

identical. The change in the TEP should be almost entirely due to the absence of a phonon drag TEP in the alloy. The appropriate measurements have also been initiated.

Third, a study similar to that reported herein but using silver as the solvent metal and impurities belonging to the silver and copper rows of the periodic table is nearing completion. If our conclusions are correct we should find that in this case the roles of copper and silver group impurities are reversed. That is, Cd, In, Sn, and Sb should not greatly influence the phonon drag TEP, whereas Zn and Ge, as well as Ga and As, should be effective in eliminating phonon drag.

Fourth and last, it will be of interest to investigate dilute ternary alloys. For example, if a dilute alloy of copper containing Cd and In is prepared, each solute element being present in sufficient abundance to eliminate phonon drag by itself, the additional influence of

the other impurity (e.g., Cd) on the TEP of the binary alloy (e.g., CuIn) should reveal itself solely as an effect on the electronic contribution to the TEP. Some studies of ternary alloys have already been initiated by Domenicali.<sup>36</sup> However, his work is not of particular usefulness to us for two reasons. First, one of the solutes in each of his ternary alloys is a member of the transition group. Second, his measurements span that temperature region (room temperature and above) in which the phonon drag effect in the pure metal is already quite small. It is significant, however, that Domenicali is able to predict with a fair degree of reliability the thermoelectric behavior of ternary alloys from a knowledge of the TEP of the binary alloys.

We wish to thank Professor M. Garber for his valuable assistance particularly with the measurements at low temperatures.

<sup>36</sup> C. A. Domenicali, *Phys. Rev.* **112**, 1863 (1958).

## Relativistic Self-Consistent Solutions for Atoms of Large Atomic Number\*

STANLEY COHEN†

*The RAND Corporation, Santa Monica, California, and  
Lawrence Radiation Laboratory, University of California, Berkeley, California*

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Relativistic self-consistent solutions, without exchange, have been obtained for several atoms of large atomic number by use of a general program for a high speed computing machine. A short description of this program and of the self-consistent calculation is given. Eigenvalues for the individual electron subshells of the self-consistent mercury, tungsten, platinum, and uranium atoms are presented. A comparison of the calculation with previous results for the mercury atom is also included.

### I. INTRODUCTION

THE wave function for an atomic system can be obtained by several methods. For atoms of small atomic number one method that has met with much success is the self-consistent field calculation of Hartree.<sup>1</sup> In the usual self-consistent calculations, electronic wave functions that satisfy the Schrödinger equation make up the product wave function for the atom. For atoms of large atomic number these calculations suffer from the neglect of relativistic effects, particularly in the inner shells of the atoms. In the present calculation the method of Hartree is used to obtain the self-consistent wave function for the atom. The single-particle wave functions are, however, assumed to be solutions to the relativistic Dirac equation. Many sizeable relativistic corrections are

therefore contained in these solutions. Exchange effects are, however, not included.

Because a modern high-speed computing machine (IBM type 704) was used for the numerical calculations, it was possible to obtain self-consistent solutions of high accuracy. Not only were a large number of grid points used in the calculations but the solutions were iterated many times to assure valid self-consistency. For reasons of flexibility the computations were carried out without the introduction of the usual numerical trial solution to begin the iterations. An iterative procedure was included in the machine program which made the calculation itself entirely automatic. The program used in these calculations may therefore be used for the calculation of the self-consistent solution of an atom of arbitrary electron configuration and atomic number.

Contained in this paper is a description of the method for obtaining the relativistic self-consistent solutions and the numerical techniques used. Also included are results obtained for the solutions to the ground states of several atoms. These include tungsten,

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† Present address: Physics Division, Argonne National Laboratory, Lemont, Illinois.

<sup>1</sup> Douglas R. Hartree, *Proc. Cambridge Phil. Soc.* **24**, 89 (1928).

platinum, mercury, and uranium. Because the complete tabular results of these calculations are lengthy they have not been included in this paper but are available elsewhere.<sup>2</sup> A comparison of the results of the calculation of the mercury atom with previous calculations is given.

