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The Effect of Correlation on Spectra of the Lanthanides: Pr^{3+}

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Abstract: The effect of correlation on the spectra of lanthanide ions has been investigated using variational methods based on multiconfiguration Dirac–Hartree–Fock (MCDHF) theory. Results from several computational models are reported for Pr^{3+}. The first assumes an inactive Cd-like $4d^{10}$ core with valence electrons in $4f^2 5s^2 5p^6$ subshells. Additional models extend correlation to include core effects. It is shown that, with such models, the difference between computed energy levels and those from observed data increases with the energy of the level, suggesting that correlation among outer electrons should also be based on the correlated core of excited configuration state functions (CSFs). Some M1 transition probabilities are reported for the most accurate model and compared with predictions obtained from semi-empirical methods.

Keywords: correlation; energy levels; lanthanides

1. Introduction

The effect of correlation in the atoms and ions of lanthanides and actinides is not well understood. Though O'Malley and Beck [1,2] have studied the effect of valence correlation of lanthanide anion binding energies, very few spectra of lanthanide atoms and ions have been investigated. The periodic table makes atomic structure changes clear, in that new shells appear before an earlier shell is filled. In addition, the number of levels in the f^n configurations of lanthanides and actinides increases rapidly with n ($n \leq 7$), and resulting spectra consist of numerous closely spaced levels. The simplest case has a $4f^2$ ground configuration with 13 levels. The lanthanides are among the lighter atomic systems where both correlation and relativistic effects require full relativistic treatment.

The spectrum for Pr^{3+} is one of the few where levels for several configurations have been classified. Spectra were published in 1965 by both Sugar [3] and Crosswhite et al. [4]. Levels of $4f^2$, $4f5d$, $4f6s$, and $4f6p$ configurations for the neutral atom were identified. Theoretical studies in those days, as exemplified by the paper published by Morrison and Rajnak [5], were based on effective operators for the f-shell group used to classify the symmetry of f^n states.

In an early publication [6], Pr^{3+} was selected as a test case for a multiconfiguration Dirac–Hartree–Fock program capable of including the effects of correlation on wave function expansions in terms of a few thousand configuration state functions. Results based on simplifying assumptions were reported, compared with observation, and important interactions identified. A few years later, Eliav et al. [7] reported results from a relativistic coupled cluster method for both Pr^{3+} ($4f^2$) and U^{4+} ($5f^2$) with improved accuracy.

Seth et al. [8] took a broader approach to the prediction of spectra with errors in the levels less than $500 \, \text{cm}^{-1}$ using a multiconfiguration Dirac–Hartree–Fock configuration interaction (MCDHF-CI)

method for lanthanide or actinide cases with subshells nf^k and additional $(n + 1)$-subshell electrons. Classes of excitations were considered for the test cases $Pr^{3+}(4f^2)/U^{4+}(5f^2)$, $Pm^{3+}(4f^4)/Np^{3+}(5f^4)$, and $Eu^{3+}(4f^6)/Am^{3+}$ $(5f^6)$ on a trial and error basis. The largest expansion size was about 150,000 CSFs. For Pr^{3+}, the average error in the 13 levels was 448 cm^{-1}.

More recently, Safronova et al. [9] applied higher-order perturbation methods to the study of correlation effects in La, Ce, and lanthanide ions using hybrid methods that combine configuration interaction (CI) with second-order perturbation theory and linearized coupled cluster all-order methods. In Ce^{2+}, only the 5 lowest levels were reported with the error increasing with the degree of excitation.

Semi-empirical relativisitic Hartree–Fock methods have been applied to the analysis of some spectra for lanthanides. Wyart et al. [10] used a group theoretical description of energy levels for $4f^n$ systems in terms of parameters that take into account Coulomb interactions, spin-dependent interactions, and other interactions. Nd^{3+}, Pr^{3+}, and Nd^{4+} were investigated. A least squares fit of parameters to observed energy levels yielded excellent agreement between theory and experiment. For the highest level of Pr^{3+}, namely $4f^2$ ^1S, an energy level of 48044.66 ± 1.29 cm^{-1} was predicted, a value that differs appreciably from the 50090.29 cm^{-1} reported by Crosswhite et al. [4]. Sugar [3] did not include this level in his publication, nor is it reported in the Atomic Spectra Database (ASD) [11]. These semi-empirical methods were applied by Yoca and Quinet [12] to the study of decay rates in Pr^{3+} and by Li et al. [13] to parity forbidden transitions in several lanthanides, including Pr^{3+}.

