

## Self-Consistent Wave Functions for Ytterbium

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Wave functions for the thirteen electron groups of ytterbium have been calculated in the nonrelativistic approximation without exchange. Certain innovations in the numerical procedures are described and discussed. In particular, the use of backward integrations is essentially eliminated from the procedure for determining the energy-related eigenparameters. Wave functions are tabulated for the outermost four subshells, and Slater integrals for the  $4f$  group. The  $4f^{14} 6s^2$  configuration is assumed.

### INTRODUCTION

THE growing interest in the lanthanides has prompted the undertaking of a program to calculate the radial wave functions and atomic form factors of these elements.<sup>1</sup> The initial phase aims at obtaining reasonably good values as rapidly as possible. Thus, these first calculations are nonrelativistic and do not include exchange effects. Better approximations will be attempted in a subsequent phase of this work.

This paper describes the methods employed in making these calculations and presents the results obtained for ytterbium. The choice of this element as a starting point was dictated to some extent by the fact that all of its electron groups are complete. Further, since its atomic number does not differ too greatly from those of other heavy elements whose wave functions have already been calculated, it was hoped that reasonably good initial approximations to the contributions to  $Z(r)$  could be made and the calculations launched without undue difficulty.

### THEORY

The calculations follow essentially the scheme described by Hartree<sup>2</sup> and involve repeated solution of the equations

$$W_m(nl; r)P_m(nl; r) = 0, \quad (1)$$

where the operator  $W$  is given by

$$W_m(nl; r) = \frac{d^2}{dr^2} + \frac{2}{r} [Y_m(r) + Y_m^0(nl; r)] - \epsilon(nl) - l(l+1)/r^2. \quad (2)$$

There is one such equation for each electron group in the atom under consideration. These equations are coupled through the relations

$$\frac{d}{dr} Y_m(r) = \frac{1}{r} [Y_m(r) - Z_{m-1}(r)], \quad (3)$$

$$\frac{d}{dr} Y_m^0(nl; r) = \frac{1}{r} \left[ Y_m^0(nl; r) + \frac{Z_{m-1}^0(nl; r)}{Z^0(nl; 0)} - 1 \right], \quad (4)$$

<sup>1</sup> For the atomic scattering factors for ytterbium, see E. L. Eichhorn and M. W. Holm, *Acta Cryst.* **15**, 294 (1962).

<sup>2</sup> D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

$$Z_m(r) = \sum_{nl} Z_m^0(nl; r) = \sum_{nl} q(nl) \int_r^\infty P_m^2(nl; s) ds. \quad (5)$$

The terminology is substantially that of Hartree save for the substitution of  $Y^0(nl; r)$  and  $Z^0(nl; r)$ , respectively, for  $Y_0(nl; r)$  and  $Z_0(nl; r)$  to avoid subscripted subscripts. In what follows, the zero superscripts are dropped since the arguments indicate clearly which functions are intended.

Thus,  $Z(nl; r)$  is the contribution to  $Z(r)$  arising from the electrons in the  $nl$  subshell;  $q(nl)$  is the number of electrons occupying this subshell;  $\epsilon(nl)$  is an eigenparameter related to the energy;  $P(nl; r)$  is the radial wave function sought;  $r$  is in Bohr units;  $m$  denotes the iteration in progress.

### NUMERICAL PROCEDURES

The zero-order approximations to the contributions to  $Z$ ,  $Z_0(nl; r)$ , and their sum  $Z_0(r)$  were obtained from data on mercury published by Mayers<sup>3</sup> and using a method described by Ridley.<sup>4</sup> These values constituted the input data to Eqs. (3) and (4) for the first iteration. Runge-Kutta integrations starting with large values of  $r$  and working back to essentially  $r=0$  gave the functions  $Y_1(r)$  and  $Y_1(nl; r)$ , the first input data to Eq. (1). Solutions of Eq. (1) then provided the first approximations to the wave functions  $P_1(nl; r)$ , the input data for Eq. (4). Solution of Eq. (4) completes one stage or iteration. Basically, the problem from this point on is merely to repeat the cycle outlined above until the output contributions to  $Z$  at some stage do not differ from the input values by more than some small, predetermined number (ideally zero). The wave functions are then self-consistent and constitute the best representation of the true wave functions possible with the given model and numerical methods.

