac{(E_k + \delta E_k^i)(P_k + \delta P_k^i) + (E_k + \delta E_k^{i-1})(P_k + \delta P_k^{i-1})}{2E_k + \delta E_k^i + \delta E_k^{i-1}} \\
 &= P_k \left(1 - \frac{y}{2E_k}\right) + P_k \frac{y}{2E_k} \left(1 - \frac{y}{2E_k}\right) \\
 & \quad + \frac{x}{2} \left(1 - \frac{y}{2E_k}\right) + O(\delta^2) \\
 &= P_k + \frac{1}{2}x + O(\delta^2). \tag{11}
 \end{aligned}$$

Near a solution, considering the behavior shown earlier for  $\delta E_k^i$ , we will have  $\delta E_k^i \simeq -\delta E_k^{i-1}$  and  $\delta P_k^i \simeq -\delta P_k^{i-1}$ , so that  $P_k^{i+1}$  will be a near solution.

The convergence for the entire system of equations is aided by the fact that the inner orbitals are not severely affected by small changes in charge distribution due to the proximity of the large nuclear charge; also, the convergence is accelerated by the  $1/E$  behavior in the higher order correction in Eq. (11).

#### THE CALCULATIONS

Self-consistency was measured by the stability of the individual eigenvalues:

$$\% \text{ variation} \equiv 200 \left| \frac{E_k^i - E_k^{i-1}}{E_k^i + E_k^{i-1}} \right|. \tag{12}$$

The lower the percent variation, the more self-consistent the system is. The iterations were continued according to (10) until all the orbitals were stable within a prescribed percent.  $\text{Pr}^{3+}$ ,  $\text{U}^{4+}$ , and  $\text{Np}^{4+}$  were carried to 0.1%, and the remainder of the calculations were held to 1.0%. The higher self-consistency was not sought, because the matrix elements did not vary sufficiently between the 0.1 and 1.0% solutions to warrant the additional accuracy.

From the initiation of these calculations, it was felt that one principal result would be a representative indication of the variation with atomic system of any radial matrix elements that would be calculated. To test this, the ratios of the spin-orbit parameters for  $\text{U}^{3+}$  and  $\text{U}^{4+}$  were compared with values measured in the UCLA laboratory. These values agreed within 4%.

TABLE II. Matrix elements and spin-orbit parameter.

Element	$\langle r^2 \rangle$ (a.u.)	$\langle r^4 \rangle$ (a.u.)	$\langle r^6 \rangle$ (a.u.)	$\langle r^{-3} \rangle$ (a.u.)	$\zeta$ (cm <sup>-1</sup> )	$F^2$ (a.u.)	$F^4$ (a.u.)	$F^6$ (a.u.)
$\text{Th}^{3+} (f^3)$	2.61	14.3	148	5.15	1816	0.307	0.198	0.145
$\text{Pa}^{3+} (5f^2)$	2.03	7.75	51.2	6.47	2329	0.349	0.228	0.167
$\text{U}^{3+} (5f^3)$	1.86	6.47	39.1	7.24	2652	0.365	0.238	0.175
$\text{U}^{4+} (5f^2)$	1.68	5.00	24.4	7.82	2874	0.384	0.253	0.186
$\text{U}^{4+} (6d^2)$	5.05	37.1		9.05	4266	0.232	0.158	
$\text{Np}^{3+} (5f^3)$	1.74	5.72	32.7	7.89	2940	0.876	0.246	0.181
$\text{Np}^{4+} (5f^2)$	1.57	4.36	20.0	8.57	3202	0.3973	0.262	0.193
$\text{Pu}^{3+} (5f^3)$	1.56	9.50	22.5	9.00	3411	0.399	0.262	0.193
$\text{Am}^{3+} (5f^3)$	1.46	3.97	18.7	9.78	3767	0.411	0.270	0.199
$\text{Cm}^{3+} (5f^2)$	1.40	3.66	16.7	10.4	4079	0.420	0.276	0.202
$\text{Bk}^{3+} (5f^3)$	1.32	3.28	14.2	11.2	4466	0.432	0.284	0.209
$\text{Cf}^{3+} (5f^3)$	1.24	2.86	11.6	12.2	4928	0.407	0.294	0.217

In all, the matrix elements calculated were

$$\langle r^k \rangle = \langle 5f | r^k | 5f \rangle, \tag{13}$$

$$F^k = \langle 5f, 5f | r_{<}^k / r_{>}^{k+1} | 5f, 5f \rangle, \tag{14}$$

$$\langle r^{-3} \rangle = \langle 5f | r^{-3} | 5f \rangle, \tag{15}$$

and the spin-orbit parameter

$$\zeta = \langle 5f | Z_F(r) / r^3 | 5f \rangle, \tag{16}$$

where

$$\begin{aligned}
 Z_F(r) = Z - \sum_{i \neq 5f} N_i \int_0^r P_i^2(q) dq \\
 + (N_{5f} - 1) \int_0^r P_{5f}^2(q) dq. \tag{17}
 \end{aligned}$$

These values are presented in Table II.

The wave functions themselves will not be presented in this paper due to their lengthiness. A complete tabulation of these functions is being prepared as a UCLA Technical Report<sup>15</sup> and the set of computer programs used in the calculations will be presented in manual form for a contribution to the UCLA series in numerical analysis.<sup>9a</sup>

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<sup>15</sup> In preparation.