This paper reports preliminary ab initio systematic studies of the many-body effects in the $4f^2$ manifold for Pr^{3+}, where observed energy levels have been classified, although the highest $^1S_0$ level is uncertain. M1 transition rates are predicted and compared with semi-empirical values. All calculations were done using the GRASP2K program [14].

2. Underlying Theory

In the multiconfiguration Dirac–Hartree–Fock (MCDHF) method [15], as implemented in the GRASP2K package [14], the wave function $\Psi(\gamma P J M_J)$ for a state labeled $\gamma P J M_J$, where J and M_J are the angular quantum numbers and P the parity, is expanded in antisymmetrized and coupled CSFs:

$$\Psi(\gamma P J M_J) = \sum_{j=1}^{M} c_j \Phi(\gamma_j P J M_J). \tag{1}$$

The labels $\{\gamma_j\}$ denote other appropriate information about the CSFs, such as orbital occupancy and coupling scheme. The CSFs are built from products of one-electron orbitals, having the general form

$$\psi_{n\kappa,m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa,m}(\theta, \varphi) \\ \imath Q_{n\kappa}(r)\chi_{-\kappa,m}(\theta, \varphi) \end{pmatrix}, \tag{2}$$

where $\chi_{\pm\kappa,m}(\theta, \varphi)$ are two-component spin-orbit functions. The radial functions $\{P_{n\kappa}(r), Q_{n\kappa}(r)\}$ are represented numerically on a grid.

In spectrum calculations, where only energy differences relative to the ground state are important, wave functions for a number of targeted states are determined simultaneously in the extended optimal level (EOL) scheme. Given initial estimates of the radial functions, the energies E and expansion coefficients $\mathbf{c} = (c_1, \ldots, c_M)^t$ for the targeted states are obtained as solutions to the configuration interaction (CI) problem,

$$\mathbf{Hc} = E\mathbf{c} \tag{3}$$

where $\mathbf{H}$ is the CI matrix of dimension $M \times M$ with elements

$$H_{ij} = \langle \Phi(\gamma_i P J M_J)|H|\Phi(\gamma_j P J M_J)\rangle. \tag{4}$$

Radial functions are solutions of systems of differential equations that define a stationary state of an energy functional for one or more wavefunction expansions. It is possible to derive the MCDHF equations from the usual variational procedure by varying both the large and small components so that

$$
w_a \begin{bmatrix} V(a;r) & -c\left[\frac{d}{dr} - \frac{\kappa_a}{r}\right] \\[2ex] c\left[\frac{d}{dr} + \frac{\kappa_a}{r}\right] & V(a;r) - 2c^2 \end{bmatrix} \begin{bmatrix} P_a(r) \\[1ex] Q_a(r) \end{bmatrix} = \sum_b \epsilon_{ab}\, \delta_{\kappa_a \kappa_b} \begin{bmatrix} P_b(r) \\[1ex] Q_b(r) \end{bmatrix}
\tag{5}
$$

where $V(a;r) = V_{nuc}(r) + Y(a;r) + \bar{X}(a;r)$ is a potential consisting of nuclear, direct, and exchange contributions arising from both diagonal and off-diagonal $\langle \Phi_\alpha | \mathcal{H}_{DC} | \Phi_\beta \rangle$ matrix elements [15]. In each κ-space, Lagrange-related energy parameters $\epsilon_{ab} = \epsilon_{n_a n_b}$ are introduced to impose orthonormality constraints in the variational process.