Equation (1) is frequently broken down into two first-order equations which are then solved simultaneously. However, since there is no first derivative term, there are Runge-Kutta type algorithms<sup>5</sup> (and

<sup>3</sup> D. F. Mayers, *Proc. Roy. Soc. (London)* **241**, 93 (1957). Slightly faster convergence would probably have been obtained using the values for  $Tm^{3+}$  reported by Ridley. (See reference 6).

<sup>4</sup> E. C. Ridley, *Proc. Cambridge Phil. Soc.* **51**, 693 (1955).

<sup>5</sup> See, for example, J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins University Press, Baltimore, 1958), 4th ed., pp. 316-7.

others) which will solve the equation as it stands. Such a method was used in this study. The primary problem at this point, however, is not the solution of Eq. (1) *per se*, but rather the determination of a value of  $\epsilon(nl)$  which possesses a wave function with the number of nodes appropriate to the given values of  $n$  and  $l$ .

Commonly, Eq. (1) is solved by integrating backwards from a large value of  $r$  (where the wave function is effectively zero) to some intermediate value; integrating forward from  $r=0$  to this same value; then adjusting  $\epsilon$  and the starting slopes until continuity is achieved at the intermediate point. By taking advantage of a pathological feature of the behavior of numerical solutions to the wave equation, however, it is possible to eliminate the backward integration and simplify the procedure for determining the eigenvalues  $\epsilon(nl)$ . Figure 1 illustrates the instability just referred to. Here are shown the numerical approximations to the solution of Eq. (1) for the  $2s$  subshell at the fifth stage for two values of  $\epsilon(2s)$  differing by only unity in the least significant digit of an eight-digit representation. The solution may be divided conveniently into four sections: (i) a region in which the behavior of the solution is that of a traveling wave; (ii) a region in which the behavior is that of a damped wave with a near-exponential approach to the  $r$  axis; (iii) a region where the solution is essentially zero; (iv) a region in which the solution tends to plus or minus infinity.

The computer was programmed to take an initial estimate of  $\epsilon$  and, by observing the behavior of the fourth region as test changes in  $\epsilon$  are made, to refine this value until a change of unity in the least significant digit resulted in a change of sign of the infinity-seeking tail. Satisfactory approximations to the wave functions at that stage of the calculations could then be obtained by discarding the third and fourth regions of those solutions in which the infinity-seeking tail had the same algebraic sign as the last maximum (or minimum) in the first region.

Where the approach to zero in the third region was not sufficiently close, an exponential tail-off was substituted for the extreme right portion of the second region. Numerically,

$$P(nl; r_{j+1}) = P(nl; r_j)R(k)^{H(j)}, \quad (6)$$

where

$$H(j) = r_{j+1} - r_j,$$

(the  $j$ th abscissal increment) and

$$R(k) = [P(nl; r_k)/P(nl; r_{k-1})]^{1/H(j-1)}.$$

By starting this tail-off at that radius value for which  $R(k)$  is a minimum (in the second region), wave functions at only those points not in agreement with values which would be obtained with a backward integration are calculated. An exception is provided by the  $4f$  wave function where a starting point midway between that of the  $4d$  and  $5s$  functions must be used to obtain a

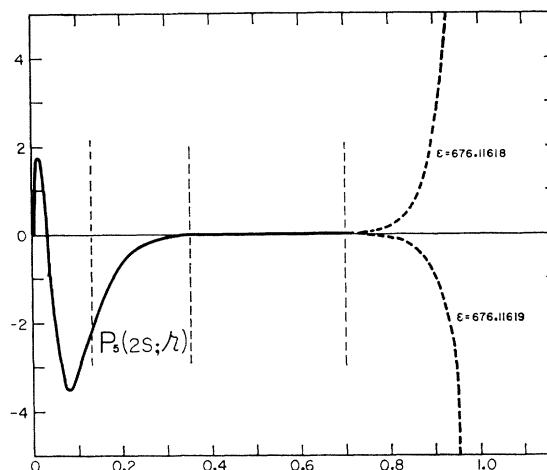


FIG. 1. Behavior of numerical solution to wave equation.

tail-off which is a satisfactory approximation to that of a backward integration.

