Accurate Numerical Hartree-Fock Self-Consistent-Field Wave Functions for Ce^{3+}, La^{2+}, Yb^{3+}, Tm^{2+}, and Yb^{2+}

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(Received 26 April 1971; revised manuscript received 29 September 1971)

Accurate numerical Hartree-Fock (HF) self-consistent-field (SCF) wave functions have been obtained for Ce^{3+} $(4f^1)$ ^2F, La^{2+} $(4f^1)$ ^2F, Yb^{3+} $(4f^{13})$ ^2F, Tm^{2+} $(4f^{13})$ ^2F, and Yb^{2+} $(4f^{14})$ ^1S rare-earth ions. In each case, the virial theorem is satisfied to at least six digits and the P_{nl} radial functions are self-consistent and without "tail-oscillations" to three decimal places. Several HF parameters are also evaluated with these wave functions.

INTRODUCTION

The rare-earth ions, with f^N-electron config-uration, are of great importance in connection with the development of solid-state devices such as lasers. Accurate descriptions of their electronic structures are therefore valuable. Recently, we have reported accurate numerical Hartree-Fock self-consistent-field (HF-SCF) wave functions for a large number of triply and doubly ionized lan-thanides having $4f^N(N=2-12)$-electron configura-tions.[1] The purpose of this paper is to report the results of similar calculations for doubly and triply ionized rare-earth ions having $4f^1$-, $4f^{13}$-, and $4f^{14}$-electron configurations, for which several enquiries were received.

As in our previous work, the calculations were performed in double-precision on an IBM 360/50K computer using the program written by Froese-Fischer.[2] All these calculations correspond to the ground states of the respective normal f^N config-urations. Additional HF parameters are the fol-lowing: $A(nl) = \lim_{r \to 0}[P_{nl}(r)/r^{l+1}]$; $S(nl) = Z - [\langle r_{Hyd}\rangle_{nl} / \langle r_{HF}\rangle_{nl}]$, screening numbers; integrals $\langle r^N\rangle_{nl}$'s for $N = -3, -1, 0, 1,$ and 2; $R2(nl) = \int_0^\infty P_{nl}^4(r)r^{-2}\,dr$ integrals[3]; $F^k(4f, 4f)$'s, the Slater integrals ζ_{4f}'s, the spin-orbit parameters,[4] and $M^k(4f, 4f)$'s, the spin-spin parameters,[5] have also been obtained with the present nl wave functions.

RESULTS AND DISCUSSION

The relevant features of the program used have been given in our earlier paper.[1] Specific details such as initial estimates, etc., of the present calculations are also similar to those of the pre-vious work.[1] The convergence tolerance in the orbital-energy (E_{nl}) iterations were specified to be $2[Z - S(nl)]^2 \times 10^{-7}$, Z being the atomic number. Thus, as we go to the outer shells the convergence tolerance in the corresponding E_{nl} iterations de-creases. But, it is to be kept in mind that $|E_{nl}|$ also decreases as we go to the outer shells, $|E_{1s}|$ being the largest. The E_{1s} values are self-con-sistent to almost seven significant digits and the accuracy of the total energy E mostly depends on the accuracy to which E_{1s} can be determined. Convergence tolerance in the normalization itera-tions was set to be $4 \times 10^{(n-9)}$, n being the principal quantum number of the shell in question.