3. Computational Procedures

What distinguishes the f^n manifolds computationally is the rapid (almost explosive) increase in the number of CSFs as single- (S) and double- (D) excitations are applied, compared with lighter systems such as the C-, N-, and O-like systems. For the latter, excellent results have been reported both for the spectrum and the transitions rates of interest in astrophysical applications [16,17]. Questions then arise about whether such large expansions are needed. The JJGEN program in GRASP2K generates excitations in terms of configurations and, for a given configuration, produces all the CSF basis states associated with the configuration. The $4d^{10}4f^2$ manifold has 13 basis states, whereas $4d^84f^4$ (produced by the $4d^2 \to 4f^2$ excitation) has 3121 basis CSFs over the same range of J, namely $J = 0, \ldots, 6$, which interact with one or more CSFs of $4d^{10}4f^2$. For a small orbital set, these expansions can readily be dealt with on current computers. Difficulties arise with larger orbital sets with multiple "layers" (orbitals with the same "n"), and a range of angular symmetries are used. GRASP calculations are systematic in that the set is increased by successively adding an extra layer of orbitals to an existing set, where each new layer is orthonormal. Associated with this systematic method is the notion of convergence. Thus, at some point, the corrections to an existing result become small. Thus, it is helpful to partition the wave function expansion into a zero-order approximation and its first-order correction whose expansion coefficients are small. In perturbation theory, the interaction between CSFs of the first-order correction for the wave function is ignored.

Two types of expansions may be used—in the past, both have been the same, but for large calculations there are advantages to relaxing this restraint and allowing expansions to be different.

(1) The first is the expansion that determines the radial functions using the RSCF program of the GRASP2K package that determines radial functions. For occupied orbitals, optimized radial functions can be obtained by applying the variational principal to an energy expression or functional. However, for correlation orbitals, the most important interactions appear as contributions to the functions $\bar{X}(a;r)$ that are in the same region of space as the occupied orbitals. This has been shown in partitioned configuration interaction (PCFI) studies [18]. In fact, solutions to the variational equations produce orbitals in a region of space determined by $\bar{X}(a;r)$ for a given orbital. This can be used effectively in tailoring the orbital to an interaction.

(2) The second is an expansion for the RCI program that determines the wavefunction and its associated energy for a given Hamiltonian based on a given orbital basis. In the present work, the Hamiltonian for RCI was the Dirac–Coulomb Hamiltonian (DC) plus the transverse photon interaction (DCB), the vacuum polarization effects as accounted for by the Uehling potential, and electron self-energies as calculated with the screened hydrogenic formula [15,19], referred to as the DCBQ Hamiltonian. The RCI program is relatively simple to parallelize efficiently [20] using message passing. As a result much larger expansions are possible for RCI calculations than RSCF

calculations that build the orbital basis. Present calculations were performed using, for larger cases, 48 processors.

4. Systematic Studies for Pr^{3+}

4.1. A Simple EAL Approximation

The $4f^25s^25p^6$ configuration of Pr^{3+} consists of filled shells and two-electrons in the open $4f$-subshell. When the MCDHF approximation is computed without any Lagrange multipliers, all orbitals will decrease exponentially radially without any extra nodes. GRASP2K provides such a solution when the valence electrons consist only of $4f^2$ and all other subshells are in the inactive core. In the extended-average-level (EAL) approximation, only the diagonal matrix elements define the energy functional, avoiding any cancellation in the definition of the energy functional. Though the difference between extended-optimal-level (EOL) and EAL is small, this study is based on the EAL solution for the Cd-like core. The mean-radii of the orbitals (shown in Table 1) are such that the $4f$-orbitals are like core orbitals in the sense that their mean radii are closer to the other $n = 4$ orbitals than either $5s$ or $5p$. At the same time, these orbitals define the spectrum. Computationally, it is more convenient to specify the configuration in terms of orbitals in their standard order, as in $4f^25s^25p^6$. In this work, the CSF's of the $4f^25s^25p^6$ configuration define the multireference (MR) set, and $4f, 5s, 5p$ electrons are considered to be valence electrons.

The core orbitals $1s, \ldots, 4d$ were fixed in all subsequent calculations.

Table 1. Mean radii, $r(nl)$, and generalized occupation numbers, $w(nl)$, of the $n = 4$ and 5 orbitals of Pr^{3+}.

nl	$r(nl)$	$w(nl)$
4s	6.21000D-01	2.00000D+00
4p-	6.39294D-01	2.00000D+00
4p	6.64991D-01	4.00000D+00
4d-	7.18376D-01	4.00000D+00
4d	7.28007D-01	6.00000D+00
4f-	9.78187D-01	9.23077D-01
4f	9.86245D-01	1.07692D+00
5s	1.48902D+00	2.00000D+00
5p-	1.64179D+00	2.00000D+00
5p	1.71177D+00	4.00000D+00

4.2. Case 1—SD Excitations from $4f^25s^25p^6$

A series of calculations were performed in which the expansions consisted of CSFs that interact with the MR set. The latter were obtained from excitations to orbital sets of increasing size by n, with orbital quantum numbers restricted to $l \leq 4$. The set are referred to as ng orbital sets.