## II. DESCRIPTION OF THE CALCULATION

In a self-consistent calculation, each of the electrons of the atom is assumed to move in the combined coulombic potentials of the nuclear charge and that due to the other electrons of the atom. An approximation, the central-field approximation, is also used. In this approximation all potentials are assumed to be spherically symmetric and averages are made for all angularly dependent effects. As a consequence of this approximation, the electrons of the atom may be grouped into subshells. The wave functions of the members of a subshell have identical radial behavior but differ in their angular dependences. These differences correspond to those electron states which differ only in the projection of the total angular momentum on the  $z$  axis.

Because the wave functions for the various electrons are interrelated, a solution to a self-consistent problem is given by presenting a set of wave functions for the electrons of the atom. Such a set of self-consistent wave functions constitutes a unique solution to the problem and, in fact, can be shown to be that solution which minimizes the energy of the atom if its wave function is assumed to be a product of the individual electron wave functions.

In the present treatment the individual electron wave functions are assumed to satisfy the usual Dirac equation in a central field. The four-component spinor solutions may be written in the form

$$\psi_j^\mu(r, \theta, \phi) = \begin{pmatrix} f(r) \left( \frac{j+\mu}{2j} \right)^{\frac{1}{2}} Y_{j-\frac{1}{2}}^{\mu-\frac{1}{2}}(\theta, \phi) \\ f(r) \left( \frac{j-\mu}{2j} \right)^{\frac{1}{2}} Y_{j-\frac{1}{2}}^{\mu+\frac{1}{2}}(\theta, \phi) \\ g(r) \left( \frac{j-\mu+1}{2j+2} \right)^{\frac{1}{2}} Y_{j+\frac{1}{2}}^{\mu-\frac{1}{2}}(\theta, \phi) \\ -g(r) \left( \frac{j+\mu+1}{2j+2} \right)^{\frac{1}{2}} Y_{j+\frac{1}{2}}^{\mu+\frac{1}{2}}(\theta, \phi) \end{pmatrix} \quad (1a)$$

<sup>2</sup> Edited tabular results consisting of the normalized wave functions and individual subshell potentials of each of the normal atoms are available as Rand Corporation research memorandums. They are identified as follows: Mercury, RM-2272-AEC; Tungsten, RM-2404-AEC; Platinum, RM-2405-AEC; and Uranium, RM-2372-AEC. These tables have also been deposited as Document No. 6230 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$26.25 for photoprints or \$7.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

for  $j=l+\frac{1}{2}$  and

$$\psi_j^\mu(r, \theta, \phi) = \begin{pmatrix} f(r) \left( \frac{j-\mu+1}{2j+2} \right)^{\frac{1}{2}} Y_{j+\frac{1}{2}}^{\mu-\frac{1}{2}}(\theta, \phi) \\ -f(r) \left( \frac{j+\mu+1}{2j+2} \right)^{\frac{1}{2}} Y_{j+\frac{1}{2}}^{\mu+\frac{1}{2}}(\theta, \phi) \\ g(r) \left( \frac{j+\mu}{2j} \right)^{\frac{1}{2}} Y_{j-\frac{1}{2}}^{\mu-\frac{1}{2}}(\theta, \phi) \\ g(r) \left( \frac{j-\mu}{2j} \right)^{\frac{1}{2}} Y_{j-\frac{1}{2}}^{\mu+\frac{1}{2}}(\theta, \phi) \end{pmatrix} \quad (1b)$$

for  $j=l-\frac{1}{2}$ .

Here  $Y_l^m$  denotes the normalized spherical harmonics describing the angular dependences of the wave functions,  $j$  is the total angular momentum, and  $\mu$  is the projection of this angular momentum on the  $z$  axis. The radial dependence of the large and small components of the wave function are given by  $f(r)$  and  $g(r)$ , respectively. These radial parts of the wave functions are the solutions to the simultaneous differential equations

$$\frac{E_i - E_0 + V_i(r)}{c} F = -\frac{dG}{dr} - \frac{k}{r} G, \quad (2a)$$

and

$$\frac{E_i + E_0 + V_i(r)}{c} G = \frac{dF}{dr} - \frac{k}{r} F, \quad (2b)$$

where  $F$  is  $rf(r)$  and  $G$  is  $irg(r)$ . Here  $E_0$  is the rest energy of the electron,  $mc^2$ , and  $k$  is the quantum number associated with angular momentum, having the properties

$$\begin{aligned} k > 0; \quad k = j + \frac{1}{2}, \quad j = l + \frac{1}{2}, \\ k < 0; \quad k = -(j + \frac{1}{2}), \quad j = l - \frac{1}{2}, \\ k = \pm 1, \pm 2, \pm 3 \dots \end{aligned} \quad (3)$$

