terest the symmetric distortion terms are also small. So, a frequency shift can occur without being accompanied by a comparable distortion in the line shape.

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Accurate Analytical Self-Consistent-Field Wave Functions for Pr$^{3+\dagger}$

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Ab initio calculations by the analytical-expansion self-consistent-field method were carried out for the ground state of the laser-active ion Pr^{3+} ($Z=59$), $4f^{2}, {}^{3}H$. The results represent the most accurate wave functions for Pr^{3+} available at this time. The knowledge of these wave functions is shifting the frontier of accurate analytical calculations into the group of rare earths. The numbers of basis functions in the analytical expansions were 10, 8, 5, and 6 for the symmetries s, p, d, and f, respectively. All the basis-function exponents were subjected to careful and exhaustive optimizations.

INTRODUCTION

Accurate analytical self-consistent-field (SCF) wave functions for the laser-active ion of praseodymium are needed for crystal-field studies in solid-state physics, and for other applications, as is evidenced by a considerable research interest in applied areas concerning this ion.[1,2]

The knowledge of the presented wave functions is shifting the frontier[3] of accurate analytical calculations significantly further into the periodic system, from the silver ion[3] into the group of rare earths. This will enable further advancement of the present frontier through extrapolation, as well as calculations of lighter atomic systems through interpolation (followed, of course, by an SCF process).

We carried out *ab initio* calculations for the ground state of Pr^{3+} ($Z=59$), $4f^{2}, {}^{3}H$, by means of the analytical-expansion SCF method.[4] This implies that the full exchange effect for all the 56 electrons entering the calculation was included in our SCF process; no approximations were added either for the exchange effect or for the off-diagonal Lagrange multipliers.

The computation was done with a program[4] for the IBM-7094-7044-II direct-channel coupling computing facility.[5]

All of 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 $4f^{2}, {}^{3}H$, was characterized by the vector-coupling coefficients $K_{\lambda\mu\nu}$.[6]

RESULTS AND DISCUSSION

The terminology, the atomic units,[7] and the notation[4] used are the usual ones.[3, 8]

The most important results are presented in Tables I and II; these tables are representing orbital wave functions as analytical expansions. 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 $P_{i\lambda}(r)$.

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 six significant figures.

The cusp-condition[11] restriction[12] on the choice of the basis set was released in this calculation. This was desirable because of the computer time economy, since the identical satisfaction of the cusp condition would require additional basis functions. It was not expected to satisfy the cusp condition too accurately for such a heavy atomic system. This release of the cusp-condition restriction, however, meant that the extrapolation from the silver ion, and other lighter systems, accurately calculated before,[3, 8, 13] could not be used since these systems were "cusp-restricted". Hence, to obtain the first well-converging run for Pr^{3+} saturated set was rather laborious; it required building the system up from much lighter systems, step by step. Incidentally, in this process "cusp-unrestricted" SCF runs for Ag^{+} ($Z = 47$) and I^{-} ($Z = 53$) were gradually obtained and used as intermediate results for further extrapolation to Pr^{3+} ($Z = 59$).

In our calculations, we tried to execute any adjustments of the orbital wave functions that were required by the variation principle under given conditions. 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; finally, the maximum amplitudes of the radial-function oscillations in the tail region (called "wobbling") never exceeded 0.0004. In other words, there were nodes and loops beyond those required by the radial-function orthogonality; however, the magnitudes of the minima and/or maxima of these loops never exceeded a comparatively tight norm. Experience with this and previous calculations shows that the variation principle, under given conditions, dictates a strong reduction of the tail "wobbling"; yet, it would not be practical to try to eliminate the "wobbling" to a considerably higher degree of accuracy. Namely, other effects would decrease considerably the meaning of higher decimal places of the radial functions; among these effects are the correlation and relativistic effects, and a limited basis set for the usual analytical expansion; besides these effects there is a nontrivial long-range behavior[14] even for the absolute Hartree-Fock orbitals.[15] In addition to these factors there is, of course, also the effect of single-precision computer representation and its corresponding accumulated round-off errors, affecting the eighth significant figure of the total energy E and the fourth and fifth decimal places of the radial functions $P_{i\lambda}(r)$; however, in comparison with the effects mentioned before, it did not seem urgent enough to carry out calculations in an extended or double-precision computer representation.