Case 1 results from SD excitations from $4f^24s^25p^6$ to ng orbital sets are given in Table 2.

The $n = 4$ calculation is an RCI calculation based on the radial functions from the variational EAL calculation. Note that the spectrum has two $J = 4$ adjacent states that are not in their final order.

Table 2. Case 1: spectrum for SD expansions from $4f^25s^25p^6$ to ng orbital sets, $n = 4, 5, 6, 7$.

J	LS	$n = 4$	$n = 5$	$n = 6$	$n = 7$
4	^3H	0	0	0	0
5	^3H	2000	2026	2005	2004
6	^3H	4124	4108	4055	4049
2	^3F	6722	5837	5636	5584
3	^3F	7970	7138	6923	6872
4	^3F	10716	7320	7149	7090
4	^1G	7958	10100	9911	9842
2	^1D	23135	20224	19709	19518
0	^3P	29218	25093	24406	24217
1	^3P	29720	25606	24912	24721
6	^1I	27564	25007	24940	24818
2	^3P	30644	26566	25856	25661
0	^1S	64078	54907	53027	52453
CSFs		13	26180	95732	209005

4.3. Case 2—SD Excitations from $4d^{10}4f^25s^25p^6$

The valence correlation calculation omitted the very strong interactions within the $n = 4$ complex, particularly the interactions between $4d^2$ and $4f^2$. By extending the active subshells to include $4d^{10}$, we are including some of the correlations in the core. At the same time, the expansion size increased significantly by a factor of about four for $n = 7$. Again, only CSFs that interacted with the MR set were included. For the RSCF calculation, only the interaction with the MR set was used to determine the correlation orbitals. The convergence of these results are shown in Table 3, where the total number of CSFs are also reported for each n.

Table 3. Case 2: spectrum for SD expansions from $4d^{10}4f^25s^25p^6$ to ng orbital sets, $n = 4, 5, 6, 7$.

J	LS	$n = 4$	$n = 5$	$n = 6$	$n = 7$
4	^3H	0	0	0	0
5	^3H	2004	2119	2134	2138
6	^3H	4122	4279	4247	4241
2	^3F	6083	5754	5766	5758
3	^3F	7339	7108	7110	7103
4	^3F	7411	7333	7293	7274
4	^1G	10152	10228	10155	10129
2	^1D	21398	20160	20012	19928
6	^1I	27373	24738	24548	24443
0	^3P	27141	24740	24760	24682
1	^3P	27643	25191	25154	25066
2	^3P	28561	26198	26111	26016
0	^1S	58748	54847	54340	53861
CSFs		6134	194186	824921	1886931

4.4. Case 3—SD Excitations from $4s^24p^64d^{10}4f^25s^25p^6$

This final calculation extended the active set core to include $4s^24p^6$; however, because of the size of the expansion, some restrictions applied. The $n = 4$ and 5 expansions were full SD expansions to ng orbital sets. The $n = 6$ expansion included all SD excitations from $4s^24p^64d^{10}4f^25s^25p^6$ to the $n = 5g$ orbital set plus SD from $4d^{10}4f^25s^25p^6$ to the $n = 6g$ orbital set, whereas the $n = 7$ expansion added SD from $4d^{10}4f^25s^25p^6$ to the $n = 7g$ orbital set to the $n = 6$ expansion and also added CV excitations from $4s^24p^6$ (core) and $4f^25s^25p^6$ (valence) shells to the $n = 7g$ orbital set.

The results based on this calculation are reported in Table 4 where they are also compared with data from observation and other theory.

Table 4. Case 3: spectrum for expansions from $4s^2 4p^6 4d^{10} 4f^2 5s^2 5p^6$ to ng orbital sets, $n = 4, 5, 6, 7$. See text for details. Results are compared with observation and other theory. For $n = 7$ results, differences from observation are given in parentheses.