$V_i(r)$  is the radial dependence of the central potential. Equations (2a) and (2b) constitute an eigenvalue problem in which the proper value of the energy,  $E_i$ , is that which results in solutions satisfying the appropriate boundary conditions. These boundary conditions involve not only the asymptotic behaviors of the wave function for small and large  $r$  but also the existence of the correct number of nodes in the radial solutions.

Properly normalized solutions also satisfy the condition

$$\int_0^\infty (F^2 + G^2) dr = 1. \quad (4)$$

The potential distribution due to an electron in the  $i$ th subshell is determined from its radial wave function

and is given by

$$v_i(r) = e^2 \int_r^\infty r_1^{-2} \int_0^{r_1} (F^2 + G^2) dr_2 dr_1. \quad (5)$$

From the contribution of each of the subshells and the nuclear charge, the potential distribution for the atom as a whole is obtained, i.e.,

$$V(r) = -(Ze^2/r) + \sum_i n_i v_i(r), \quad (6)$$

where  $n_i$  is the number of electrons in the  $i$ th subshell.

The effective potential used in obtaining a wave function is the total atomic potential less the contribution due to the particular electron being treated. Thus

$$V_i(r) = V(r) - v_i(r). \quad (7)$$

If the solutions are indeed self-consistent, then for each subshell the wave function obtained by using this potential will, when integrated as in (5), lead to a  $v_i(r)$  identical to that used in determining the effective potential in (7).

In practice the method used to solve a self-consistent problem is to assume a set of trial wave functions and potentials for each of the electrons of the atom and to improve on these by successive iterations of the entire solution. As a result of the variational nature of the problem, these iterations will converge on the correct self-consistent solution.

### Calculation of the Radial Wave Functions

Integration of the radial differential equations was carried out numerically. In order to make maximum use of the available number of grid points, the calculations were carried out on a logarithmic scale in which the variable of integration  $\rho$  was defined to be

$$\rho = \ln(1000r/a_0), \quad (8)$$

where  $a_0$  is the Bohr radius in hydrogen. In terms of the new variable the radial differential equations become

$$\frac{(E_i - E_0)r - rV_i(r)}{c} F = \frac{-dG}{d\rho} - kG, \quad (9a)$$

and

$$\frac{(E_i + E_0)r - rV_i(r)}{c} G = \frac{dF}{d\rho} - kF. \quad (9b)$$

These equations were numerically integrated by the method of Milne.<sup>3</sup> In this procedure predicted values for the wave functions at a new grid point are obtained. From the differential equations, values for the predicted derivatives are obtained which are then used to determine corrected values for the wave functions and also their derivatives. The equations used require the values of the functions at the four preceding grid points

<sup>3</sup> James B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, 1950), second edition, p. 293.

and are of the form

$$Y_{\rho+\Delta\rho}^P = Y_{\rho-3\Delta\rho} + \frac{4}{3}\Delta\rho(2Y_{\rho'} - Y_{\rho-\Delta\rho}' + 2Y_{\rho-2\Delta\rho}'), \quad (10)$$

and

$$Y_{\rho+\Delta\rho}^C = Y_{\rho-\Delta\rho} + (\Delta\rho/3)(Y_{\rho+\Delta\rho}'^P + 4\rho' + Y_{\rho-\Delta\rho}'). \quad (11)$$