The numerical HF-SCF wave functions and the HF parameters have been collected, respectively, in Tables I and II deposited with a distributing agency.[6] The P_{nl} wave functions are given to six decimal places with $\rho = \ln(Zr)$ as the independent variable. The values of the maximum error MAX DIFF (nl)'s are also given in this Table I. They measure the self-consistency of the functions and are defined as: MAX DIFF $(nl) = \max \{\Delta P_{nl}(\rho_1), \Delta P_{nl}(\rho_2), \ldots, \Delta P_{nl}(\rho_{1ast})\}$, where $\Delta P_{nl}(\rho_1), \Delta P_{nl}(\rho_2), \ldots,$ etc., are the absolute differences of the $P_{nl}(\rho)$ functions obtained in the last two iterations at the various points of the mesh. In the present calculations, the largest MAX DIFF is 0.000 009. Thus, the orbital wave functions are self-consistent to at least four decimal places, the inner orbitals being always more self-consistent than the outer ones. How-ever, there are occasionally nodes in the tails of the inner wave functions beyond those required by the orthogonality restrictions. Within the accuracy of the present computations, the wave functions are without such tail-oscillations to three decimal places only. It is necessary here to assess the "tail-procedure" used by Froese-Fischer.[2,7] Re-cently Handy, Marron, and Silverstone[8] claimed that the choice of the slope of the wave functions at the outmost point in the Froese-Fischer tail-procedure[7] neglects exchange-effect contributions. In the no-tation used by Froese-Fischer,[7] a boundary condi-tion is applied at r_N by guessing a value of y_N as-suming $y_N = cy_{N-1}$. One could let $y_N = 0$ (which is actual-ly done later by Froese-Fischer) and then back sub-stitute $y_{N-1}, y_{N-2}, y_{N-3}, \ldots,$ etc. Although the wrong value of y_N introduces some error in the boundary condition, it has been shown by Froese-Fischer and Usmani[9] that the effect of this error actually reduces as one moves away from boundary.

TABLE I. Total energy E (a.u.), spin-orbit parameter ζ_{4f} (cm^{-1}), spin-spin parameters M^K $(4f, 4f)$ (cm^{-1}), Slater integrals $F^K(4f, 4f)$ (a.u.), and virial-theorem ratio (potential energy)/(kinetic energy) (PE/KE) for various systems.

System	E	PE/KE	ζ_{4f}	F^K's$(K=0,2,4,6)$	M^K's$(K=0,2,4)$
Ce$^{3+}(4f^1)$ ^2F	-8565.631	-1.9999998	782.5	$\cdots$	$\cdots$
La$^{2+}(4f^1)$ ^2F	-8220.574	-1.9999996	564.6	$\cdots$	$\cdots$
Yb$^{3+}(4f^{13})$ ^2F	-13389.95	-2.0000003	3184.0	1.349	5.738
				0.6458	3.222
				0.4061	2.189
				0.2925	$\cdots$
Tm$^{2+}(4f^{13})$ ^2F	-12939.63	-2.0000006	2742.0	1.269	4.926
				0.5994	2.754
				0.3754	1.869
				0.2700	$\cdots$
Yb$^{2+}(4f^{14})$ ^1S	-13390.90	-2.0000004	$\cdots$	1.300	$\cdots$
				0.6140	$\cdots$
				0.3846	
				0.2765	

Table II deposited with the distributing agency gives the total energy, one-electron energies (E_{nl}), potential energies (J_{nl}), kinetic energies (KE_{nl}), total potential energy, total kinetic energy, the virial-theorem[10] ratio, and the additional HF parameters metnioned earlier. All quantities are given in a.u. except the spin-orbit and spin-spin parameters which are in cm^{-1}.

Table I of the present paper summarizes the important results.

Approximate analytic HF-SCF wave functions for Ce^{3+} $(4f^1)$ ^2F and Yb^{3+} $(4f^{13})$ ^2F have been obtained by Freeman and Watson.[11] Owing to the small size of the s and p basis sets used in these calculations, the accuracy of the inner nl wave functions was limited. More emphasis has been placed on the accuracy of the inner electron distribution in the present calculations. The ζ_{4f}, $F^K(4f, 4f)$'s, and M^K $(4f, 4f)$'s values for Ce^{3+} and Yb^{3+} given in Table I of the present paper can be compared with those obtained[11,12] using the above-mentioned analytic wave functions. The F^K and M^K values agree to within 1% but the agreement in ζ_{4f} values is only within 6%. This shows that the $4f$ wave functions of Freeman and Watson are reliable. The greater disagreement in the ζ_{4f} values is probably owing to the fact that its evaluation[4] utilizes all the nl wave functions of the atomic system.

ACKNOWLEDGMENTS

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