J	LS	$n = 4$	$n = 5$	$n = 6$	$n = 7$(diff)	Obs.[a]	Eliav(diff) [b]	Seth(diff)[c]	Cai(diff)[d]
4	^3H	0	0	0	0	0.00	0(0)	0(0)	0(0)
5	^3H	2011	2207	2176	2189(37)	2152.09	2081(-71)	2237(85)	2337(185)
6	^3H	4136	4426	4312	4320(-69)	4389.09	4250(-139)	4589(200)	4733(344)
2	^3F	5714	5393	5392	5387(390)	4996.61	4842(-155)	4872(-125)	4984(-13)
3	^3F	6988	6817	6780	6782(367)	6415.24	6215(-200)	6356(-59)	6517(102)
4	^3F	7268	7221	7138	7124(269)	6854.75	6680(-175)	7010(155)	6950(95)
4	^1G	10076	10342	10171	10152(231)	9921.24	9686(-235)	10357(436)	10207(286)
2	^1D	20195	18976	18770	18693(1359)	17334.39	16867(-458)	17535(201)	18153(819)
0	^3P	25881	23558	23522	23439(2104)	21389.81	21128(-262)	21253(-137)	22776(1386)
1	^3P	26396	24004	23899	23810(1803)	22007.46	21713(-294)	21862(-145)	23450(1443)
6	^1I	26751	24302	23992	23877(1665)	22211.54	21829(-382)	22970(758)	25854(3643)
2	^3P	27333	25058	24876	24784(1623)	23160.61	22803(-357)	23171(10)	24653(1492)
0	^1S	57598	54199	53515	52939(2849)	50090.29	49061(-1029)	51007(917)	50517(427)
CSFs		12286	405557	1039966	2101976				

[a] Ref. [3,4]   [b] Ref. [7]   [c] Ref. [8]   [d] Ref. [6].

Table 4 shows theoretically the most accurate results of our study. The differences between our $n = 7$ results and observations [3,4] and similar information from other theories are also listed. The fine-structure splitting of the lowest ^3H term from the present work is more accurate than the fine-structure reported by Eliav et al. [7], who used a coupled-cluster method. In fact, the fine-structure for the ^3F term from the present work was also well predicted, except for the $J = 4$ level, which is affected by the interactions with components of the adjacent $^1G_4$ level. What is striking is that the difference observed in our present work is related to the energy of the level relative to the ground state. A similar linear dependence in the $3d^k$ levels of tungsten was shown to be related, at least in part, to the omission of core correlation [21] from the calculation. On the other hand, the differences in values reported by Eliav et al. [7] are all negative. A slightly lower energy for the ground term would have improved the accuracy (relative to the ground state) for the entire spectrum. The differences for the last two columns are more random. The present results are not sufficiently accurate for the higher levels to be able to confirm Wyart's prediction of 48044.66 ± 1.29 cm^{-1} for the highest ^1S level.

4.5. M1 Transitions

Table 5 reports the theoretical wavelengths and M1 transition probabilities for all computed levels. The transition with the largest transition rate by far is from the upper $^1S_0$ level to $^3P_1$, a transition with the largest error in our computed wavelength. Our results are shown here with the larger semi-empirical transition rates reported by Li et al. [13] as well as those reported by Yoca and Quinet [12]. The semi-empirical values are based on observed wavelengths whereas the present rates used computed values. Transition rates for M1 transitions depend largely on wavelengths giving semi-empirical methods an advantage with regard to accuracy. For the larger transition rates, there is greater agreement than expected.

Table 5. Computed wavelengths λ (in vac., in nm) and transition rates (A in s^{-1}) for M1 transitions between levels of $4d^{10}4f^25s^25p^6$ for Pr^{3+} from present work compared with semi-empirical results.