To facilitate comparison with the values obtained by Ridley<sup>6</sup> for  $\text{Pr}^{3+}$  and  $\text{Tm}^{3+}$ , Slater integrals were calculated for the  $4f$  subshell using the relations

$$F^k(4f, 4f) = \int_0^\infty \int_0^\infty \frac{r_1^{k-1}}{r_2^{k+1}} P^2(4f; r_1) P^2(4f; r_2) dr_1 dr_2; \quad (7)$$

$$F_k(4f, 4f) = F^k(4f, 4f)/D_k, \quad (8)$$

where, in particular,  $D_2 = 225$ ,  $D_4 = 1089$ , and  $D_6 = 7361.64$ .

## RESULTS

Values of  $\epsilon(nl)$  for the 13 subshells are listed in Table I. The calculated wave functions for the four outermost subshells are given in Table II.<sup>7</sup> Values of

TABLE I. Values of  $\epsilon(nl)$ .

Subshell	$\epsilon$	Subshell	$\epsilon$
1s	4204.89	4s	28.575
2s	677.95	4p	23.052
2p	650.55	4d	13.166
3s	151.23	4f	0.6707
3p	137.70	5s	3.3792
3d	113.12	5p	1.9330
		6s	0.33906

<sup>6</sup> E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

<sup>7</sup> Space limitations make it impractical to include full tables of values of the wave functions (Table II) and contributions to  $Z$  (Table IV) for all of the 13 subshells. These have been deposited as Document No. 7384 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 \$2.50 for photoprints, or \$1.75 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE II. Radial wave functions for ytterbium.

