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Hyperfine Structure Constants of $(d+s)^3$ states in La I and the Zr II and Hf II Isoelectronic Sequences

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Abstract

Accurate results for hfs constants of $(d+s)^n$ states often require the inclusion of both correlation and relativistic effects. Without these, Dirac-Fock hfs constants may have the wrong sign, and energies of uppermost d^n levels may be wrong by over 1 eV. Here, we demonstrate that these problems persist well into an isoelectronic sequence, and identify the principle configurations needed to achieve accurate results.

I. INTRODUCTION

Transition metal atoms play important roles in catalysis, as impurities in plasma fusion devices, and as deep level traps in semi-conductors. Previously, properties of $(d+s)^n$ states of these species, which form many of the ground and low lying excited states, have been rather poorly understood. Positions of d^n levels can be in error over 1 eV, independent particle hfs constants can have the wrong sign, and little ab initio work has been done on their transition probabilities.

Our hfs work on these states, which began in 1992 [1], has established the need to accurately position the $d^{n-1}s$ levels relative to those from d^n and $d^{n-2}s^2$ in order to account for the hfs constants for the latter two configurations. We may interpret this as being due to the former normally having large hfs constants arising from the contact operator contributing at the zeroth order (independent particle) level. Of course, in addition to positioning the levels correctly, the usual core polarization effects must be included.

Since relativistic effects associated with d,s electron interchanges may be several tenths of an eV [2], they can have an important impact on level positions, and so must be included in any theoretical treatment. It is also necessary to treat d^n , $d^{n-1}s$ and $d^{n-2}s^2$ levels on an equal footing, so our theory must be a multi-reference one. Furthermore, when obtaining correlated wavefunctions for these levels, one can be involved with configurations possessing a few hundreds of eigenvectors, each constructed from several hundreds of Slater determinants. This calls for some innovative ways of reducing computational costs.

II. METHODOLOGY

The wavefunctions are generated from the Dirac-Coulomb Hamiltonian, with the Breit contribution, optionally, added as a perturbation. Multi-Configurational Dirac-Fock (MCDF) solutions obtained from Desclaux's program [3] are used as zeroth order functions. These are generated from just $(d+s)^n$ levels. Correlation is introduced through Relativistic Configuration Interaction (RCI); normally a first order form is chosen, i.e. those configurations generated by making single or double excitations from outermost subshells of MCDF configurations. The question of what to use as one electron functions for unoccupied (virtual) subshells is an important one, as poor choices may lead to (partial) variational collapse into the "positron sea". This can be avoided, if the major and minor components of these functions are properly constrained (e.g. not allowed to vary separately). In our case, experience has demonstrated that use of relativistic screened (Z^*) hydrogenic functions avoid this problem, while at the same time providing an adequately converged series, if Z^* is chosen during the RCI process to minimize the energy for the root of interest.

Since much of our work deals with excited states, we prefer to work with moderately sized (< 7000) energy matrices, which we diagonalize using Weber *et al's* [4] variant of the Davidson algorithm, to which we have added some improvements [5]. We thus want to use N electron functions which are eigenstates of J^2 , J_z and parity. Formerly, we used to generate eigenstates of J^2 by direct diagonalization of that matrix, but some of the correlation configurations can involve matrices of order several thousand, and we may need a few hundred eigenvectors. In our hfs studies, we have avoided this difficulty by splitting the configuration into two separate parts, each of which we make eigenstates of J^2 and J_z , and then "paste" the parts back together using standard vector coupling theory (sums of the product of the two section functions and a single 3j symbol are involved). The procedure is very fast, and capable of dealing with large problems.

To further restrict the size of the energy matrix, we have automated a suggestion first made by Bunge [6] in a non-relativistic study of the C I atom. This recognizes that the N parents (eigenvectors) of a single configuration, generate matrix elements (with the zeroth order function) involving M radial integrals, and that M is less than N , usually. In fact, in the transition metals and rare earths, M may be 10-1000 times smaller than N . Since the theory is first order in "form", a rotation of the original set of parents can be done, such that in the new set, there are only M parents which have a non-zero interaction with the reference function. The other $N-M$ functions can then be discarded, consistent with a first order (in form) theory. Certain adjustments are made for the fact that our theory is relativistic, and multi-reference, but the approximation is both a good one (errors less than 200 cm^{-1}) and highly efficient. Further details of the methodology can be found in our Zr II paper [7].