Upper	Lower	λ	A	λ_{obs}	A [13]	A [12]
$^3H_5$	$^3H_4$	4567.5	0.2706	4644	0.258	0.247
$^3H_6$	$^3H_5$	4691.4	0.2171	4473	0.252	0.248
$^3F_3$	$^3H_4$	1474.5	0.0061	1559	0.00672	
$^3F_3$	$^3F_2$	7167.1	0.0684	7049	0.0720	0.0716 ^{a}
$^3F_4$	$^3H_4$	1403.7	0.1538	1459	0.163	0.154
$^3F_4$	$^3H_5$	2026.4	0.0508	2127	0.0512	0.0499
$^3F_4$	$^3F_3$	29235.9	0.00053			
$^1G_4$	$^3H_4$	984.9	0.1832	1008	0.180	0.173
$^1G_4$	$^3H_5$	1255.8	0.2041	1287	0.208	0.200
$^1G_4$	$^3F_3$	2966.8	0.2648	2852	0.304	0.300
$^1G_4$	$^3F_4$	3302.3	0.2196	3261	0.232	0.219
$^1D_2$	$^3F_2$	751.4	0.7956	811	0.781	0.764
$^1D_2$	$^3F_3$	839.5	1.094	916	1.03	1.00
$^3P_1$	$^3F_2$	542.7	0.01701	588	0.0208	
$^3P_1$	$^1D_2$	1954.2	0.2136	2140	0.188	0.181
$^3P_1$	$^3P_0$	2695.4	0.00091	16195		0.00467
$^1I_6$	$^3H_5$	461.0	0.4939	499	0.515	0.494
$^1I_6$	$^3H_6$	511.4	0.5119	561	0.505	0.485
$^3P_2$	$^3F_2$	515.5	0.01107	551	0.0104	
$^3P_2$	$^3F_3$	555.4	0.1350	597	0.151	
$^3P_2$	$^1D_2$	1641.7	0.6120	1716	0.614	0.618
$^3P_2$	$^3P_1$	10269.8	0.01156	8671	0.0191	0.0232
$^1S_0$	$^3P_1$	343.3	9.144			

^{a} Corrected value reported by Li et al. [13].

5. Conclusions

By comparing the energy levels of the three cases, it is clear that the energy levels of the lowest ^3H term are improving, but the higher levels are not approaching the observed levels. Since the energy level is the difference in the total energy of an excited level and the ground state, this suggests that a higher-order effect has been omitted.

Table 6 shows expansion coefficients of CSFs that contribute more than 0.1% of the wavefunction. It is immediately evident that the $^1S_0$ level has an extensive variation in angular symmetry. It is the only level where the $(4d5p) \rightarrow (4f5d)$ excitation plays a significant role. Important for all levels are the $(5p^2) \rightarrow (5d^2)$ (outer correlation) and the $(4d^2) \rightarrow (4f^2)$ (core correlation) excitations. A comparison with an expansion similar to that of Case 1 (not shown in this paper) indicates a substantial reduction in the coefficient for the $4d^{10}4f^25s^25p^45d^2$ basis states. What has changed is that CC has been included for the $4d^{10}4f^25s^25p^6$ components, essentially lowering the energy for these components, but not for the $4d^{10}4f^25s^25p^45d^2$ components.

Table 6. Wavefunction expansion coefficients for the different levels. The coupling of the CSFs from left to right is indicated in LSJ notation. LS terms that are the result of coupling are preceded by the _ symbol.

Pos	J	Parity	Energy Total	Comp. of ASF
1	0	+		
			0.95688308	4d(10)1S.4f(2)3P_3P.5s(2).5p(6)_3P
			0.07944615	4d(10)1S.4f(2)1S_1S.5s(2).5p(6)_1S
			0.05764566	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1S_3P.5d(2)1S_3P
			-0.04040785	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3F.5d(2)1D_3P
			-0.03824922	4d(8)3P.4f(4)5D_3P.5s(2).5p(6)_3P
			-0.03493664	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)3P_5D.5d(2)3P_3P
			0.03415086	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3D.5d(2)1D_3P
			0.03209335	4d(8)1S.4f(4)3P_3P.5s(2).5p(6)_3P

