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Accurate Analytical Self-Consistent-Field Wave Functions for Nd^{3+} †

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The need for an accurate description of the electronic structure of the important laser-active ion Nd^{3+} stimulated this work. We calculated self-consistent-field wave functions by the analytical-expansion method for the ground state of the laser-active ion Nd^{3+}($Z=60$), $4f^3$,^4I. The results represent the most accurate wave functions for Nd^{3+} published. All the exponents of the basis functions in the analytical expansion were exhaustively optimized. The virial theorem was satisfied to seven significant figures. Values of $\langle r^n \rangle$ for the $4f$ orbital are included.

INTRODUCTION

Accurate analytical self-consistent-field (SCF) wave functions for Nd^{3+}, one of the most important laser-active ions, are required for profound crystal-field studies in solid-state physics, as well as for other applications. This is manifested by the increasing interest in applied research involving this ion.[1,2]

The accurate description of the electronic structure of Nd^{3+} represents a further advance of accurate analytical calculations into the rare-earth group of atomic systems. These results will, as in the past,[3,4] facilitate continued progress into the heavier elemental ions by means of accurate atomic-structure calculations.

We carried out SCF calculations for the ground state of Nd^{3+} ($Z=60$), $4f^3$, ^4I, by means of the analytical-expansion method.[5] All the exponents $\zeta_{\lambda p}$ of the basis functions were subjected to careful, repeated, and exhaustive optimizations, until the calculated total energy E remained almost unchanged to eight significant figures. The open-shell state $4f^3$, ^4I was characterized by the vector coupling coefficients $K_{\lambda\mu\nu}$.[6] The computation was done with a program[5] for the IBM-7094-7044-II direct-channel coupling computing facility.[7]

RESULTS AND DISCUSSION

The terminology, the atomic units,[8] and the notation[5] used are the conventional ones.[3]

Tables I and II represent the most important results; Table II specifies the orbital exponents and eigenvector components required to construct the orbital wave functions, as prescribed by the analytical SCF expansion technique, using Slater-type orbitals as basis functions. Furthermore, from these analytical expansions the numerical tabulations of the radial functions were calculated, together with the total electronic density; the results in this form are in Tables III–VI[9]; these tables may be requested from a depository agency[9]; in these tables the radial part of the orbital wave function $\varphi_{i\lambda\alpha}(r, \vartheta, \varphi)$ multiplied by r is denoted by $P_{i\lambda}(r)$.

TABLE I. Total energy E (a.u.), the virial theorem, and the orbital energies ϵ (a.u.) for Nd^{3+}, $4f^3$, ^4I.

Quantity		Value
E		−9282.5000
E_p/E_k		−1.9999999
	1s	−1528.352
	2s	−244.562
	3s	−55.477
	4s	−12.571
	5s	−2.678
	2p	−231.397
ϵ	3p	−49.667
	4p	−10.277
	5p	−1.950
	3d	−38.979
	4d	−6.181
	4f	−1.730

We assume that the radial functions $P_{i\lambda}(r)$ represent the Hartree-Fock values to about two to three decimal places. The Hartree-Fock total energy is represented to about five significant figures. The virial theorem[10] is satisfied to seven significant figures.

The cusp condition[11] restriction[12] on the choice of the basis set was not imposed in this calculation. This restriction would have required additional basis functions, thus consuming a greater amount of costly computer time.

In these calculations, a considerable amount of computer time was spent executing the adjustments of the orbital wave functions so as to satisfy the variation principle under given conditions.[4] This was accomplished by repeated, careful, and exhaustive optimizations of the basis function exponents $\zeta_{\lambda p}$. In particular, such optimizations caused smoothing out of the tail parts of the orbital wave functions to a considerable extent[4]; finally, the maximum amplitudes of the radial-function oscillations in the tail region (called "wobbling") never exceeded 0.0004.

Previously, an approximate analytical calculation for Nd^{3+} was conducted, with minimum basis sets for the s and p symmetries, and with five and six basis functions for the d and f symmetries, respectively.[13] For the 3d, 4d, and 4f orbitals, we found that the accurate results of this work, when numerically tabulated,[9] agree with the corresponding approximate results previously obtained[13] to two decimal places. For the approximate orbitals[13] of the s and p symmetries we found, of course, larger deviations from the accurate results of this work.

The average values $\langle r^n \rangle$ for the 4f orbital are as follows: $\langle r^{-3} \rangle = 6.1659$; $\langle r^0 \rangle = 1.0000$; $\langle r \rangle = 0.8872$; $\langle r^2 \rangle = 0.9788$; $\langle r^4 \rangle = 2.1854$; and $\langle r^6 \rangle = 10.6720$.

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TABLE II. The orbital exponents $\zeta_{\lambda p}$ of the basis functions and the eigenvectors of coefficients $C_{i\lambda p}$ for Nd^{3+}, $4f^3$, ^4I.

Basis function	Exponent	Eigenvectors				
		1s	2s	3s	4s	5s
1s	61.10416	0.89439	0.00229	−0.02029	0.01069	−0.00329
1s	43.96945	0.11379	−0.52073	0.26878	−0.12940	0.05028
2s	25.46811	−0.03965	1.51001	0.00201	−0.10621	0.08008
2s	21.83292	0.03770	−0.33907	−0.96813	0.62101	−0.29981
3s	16.10059	−0.01066	0.07565	0.97108	−0.47480	0.22754
3s	11.52179	0.00710	−0.04071	0.49443	−0.65313	0.25674
4s	9.21916	−0.00337	0.01664	−0.04797	0.85513	−0.35864
4s	6.58402	0.00164	−0.00763	0.01882	0.56134	−0.44393
5s	5.22214	−0.00049	0.00217	−0.00437	0.00215	0.51294
5s	3.29945	0.00009	−0.00039	0.00059	0.00257	0.75601

TABLE II. *(continued)*.

Basis function	Exponent	Eigenvectors			
		2p	3p	4p	5p
2p	36.22722	0.20837	−0.04583	0.01741	−0.00422
2p	25.45896	0.80198	−0.51283	0.24866	−0.09777
3p	15.34649	−0.01243	0.23420	0.16182	−0.02042
3p	13.77824	0.01973	0.89341	−0.91709	0.30970
4p	9.34953	−0.00573	0.05029	0.47913	−0.16101
4p	6.69853	0.00336	−0.00927	0.74079	−0.46152
5p	4.96713	−0.00101	0.00153	0.03539	0.42647
5p	2.97237	0.00024	−0.00022	0.00063	0.78977
		3d	4d		
3d	23.33333	0.16458	−0.07415		
3d	13.93005	0.82346	−0.39763		
4d	8.99526	0.08177	0.34229		
4d	6.39608	−0.02647	0.60969		
4d	4.39476	0.00610	0.19626		
		4f			
4f	14.59345	0.05497			
4f	9.15764	0.17629			
4f	6.64639	0.30773			
4f	4.87307	0.25520			
4f	3.25600	0.35575			
4f	1.59394	0.03608			

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[9] Tables III, IV, and V of the radial functions $P_{i\lambda}(r)$ and Table VI of the total electronic density, numerically tabulated to five decimal places, are not printed in this article. These tables may be requested by ordering NAPS Document from National Auxiliary Publications Service, American Society for Information Sciences, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for Microfiche or $ 6.50 for photocopies.

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