$r$	$4f$	$5s$	$5p$	$6s$	$r$	$4f$	$5s$	$5p$	$6s$
0.0000	0.000	0.0000	0.0000	0.0000	0.28	0.830	-0.0603	0.0816	-0.0156
0.0005	0.000	0.0157	0.0001	0.0038	0.30	0.893	-0.1699	0.1663	-0.0421
0.001	0.000	0.0303	0.0005	0.0073	0.32	0.948	-0.2694	0.2424	-0.0662
0.002	0.000	0.0565	0.0021	0.0137	0.34	0.995	-0.3546	0.3074	-0.0866
0.003	0.000	0.0787	0.0045	0.0190	0.36	1.034	-0.4230	0.3598	-0.1029
0.004	0.000	0.0973	0.0078	0.0236	0.38	1.065	-0.4735	0.3990	-0.1148
0.005	0.000	0.1126	0.0117	0.0273	0.40	1.090	-0.5061	0.4251	-0.1222
0.006	0.000	0.1248	0.0163	0.0302	0.45	1.127	-0.5152	0.4375	-0.1229
0.007	0.000	0.1342	0.0214	0.0325	0.50	1.133	-0.4401	0.3878	-0.1030
0.008	0.000	0.1411	0.0270	0.0342	0.55	1.120	-0.3082	0.2947	-0.0694
0.009	0.000	0.1456	0.0330	0.0353	0.60	1.092	-0.1445	0.1752	-0.0282
0.010	0.000	0.1480	0.0393	0.0358	0.65	1.055	0.0316	0.0429	0.0156
0.012	0.000	0.1471	0.0527	0.0356	0.70	1.013	0.2059	-0.0921	0.0583
0.014	0.000	0.1398	0.0667	0.0339	0.75	0.968	0.3692	-0.2229	0.0976
0.016	0.000	0.1274	0.0810	0.0308	0.80	0.921	0.5157	-0.3449	0.1320
0.018	0.000	0.1109	0.0953	0.0268	0.85	0.874	0.6423	-0.4552	0.1607
0.020	0.001	0.0913	0.1093	0.0221	0.90	0.828	0.7482	-0.5525	0.1833
0.022	0.001	0.0694	0.1227	0.0168	0.95	0.783	0.8334	-0.6362	0.2000
0.024	0.001	0.0460	0.1354	0.0111	1.00	0.740	0.8991	-0.7065	0.2111
0.026	0.002	0.0216	0.1473	0.0052	1.10	0.658	0.9789	-0.8097	0.2178
0.028	0.002	-0.0032	0.1581	-0.0008	1.20	0.585	1.0027	-0.8697	0.2077
0.030	0.003	-0.0279	0.1679	-0.0068	1.30	0.519	0.9859	-0.8950	0.1847
0.032	0.003	-0.0522	0.1765	-0.0127	1.40	0.462	0.9414	-0.8941	0.1526
0.034	0.004	-0.0758	0.1840	-0.0184	1.50	0.411	0.8798	-0.8740	0.1143
0.036	0.005	-0.0983	0.1902	-0.0238	1.60	0.367	0.8088	-0.8405	0.0721
0.038	0.006	-0.1196	0.1951	-0.0290	1.70	0.328	0.7341	-0.7981	0.0280
0.040	0.007	-0.1394	0.1988	-0.0338	1.80	0.295	0.6596	-0.7503	-0.0169
0.045	0.010	-0.1819	0.2027	-0.0441	1.90	0.265	0.5878	-0.6997	-0.0614
0.050	0.014	-0.2134	0.1992	-0.0517	2.0	0.238	0.5202	-0.6482	-0.1049
0.055	0.019	-0.2336	0.1890	-0.0565	2.2	0.195	0.4009	-0.5475	-0.1867
0.060	0.025	-0.2426	0.1729	-0.0587	2.4	0.160	0.3039	-0.4549	-0.2597
0.065	0.032	-0.2413	0.1519	-0.0584	2.6	0.132	0.2274	-0.3733	-0.3228
0.070	0.041	-0.2306	0.1267	-0.0558	2.8	0.110	0.1685	-0.3033	-0.3755
0.075	0.050	-0.2120	0.0985	-0.0513	3.0	0.092	0.1238	-0.2445	-0.4182
0.080	0.060	-0.1865	0.0679	-0.0451	3.5	0.059	0.0559	-0.1389	-0.4855
0.085	0.071	-0.1555	0.0358	-0.0376	4.0	0.039	0.0246	-0.0768	-0.5073
0.090	0.084	-0.1203	0.0031	-0.0290	4.5	0.025	0.0106	-0.0416	-0.4971
0.095	0.097	-0.0821	-0.0298	-0.0198	5.0	0.017	0.0045	-0.0223	-0.4668
0.100	0.111	-0.0419	-0.0621	-0.0100	6.0	0.008	0.0008	-0.0063	-0.3786
0.110	0.142	0.0402	-0.1232	0.0099	7.0	0.003	0.0001	-0.0017	-0.2857
0.12	0.177	0.1195	-0.1770	0.0291	8.0	0.002	0.0000	-0.0005	-0.2056
0.13	0.214	0.1909	-0.2215	0.0463	9.0	0.001		-0.0001	-0.1431
0.14	0.253	0.2509	-0.2554	0.0609	10.0	0.000		-0.0000	-0.0971
0.15	0.294	0.2977	-0.2782	0.0721	12.0				-0.0423
0.16	0.337	0.3302	-0.2902	0.0799	14.0				-0.0174
0.17	0.381	0.3483	-0.2917	0.0843	16.0				-0.0069
0.18	0.425	0.3527	-0.2837	0.0852	18.0				-0.0027
0.19	0.469	0.3443	-0.2671	0.0831	20.0				-0.0010
0.20	0.514	0.3245	-0.2431	0.0782	22				-0.0004
0.22	0.600	0.2569	-0.1777	0.0617	24				-0.0001
0.24	0.683	0.1625	-0.0965	0.0386	26				-0.0000
0.26	0.760	0.0533	-0.0077	0.0120					

the Slater integrals for the  $4f$  subshell will be found in Table III. The degree of self-consistency achieved was

TABLE III. Values of the Slater integrals.

$F^2$	0.5465	$F_2$	0.002429		
$F^4$	0.3398	$F_4$	0.0003120	$F_4/F_2$	0.1284
$F^6$	0.2436	$F_6$	0.00003309	$F_6/F_2$	0.01362

such that the largest difference between the input and output contributions to  $Z$  at the last iteration was less than 0.0005 for the  $4f$  subshell, and less than 0.0001 for all other subshells. This means that these calculations were carried farther than the nonrelativistic approximation without exchange would normally justify.

Most of the wave functions of the remaining rare-earth elements are not being calculated with this accuracy. However, as indicated in the first paragraph

of this report, calculations of these wave functions using better approximations will be attempted when, shortly, a more powerful computer becomes available. In the case of ytterbium, at least, it will then be possible to determine with considerable accuracy the magnitudes of the relativistic and exchange effects. Further, it becomes possible to study in some detail certain fairly simple transformations which when applied to the corresponding hydrogen-like wave functions produce

remarkably good approximations to the self-consistent field (SCF) functions.