Table 6. *Cont.*

Pos	J	Parity	Energy Total	Comp. of ASF
2	0	+		
			0.95439158	4d(10)1S.4f(2)1S_1S.5s(2).5p(6)_1S
			-0.07966975	4d(10)1S.4f(2)3P_3P.5s(2).5p(6)_3P
			0.07779345	4d(9)2D.4f(3)2F_1P.5s(2).5p(5)_2D.5d_1S
			-0.06276546	4d(10)1S.4f(2)1S_1S.5s(2).5p(4)3P_3P.5d(2)3P_1S
			-0.05857617	4d(10)1S.4f(2)1S_1S.5s(2).5p(4)1D_1D.5d(2)1D_1S
			0.05552689	4d(10)1S.4f(2)1S_1S.5s(2).5p(4)1S_1S.5d(2)1S_1S
			-0.05095911	4d(8)3P.4f(4)3P_1S.5s(2).5p(6)_1S
			0.04940667	4d(8)1S.4f(4)1S_1S.5s(2).5p(6)_1S
			0.04804989	4d(10)1S. .5s(2).5p(6).5d(2)1S0_1S
			-0.04366450	4d(8)3F.4f(4)3F_1S.5s(2).5p(6)_1S
			0.04186055	4d(10)1S.4f(2)1D_1D.5s_2D.5p(6).5d_1S
			-0.04109111	4d(10)1S.4f(3)2F_2F.5s_3F.5p(5)_2D.5d_1S
			0.03853116	4d(10)1S.4f(1)2F_2F.5s(2).5p(6).5f_1S
			-0.03610536	4d(10)1S.4f(2)1S_1S.5s_2S.5p(5)_1P.5d_2F.5f_1S
			-0.03452111	4d(10)1S.4f(4)1S_1S.5s(2).5p(4)1S_1S
			-0.03441194	4d(8)1G.4f(4)1G_1S.5s(2).5p(6)_1S
			-0.03418894	4d(8)1D.4f(4)1D_1S.5s(2).5p(6)_1S
			-0.03370734	4d(10)1S. .5s(2).5p(6).5f(2)1S1_1S
			-0.03340972	4d(10)1S.4f(2)1D_1D.5s(2).5p(5)_2F.5f_1S
			-0.03298434	4d(10)1S.4f(1)2F_2F.5s(2).5p(5)_1G.5d(2)1G_1S
			0.03284105	4d(8)3P.4f(3)2F_2F.5s(2).5p(6).5f_1S
1	1	+		
			0.96000734	4d(10)1S.4f(2)3P_3P.5s(2).5p(6)_3P
			0.05783129	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1S_3P.5d(2)1S_3P
			-0.04050954	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3F.5d(2)1D_3P
			-0.03675295	4d(8)3P.4f(4)5D_3P.5s(2).5p(6)_3P
			-0.03507024	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)3P_5D.5d(2)3P_3P
			0.03425834	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3D.5d(2)1D_3P
			0.03213372	4d(8)1S.4f(4)3P_3P.5s(2).5p(6)_3P
1	2	+		
			0.95268304	4d(10)1S.4f(2)3F_3F.5s(2).5p(6)_3F
			0.13065275	4d(10)1S.4f(2)1D_1D.5s(2).5p(6)_1D
			0.05766997	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1S_3F.5d(2)1S_3F
			-0.03322783	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1D_3H.5d(2)1D_3F
			0.03183390	4d(8)1S.4f(4)3F_3F.5s(2).5p(6)_3F
2	2	+		
			-0.91699186	4d(10)1S.4f(2)1D_1D.5s(2).5p(6)_1D
			0.25549718	4d(10)1S.4f(2)3P_3P.5s(2).5p(6)_3P
			0.12899064	4d(10)1S.4f(2)3F_3F.5s(2).5p(6)_3F
			-0.05534533	4d(10)1S.4f(2)1D_1D.5s(2).5p(4)1S_1D.5d(2)1S_1D
			0.04077372	4d(10)1S.4f(2)1D_1D.5s(2).5p(4)3P_3F.5d(2)3P_1D
			0.03385521	4d(10)1S.4f(2)1D_1D.5s(2).5p(4)1D_1G.5d(2)1D_1D
			-0.03339539	4d(9)2D.4f(3)2H_1F.5s(2).5p(5)_2G.5d_1D
			-0.03306878	4d(10)1S.4f(2)1D_1D.5s(2).5p(4)3P_3D.5d(2)3P_1D
3	2	+		
			0.92521406	4d(10)1S.4f(2)3P_3P.5s(2).5p(6)_3P
			0.25482649	4d(10)1S.4f(2)1D_1D.5s(2).5p(6)_1D
			0.05574679	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1S_3P.5d(2)1S_3P
			-0.03919043	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3F.5d(2)1D_3P
			-0.03639504	4d(8)3P.4f(4)5D_3P.5s(2).5p(6)_3P
			0.03432540	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)1D_3D.5d(2)1D_3P
			-0.03328506	4d(10)1S.4f(2)3P_3P.5s(2).5p(4)3P_5D.5d(2)3P_3P
1	3	+		
			0.96174530	4d(10)1S.4f(2)3F_3F.5s(2).5p(6)_3F
			0.05824364	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1S_3F.5d(2)1S_3F
			-0.03482837	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1D_3H.5d(2)1D_3F
			0.03211558	4d(8)1S.4f(4)3F_3F.5s(2).5p(6)_3F