The maximum error in an integration step by this procedure is given by:

$$E \cong |Y^P - Y^C|/29$$

Because these equations use functions at several grid points, it is necessary to supply values for the functions at several points to start the integration. Power-series expressions for the wave functions for small  $r$  were used for this purpose. These series were obtained by assuming that the potential for  $\rho < \rho_0$  is that of the nuclear charge with an added constant contribution due to the external-electron cloud. With this assumption, the wave functions and their derivative can then be shown to be of the form

$$F(r) = (r/r_0)^\lambda \sum_0^\infty \alpha_m r^m,$$

$$G(r) = (r/r_0)^\lambda \sum_0^\infty \beta_m r^m, \quad (12)$$

$$dF(r)/d\rho = (r/r_0)^\lambda \sum_0^\infty (\lambda+m)\alpha_m r^m,$$

$$dG(r)/d\rho = (r/r_0)^\lambda \sum_0^\infty (\lambda+m)\beta_m r^m.$$

The  $\alpha$ 's and  $\beta$ 's satisfy the recursion relationships

$$\alpha_m = \frac{(\lambda+m+k)(E-a+E_0)\beta_{m-1} - Z\alpha(E-a-E_0)\alpha_{m-1}}{c[(\lambda+m)^2 - \lambda^2]}, \quad (13)$$

and

$$\beta_m = \frac{(\lambda+m+k)(E-a-E_0)\alpha_{m-1} + Z\alpha(E-a+E_0)\beta_{m-1}}{c[(\lambda+m)^2 - \lambda^2]},$$

where  $a$  is the constant potential due to the electrons,  $\alpha$  is the fine structure constant, and  $\lambda$  is given by

$$\lambda = +[k^2 - (Z\alpha)^2]^{\frac{1}{2}}. \quad (14)$$

The constants  $\alpha_0$  and  $\beta_0$  are related by

$$\alpha_0/\beta_0 = Z\alpha/(\lambda - k). \quad (15)$$

By the use of these relationships, the wave functions and their derivatives at the four innermost grid points were evaluated and used for starting the numerical integration.

Numerical integration of the differential equations in a classically forbidden region is inherently stable

about the solution with increasing magnitude. If the integration is attempted for the monotonically decreasing solution, propagated errors will eventually dominate over the true solution. It is therefore necessary to perform the integration in a manner that will eliminate this difficulty. For this reason a second inward integration of the differential equation was performed for the region outside the outermost classical turning point. As starting values for this set of solutions, it was assumed that the ratio of the large to the small components was  $-(E_0+E)^{1/2}/(E_0-E)^{1/2}$  and that the wave functions of the form  $e^{br}$  where  $b$  is given by  $-(E_0^2-E^2)^{1/2}/c$ .

The two sets of solutions were matched at a point,  $r_m$ , near the outermost classical turning point. Because the solutions contain an arbitrary multiplicative factor this was done by multiplying the outer solution by that factor which results in identical values for the large components at the match point. In general, because the eigenvalue used is not the correct one, the small components will not be identical. This discrepancy in the values of the small components was in fact used to determine the correction to the eigenvalue for the next calculation. The change in the eigenvalue was assumed to be

$$\Delta E = \lim_{\epsilon \rightarrow 0} \frac{cF(r_m)[G(r_m-\epsilon)-G(r_m+\epsilon)]}{\left[ \int_0^{r_m} (F^2+G^2)dr + \int_{r_m}^{\infty} (F^2+G^2)dr \right]}. \quad (16)$$

This expression is obtained by assuming that the calculated wave function is a good approximation to the correct one, and evaluating its expectation values to arrive at a better approximation to the eigenvalue. The calculation of the wave functions was repeated until this calculated change in the eigenvalue was negligible. This wave function was then used to obtain the potentials used in the problem. The integrals for the various potentials used in the calculation were evaluated from the wave functions by use of Simpson's rule. Contributions to these integrals for values of  $r$  smaller than the innermost grid point were determined from power-series expressions involving the parameters of Eq. (12) and included in the calculations.

#### Iterative Scheme

The calculations of individual subshell contributions to the total atomic potential were carried out by making each subshell internally self-consistent in the potential of the nuclear charge and that of the other subshells. At the completion of the calculation for a subshell the total atomic potential was altered to include the change in the total atomic potential introduced by the changes in that subshell. The subshells of the atom were treated successively starting with the innermost one. At the completion of each iteration of the entire atom, each subshell was tested for agreement with the results of the previous iteration. If significant

changes had occurred in any of the subshells the iterative process was continued.

Tests for self-consistency both within the subshells and for the entire solution involved an investigation of the potentials at the origin. Because the potential distributions are all monotonic, it was assumed that any significant changes in a wave function would be manifested by changes in the value of its contribution to the potential at the origin.