The numerical SCF calculations *without exchange* for Pr^{3+} were carried out by Ridley.[16] The numerically represented radial functions[9] $P_{i\lambda}(r)$ of this work, which have exchange effects included, of course, cannot be expected to agree closely with those of Ridley (after normalization). Namely, large disagreement is always expected when comparing calculations with and without exchange.[3, 8]

An analytical expansion for the $4f$ orbital, described with four basis functions, was published

TABLE I. Total energy E (a.u.), the virial theorem and the orbital energies ϵ (a.u.) for Pr^{3+}, $4f^{2}, {}^{3}H$.

Quantity		Value
E		−8919.8142
E_p/E_k		−2.0000037
ϵ	$1s$	−1475.695
	$2s$	−235.251
	$3s$	−53.186
	$4s$	−12.112
	$5s$	−2.625
	$2p$	−222.351
	$3p$	−47.518
	$4p$	−9.888
	$5p$	−1.916
	$3d$	−37.092
	$4d$	−5.921
	$4f$	−1.642

TABLE II. Orbital exponents $\xi_{\lambda p}$ of the basis functions and the eigenvectors of the coefficients $C_{i\lambda p}$ for Pr^{3+}, $4f^{2,3}H$.

Basis function	Exponents	Eigenvectors				
		1*s*	2*s*	3*s*	4*s*	5*s*
1*s*	60.073 21	0.899 41	−0.014 39	−0.010 08	0.006 68	−0.001 66
1*s*	41.873 08	0.111 08	−0.517 20	0.263 59	−0.128 09	0.049 89
2*s*	25.617 18	−0.048 22	1.341 93	−0.026 43	−0.046 93	0.051 87
2*s*	21.626 64	0.045 14	−0.148 91	−0.924 41	0.539 45	−0.262 93
3*s*	15.884 89	−0.014 62	0.068 94	0.878 00	−0.357 80	0.179 40
3*s*	11.621 13	0.010 02	−0.040 48	0.561 44	−0.750 87	0.299 32
4*s*	9.233 00	−0.004 26	0.015 59	−0.043 18	0.813 24	−0.343 64
4*s*	6.458 36	0.001 96	−0.007 05	0.018 41	0.622 47	−0.466 43
5*s*	5.042 25	−0.000 61	0.002 17	−0.004 86	−0.010 13	0.537 77
5*s*	3.214 61	0.000 13	−0.000 45	0.000 84	0.004 99	0.731 56
		2*p*	3*p*	4*p*	5*p*	
2*p*	36.786 44	0.167 75	−0.033 76	0.013 07	−0.002 86	
2*p*	25.351 87	0.838 39	−0.514 89	0.246 14	−0.097 21	
3*p*	14.984 36	0.004 76	0.025 25	0.383 95	−0.093 29	
3*p*	13.751 18	0.006 81	1.088 54	−1.128 38	0.379 58	
4*p*	9.232 41	−0.004 76	0.055 80	0.457 67	−0.148 72	
4*p*	6.545 90	0.003 02	−0.010 11	0.762 52	−0.483 93	
5*p*	4.902 92	−0.001 01	0.001 73	0.029 96	0.430 10	
5*p*	2.926 30	0.000 24	−0.000 24	0.002 19	0.794 79	
		3*d*	4*d*			
3*d*	22.964 06	0.162 83	−0.072 98			
3*d*	13.636 14	0.823 64	−0.394 83			
4*d*	8.838 69	0.084 78	0.316 39			
4*d*	6.300 87	−0.026 87	0.624 12			
4*d*	4.304 46	0.005 92	0.205 04			
		4*f*				
4*f*	14.021 82	0.059 72				
4*f*	8.899 06	0.140 93				
4*f*	6.514 28	0.371 69				
4*f*	4.457 41	0.192 16				
4*f*	3.273 82	0.375 55				
4*f*	1.591 80	0.048 93				

by Freeman and Watson.[2] We are presenting analytical SCF expansions for all the orbitals; all the orbitals are described accurately; the 4*f* orbital was described with six basis functions. Similar statements can be made with respect to the approximate results numerically obtained by Sovers[17] from the results of Freeman and Watson[2] for the 4*f* orbital. Our analytical orbitals are the most accurate ones available at this time.

Previously, an approximate analytical calculation for Pr^{3+} was carried out, with minimum basis sets for the *s* and *p* symmetries, and with five and six basis functions for the *d* and *f* symmetries, respectively (exponents optimized).[18] For the 3*d*, 4*d*, and 4*f* orbitals we found that the accurate results of this work, numerically tabulated,[9] agree with the corresponding approximate results published before[18] to two decimal places. For the approximate orbitals[18] of the *s* and *p* symmetries we found, of course, larger deviations from the accurate results of this work.

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