The calculations reported on in this paper were carried out on a Burroughs 220 10K computer equipped with card input and output for data handling, and an IBM 407 for printed output. In addition, two magnetic tape units were required to accommodate the ALGOL compiler. Compile and running times for a typical iteration on 13 subshells total a little under three hours.

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## Hyperfine-Structure Measurements on Silver-105†

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The hyperfine-structure separation in the  $^2S_{1/2}$  electronic ground state of  $\text{Ag}^{105}$  (40 day;  $I=\frac{1}{2}$ ) has been measured by atomic-beam methods. The result is  $\Delta\nu = 1529.057(20)$  Mc/sec, assuming either a positive or a negative nuclear moment. Combining this measurement with the known constants of  $\text{Ag}^{107}$  gives a nuclear magnetic moment of magnitude  $|\mu_I|_{\text{uncorrected}} = 0.1009(10)$  nuclear magneton.

### I. INTRODUCTION

ATOMIC-BEAM measurements on the “field-independent”  $\Delta F=1$  hyperfine transition have given a new precision to the measured value of the hyperfine-structure (hfs) separation of 40-day  $\text{Ag}^{105}$ . Preliminary work was done at several fields up to about 380 G, using the  $\Delta F=0$  “standard transition.” When the hfs separation was known well enough, a search for direct ( $\Delta F=1$ ) transitions was made successfully. Both  $\Delta F=1$  lines were measured at low fields.

### II. THEORY OF THE EXPERIMENT

The theory of atomic-beam magnetic-resonance experiments has been developed in some detail since the method was introduced by Rabi.<sup>1</sup> Measurements of transition frequencies between pairs of hyperfine sublevels as split by a known magnetic field lead directly to a calculated value of the zero-field hfs separation. The hfs splitting, in turn, is a measure of the strength of the interaction between the electromagnetic moments of the nucleus and the electrons. If the electronic moments are known, the nuclear moments can be calculated. The results can then be compared with the predictions of various nuclear models.

For the alkali and alkali-like elements of Column I in the periodic table, the electronic ground state is  $^2S_{1/2}$ . The only electron-nuclear interaction is then the contact

interaction between the magnetic moments of the single-valence electron and the nucleus. The behavior of such a coupled spin system when a magnetic field is applied has been described by Breit and Rabi.<sup>2</sup> At low fields the two spins are tightly coupled and their resultants  $F=I\pm\frac{1}{2}$  behave like single dipoles, whose magnetic sublevels are split linearly by the field. At higher fields, the two spins are gradually decoupled until their magnetic splittings are virtually independent. The Breit-Rabi equation is an analytic description of this field behavior when  $J=\frac{1}{2}$ . If the nuclear moment  $\mu_I = g_I\mu_0 I$  and the electronic moment  $\mu_J = g_J\mu_0 J$  (where  $\mu_0$  is the magnitude of the Bohr magneton), then the energy of a magnetic sublevel is given by

$$\frac{W(H)}{h} = \frac{-\Delta\nu}{4(I+\frac{1}{2})} - g_I \frac{\mu_0}{h} H m \pm \frac{1}{2} [(\Delta\nu)^2 + 2(\Delta\nu)\rho f + f^2]^{1/2}, \quad (1)$$

with

$$f = (-g_J + g_I)(\mu_0/h)H \quad \text{and} \quad \rho = m/F_{\text{max}} = \frac{m}{I+\frac{1}{2}},$$

where  $h\Delta\nu = W_{I+1/2}(0) - W_{I-1/2}(0)$  is the zero-field hfs splitting between the two levels for  $F=I\pm\frac{1}{2}$  and  $f$  is a field parameter. The sign of the root is chosen positive or negative, respectively, depending on whether the level belongs to the group having larger or smaller  $F$ . Figure 1 illustrates this field dependence of the hyperfine sublevels for an isotope with  $I=\frac{1}{2}$  and a negative nuclear moment. (The assumption of a negative nuclear moment is proper for the stable silver isotopes  $\text{Ag}^{107}$  and  $\text{Ag}^{109}$ , and is probably correct for  $\text{Ag}^{105}$  as well.)

<sup>2</sup> G. Breit and I. I. Rabi, Phys. Rev. 38, 2082 (1931).

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<sup>1</sup> I. I. Rabi, J. R. Zacharias, S. Millman, and P. Kusch, Phys. Rev. 53, 318 (1938).