In a calculation of the self-consistency of a subshell three successive iterations of that subshell were required to agree before the subshell was considered self-consistent. For the atom as a whole, agreement between all of the individual subshell contributions for two successive iterations was required.

#### Computation

Because the self-consistent calculations were carried out on a modern high-speed computer (IBM-704), it was decided to make the calculation as flexible as possible. Therefore no attempt to supply a trial set of wave functions was made. Instead, a rather crude first approximation for the solution was computed by starting with the totally ionized atom and adding one subshell of electrons at a time. During this process the individual subshells were made self-consistent in the potential of the nuclear charge and that of the other subshells already included. In this manner the required information for the starting a self-consistent calculation was minimized and consisted only of the desired configuration of the atom.

Although the calculations varied, seven or eight iterations of the solutions were generally sufficient to obtain self-consistent results that were limited in accuracy only by roundoff errors in the numerical calculations.

When the final self-consistent solutions were obtained, the results were stored on magnetic tape suitable for use on an IBM-704 computer. These results include the wave functions for each of the subshells of the atom and also the potentials due to each of the subshells.

### III. RESULTS FOR MERCURY

In this calculation 541 grid points were used for the numerical integrations. The grid spacing was chosen as  $\Delta\rho=1/36$  with an innermost value of  $\rho=-4.00000$ . The range in values of  $r$  is therefore from  $r_{\min}=1.83156 \times 10^{-4}a_0$  to  $r_{\max}=59.8741a_0$ . For this particular calculation iterations were carried out until successive values of the individual subshell contributions at the origin were constant to at least 2 parts in  $10^7$ . Six-figure accuracy on all of the eigenvalues was obtained as indicated by the values in successive iterations.

In order to obtain estimates of the accuracy of the wave functions, the hydrogenlike wave function for the 1S electron in an ionized mercury atom was computed. This wave function was accurate to at

least six figures inside the classical turning point and to at least one part in  $10^6$  of the value of the functions at the turning point for points outside. In addition in order to obtain estimates of the accuracy of the self-consistent calculations as a whole the entire calculation was repeated with half the number of grid points and a grid spacing of  $\Delta\rho=1/18$ . The results of this calculation were found to be in excellent agreement with the previous calculation. The energy eigenvalues for the individual subshells agreed to at least six figures for  $K$ ,  $L$ , and  $M$  shells and deviated by less than  $0.0002 Ry$  for the other electrons. At least four figure agreement was found in all the potential functions and wave functions for the individual subshells.

The eigenvalues obtained for the normal mercury atom are given in Table I. Also included in this table

TABLE I. Comparative results for the energy-term values in the normal mercury atom, in rydbergs.

Subshell	Experimental energy-term value	Previous non-relativistic results	Previous relativistic results	This calculation
1S	6115.9	5553		6145.7
2S	1093.3	925		1081.8
2P <sub>1/2</sub>	1046.9	}892		1041.7
2P <sub>3/2</sub>	905.0			897.9
3S	262.5	216.9		255.7
3P <sub>1/2</sub>	241.7	}200.6		236.1
3P <sub>3/2</sub>	209.8			204.7
3D <sub>3/2</sub>	176.0	}170.5		173.2
3D <sub>5/2</sub>	169.3			166.4
4S	59.3	46.07		55.86
4P <sub>1/2</sub>	50.2	}38.89		47.42
4P <sub>3/2</sub>	42.7			39.81
4D <sub>3/2</sub>	28.3	}25.79		26.19
4D <sub>5/2</sub>	26.7			24.78
4F <sub>5/2</sub>	7.8	}8.39		7.44
4F <sub>7/2</sub>	6.9			7.13
5S	9.2	6.93	8.01	8.806
5P <sub>1/2</sub>	...	}4.60	5.58	5.997
5P <sub>3/2</sub>	...		4.92	4.626
5D <sub>3/2</sub>	1.1	}0.920	1.021	0.858
5D <sub>5/2</sub>	...		0.981	0.712
6S <sub>1/2</sub>	0.7682 <sup>a</sup>	0.471	0.536	0.5665

<sup>a</sup> The value was obtained from the first ionization potential.

are previous nonrelativistic results,<sup>4</sup> a previous relativistic calculation<sup>5</sup> and experimental energy terms for this atom.<sup>6</sup> As expected, the relativistic results are in considerably better agreement for the inner electrons. It is apparent that some improvement is also present for the outer electrons. Table II contains similar information for the Hg<sup>++</sup> ion.