Table 6. *Cont.*

Pos	J	Parity	Energy Total	Comp. of ASF
1	4	+		
			0.94974464	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.15137535	4d(10)1S.4f(2)1G_1G.5s(2).5p(6)_1G
			0.05756326	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1S_3H.5d(2)1S_3H
			0.03172136	4d(8)1S.4f(4)3H_3H.5s(2).5p(6)_3H
			-0.03163263	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1D_3K.5d(2)1D_3H
2	4	+		
			0.77949362	4d(10)1S.4f(2)3F_3F.5s(2).5p(6)_3F
			-0.55255416	4d(10)1S.4f(2)1G_1G.5s(2).5p(6)_1G
			0.10985122	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.04720553	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1S_3F.5d(2)1S_3F
			-0.03348741	4d(10)1S.4f(2)1G_1G.5s(2).5p(4)1S_1G.5d(2)1S_1G
3	4	+		
			0.77273818	4d(10)1S.4f(2)1G_1G.5s(2).5p(6)_1G
			0.56262158	4d(10)1S.4f(2)3F_3F.5s(2).5p(6)_3F
			-0.10753810	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.04687515	4d(10)1S.4f(2)1G_1G.5s(2).5p(4)1S_1G.5d(2)1S_1G
			0.03410347	4d(10)1S.4f(2)3F_3F.5s(2).5p(4)1S_3F.5d(2)1S_3F
1	5	+		
			0.96220777	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.05836490	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1S_3H.5d(2)1S_3H
			-0.03284413	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1D_3K.5d(2)1D_3H
			0.03211299	4d(8)1S.4f(4)3H_3H.5s(2).5p(6)_3H
1	6	+		
			0.96113767	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.05833222	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1S_3H.5d(2)1S_3H
			-0.04478581	4d(10)1S.4f(2)1I_1I.5s(2).5p(6)_1I
			-0.03214745	4d(10)1S.4f(2)3H_3H.5s(2).5p(4)1D_3K.5d(2)1D_3H
			0.03207693	4d(8)1S.4f(4)3H_3H.5s(2).5p(6)_3H
2	6	+		
			-0.95979783	4d(10)1S.4f(2)1I_1I.5s(2).5p(6)_1I
			-0.05797893	4d(10)1S.4f(2)1I_1I.5s(2).5p(4)1S_1I.5d(2)1S_1I
			-0.04484692	4d(10)1S.4f(2)3H_3H.5s(2).5p(6)_3H
			0.03800845	4d(10)1S.4f(2)1I_1I.5s(2).5p(4)3P_3K.5d(2)3P_1I
			-0.03396403	4d(10)1S.4f(2)1I_1I.5s(2).5p(4)3P_3I.5d(2)3P_1I
			-0.03239597	4d(10)1S.4f(2)1I_1I.5s_2I.5p(6).5d_1I
			-0.03211047	4d(8)1S.4f(4)1I_1I.5s(2).5p(6)_1I
			0.03179904	4d(10)1S.4f(2)1I_1I.5s(2).5p(4)1D_1L.5d(2)1D_1I

Correlation in the core defines the potential ($V(a; r)$ of Equation (5)) for the outer electrons. This suggests that all major contributors to the wave function such as $4d^{10}4f^25s^25p^45d^2$ should be built on a correlated core but that the correlation between core-correlation CSFs may not be important. This is similar to the CI-RMBPT method [22], where effective operators are used for the calculation of an interaction matrix for the outer correlation. The effective operators include the effect of core correlation. With this model, the expansion for even $J = 0$ is about 3 million for an $n = 5$ calculation. Further studies are needed to determine how core correlation can be included efficiently in such cases.

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