#### IV. RESULTS FOR TUNGSTEN

In this calculation 541 grid points were used for the numerical integrations. The grid spacing chosen was

<sup>4</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A149, 210 (1935).

<sup>5</sup> D. F. Mayers, Proc. Roy. Soc. (London) A241, 93 (1957).

<sup>6</sup> H. H. Landolt and R. Bornstein, *Zahlenwerte und Funktionen*, (Springer-Verlag, Berlin, 1950), 6th ed., Vol. 1, p. 228.

TABLE II. Energy-term values for Hg<sup>++</sup>, in rydbergs.

Subshell	Previous nonrelativistic results	Previous relativistic results	This calculation
1S		6181	6147.00
2S		1102	1083.08
2P <sub>1/2</sub>		1061	1042.98
2P <sub>3/2</sub>		917	899.17
3S		263.8	257.02
3P <sub>1/2</sub>		244.4	237.41
3P <sub>3/2</sub>		212.5	206.00
3D <sub>3/2</sub>		181.2	174.47
3D <sub>5/2</sub>		175.5	167.70
4S		57.73	57.13
4P <sub>1/2</sub>		50.08	48.70
4P <sub>3/2</sub>		42.47	41.09
4D <sub>3/2</sub>		28.68	27.47
4D <sub>5/2</sub>		27.36	26.06
4F <sub>5/2</sub>		9.63	8.72
4F <sub>7/2</sub>		9.40	8.41
5S	8.115	10.36	10.08
5P <sub>1/2</sub>	}5.77	7.50	7.27
5P <sub>3/2</sub>		5.97	5.90
5D <sub>3/2</sub>	}2.095	2.18	2.14
5D <sub>5/2</sub>		2.03	2.00

$\Delta\rho=1/36$  with an innermost value of  $\rho=\rho_0=-4$ . The range of values of  $r$  is therefore from  $r_{\min}=r_0=1.83156 \times 10^{-4} a_0$  to  $r_{\max}=59.8741 a_0$ . The iterations of the calculation were repeated until successive values of the individual subshell contributions to the potential at the origin were constant to at least 1 part in  $10^6$ . Six-figure accuracy for all energy eigenvalues was obtained as indicated by their values in successive iterations. The energy eigenvalues obtained from this calculation are given in Table III. Also included in this table are experimental energy-term values for each of the subshells of the atom.<sup>6</sup>

TABLE III. Comparison of energy eigenvalues with experimentally determined term values for tungsten, in rydbergs.

Subshell	Number of electrons	Experimental energy-term value	Calculated eigenvalue
1S	2	5120.3	5139.0
2S	2	890.64	880.90
2P <sub>1/2</sub>	2	849.75	845.74
2P <sub>3/2</sub>	4	751.25	745.82
3S	2	207.17	202.21
3P <sub>1/2</sub>	2	189.20	185.21
3P <sub>3/2</sub>	4	167.58	163.93
3D <sub>3/2</sub>	4	137.36	136.10
3D <sub>5/2</sub>	6	132.76	131.44
4S	2	43.38	41.47
4P <sub>1/2</sub>	2	35.70	34.39
4P <sub>3/2</sub>	4	30.79	29.40
4D <sub>3/2</sub>	4	18.57	17.91
4D <sub>5/2</sub>	6	17.58	17.00
4F <sub>5/2</sub>	6	}1.99	2.701
4F <sub>7/2</sub>	8		2.529
5S	2	5.19	5.889
5P <sub>1/2</sub>	2	2.96	3.785
5P <sub>3/2</sub>	4	2.20	3.058
5D <sub>3/2</sub>	4	...	0.411
6S	2	...	0.492

TABLE IV. Comparison of energy eigenvalues with experimentally determined term values for platinum, in rydbergs.

Subshell	Number of electrons	Experimental energy-term value	Calculated eigenvalue
1S	2	5773.8	5796.7
2S	2	1021.92	1011.44
2P <sub>1/2</sub>	2	977.41	973.04
2P <sub>3/2</sub>	4	851.47	845.37
3S	2	242.60	236.76
2P <sub>1/2</sub>	2	222.46	218.05
3P <sub>3/2</sub>	4	194.73	190.38
3D <sub>3/2</sub>	4	162.01	160.11
3D <sub>5/2</sub>	6	156.01	154.11
4S	2	53.06	50.59
4P <sub>1/2</sub>	2	44.51	42.63
4P <sub>3/2</sub>	4	37.82	36.01
4D <sub>3/2</sub>	4	24.24	23.11
4D <sub>5/2</sub>	6	22.84	21.89
4F <sub>5/2</sub>	6	} 5.15	5.57
4F <sub>7/2</sub>	8		5.32
5S	2	7.29	7.666
5P <sub>1/2</sub>	2	4.51	5.102
5P <sub>3/2</sub>	4	3.51	3.980
5D <sub>3/2</sub>	4	...	0.599
5D <sub>5/2</sub>	5	...	0.486
6S	1	...	0.502

## V. RESULTS FOR PLATINUM

In this calculation 613 grid points were used for the numerical integrations. The grid spacing chosen was  $\Delta\rho=1/36$  with an innermost value of  $\rho=\rho_0=-4$ . The range of values of  $r$  is therefore from  $r_{\min}=r_0=1.83156 \times 10^{-4} a_0$  to  $r_{\max}=442.413 a_0$ . Values of  $r$  larger than 59.8741 however were of no importance because the electron cloud has an insignificant density beyond this value. The iterations of the calculation were repeated until successive values of the individual subshell contributions to the potential at the origin were constant to at least 1 part in  $10^6$ . Six-figure accuracy for all energy eigenvalues was obtained as indicated by their values in successive iterations. The energy eigenvalues obtained from this calculation are given in Table IV. Also included in this table are experimental energy-term values for each of the subshells of the atom.<sup>6</sup>

## VI. RESULTS FOR URANIUM

This calculation made use of the same parameters as the calculation of the platinum atom. Values of  $r$

between  $1.83156 \times 10^{-4} a_0$  and  $442.413 a_0$  were computed. As in that case however only values of  $r$  less than 59.8741 contained any useful information. The iterations were continued until values of the individual subshell contributions to the potential at the origin were constant to 1 part in  $10^6$ . Six-figure accuracy for all energy eigenvalues was obtained as indicated by

TABLE V. Comparison of energy eigenvalues with experimentally determined term values for uranium, in rydbergs.

Subshell	Number of electrons	Experimental energy-term value	Calculated eigenvalue
1S	2	8515.0	8562.76
2S	2	1602.44	1589.79
2P <sub>1/2</sub>	2	1542.73	1537.77
2P <sub>3/2</sub>	4	1264.32	1255.32
3S	2	408.66	399.48
3P <sub>1/2</sub>	2	381.66	373.79
3P <sub>3/2</sub>	4	316.90	309.50
3D <sub>3/2</sub>	4	274.42	270.05
3D <sub>5/2</sub>	6	261.51	256.95
4S	2	106.00	101.01
4P <sub>1/2</sub>	2	93.69	89.40
4P <sub>3/2</sub>	4	76.79	72.71
4D <sub>3/2</sub>	4	57.43	54.45
4D <sub>5/2</sub>	6	54.36	51.40
4F <sub>5/2</sub>	6	28.5	27.69
4F <sub>7/2</sub>	8	27.6	26.89
5S	2	23.94	22.62
5P <sub>1/2</sub>	2	18.86	18.11
5P <sub>3/2</sub>	4	13.59	14.11
5D <sub>3/2</sub>	4	} 7.12	7.58
5D <sub>5/2</sub>	6		7.00
5F <sub>5/2</sub>	3	...	0.274
6S	2	5.32	3.598
6P <sub>1/2</sub>	2	2.04	2.287
6P <sub>3/2</sub>	4	...	1.625
6D <sub>3/2</sub>	1	0.27	0.225
7S	2	...	0.379

their values on successive iterations. The results are given in Table V.

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