Computational Strategy

Our calculations begin by doing RCI calculations built from single and double excitations from the valence (e.g. $4d, 5s$ in Zr II) subshells into virtuals of symmetries s, p, d, g (one radial for each type). These excitations are significant contributors to energy differences, and sensitive to orthogonalization order (if core excitations are done first, it is difficult to recover

energy lost from valence virtuals due to orthogonalization to core virtuals). Now the 4d and 5s radial functions can vary substantially between $(4d)^3$, $(4d)^25s$ and $4d(5s)^2$ configurations. To account for this, we do the MCDF calculation for the root of most interest (e.g. $(4d)^3$ $J=3/2$ was chosen in Zr II, as this was the subject of a recent measurement [7]), and use “Brillouin” type excitations, viz $4d \rightarrow vd$, $5s \rightarrow vs$ (and eventually $4p \rightarrow vp$) to improve the description of the other roots.

After the first set of valence virtuals is determined, a second set, associated with these same single and double valence excitations is added; this normally provides sufficient radial saturation of the valence space. The larger triple excitations are also added in at this time.

In the next calculational layer, we begin to make single and double excitations from the shallow core, viz the 4s and 4p subshells, adding in a third set of virtuals, with larger effective Z^* (determined during the RCI process). Important excitations include $4p \rightarrow vp + vf$, and $4s \rightarrow 5s + vs$, $4d + vd$. Decisions on what to include are based on the criteria that we are seeking energy contributions which are differentially large, or make substantial contributions to hfs. These single excitations generally fall into both categories.

At this stage, errors in relative energy differences were still too large, on the order of a few tenths of an eV. We may reasonably expect the next most important corrections to come from the classes of excitations: $4p(4d + 5s) \rightarrow$, but in fact these have a differentially modest effect. Next, we looked at double excitations from $4p^6$. The most important of these, differentially, turn out to be $4p^2 \rightarrow 4d^2 + 4dvd$, which we may ascribe to (1) the fact that $l^2 \rightarrow (l+1)^2$ are among the largest [8], and (2) Pauli exclusion effects are involved, i.e. the 4d subshells are already partially occupied, and this tends to reduce the contribution in varying amounts, depending on the occupancy of the 4d subshell for the level of interest. This finding is valid for all transition metal spectra studied to date, and was first noted in the Zr II work [7].

By using intermediate normalization $\langle \Phi | \Psi \rangle = 1$, where Φ is the zeroth order function, and Ψ is the RCI function, it is possible to assign energy contributions to each correlation vector. These are collected in Table I, for Zr II for all configurations contributing .025 eV or more to at least one root. The excitations present in Table I, reduce the average energy difference error to .075 eV ($\sim 600 \text{ cm}^{-1}$). On simpler systems, e.g. La II, we have reduced the error to .02 eV or $\sim 160 \text{ cm}^{-1}$ [9].

III. RESULTS

A. The Zr II Isoelectronic Sequence

In this sequence, we avoid Y I because of the interpenetrating manifolds $5s^2 6s$ and $4d 5s 6s$ [10] which would increase the number of reference functions needed. In a relativistic treatment such as this, each J is a separate problem. We chose to study $J=3/2$ because it had the greatest number of reference functions (10), thus making it challenging, and because several $J=3/2$ levels were just being measured for Zr II [11]. Results for Zr II have already appeared [7,11], but we reproduce them here in Table II, as this species can provide a benchmark for the other sequence members for which no hfs measurements exist. It can be seen that the average error for the RCI A results is 9.2% , in contrast to the DF values, for which two of the three results have the wrong sign. We also note that we are in agreement with the corrections of Kiess [12] to the Moore [10] energy levels.

In Table III we present results for the Nb III member of the $J=3/2$ isoelectronic sequence. For the 5 known energy differences [10], the theoretical error is .050 eV (410 cm^{-1}); note that we have predicted the positions of 4 new levels, not available from experiment [10,13]. Though there is greater agreement between the DF and RCI results for A than in Zr II, there are still 2 levels exhibiting a sign reversal. The one and N electron basis sets used to generate the results are the same as that used for Zr II, with the obvious changes in radial functions (MCDF and virtuals, viz Z^*).

In Table IV, are presented the results for Mo IV $J=3/2$ using the same 1 and N electron basis sets (radial sets suitably adjusted). These calculations along isoelectronic sequences were considerably eased by the fact that almost the entire data sets (several thousand lines) could be reused from one member to the next. Here, the average error for the 8 known [10,14] energy levels is somewhat larger: .107 eV or 860 cm^{-1} , and just 1 new level has been identified. We may note that there is still 1 value of A for which the DF and RCI results have different signs.

B. The Hf II Isoelectronic Sequence

Discussion of La I is postponed to the next section, as it is a thoroughly measured system and we have done calculations for several J's. The first member of the series considered here is Hf II, whose results are presented in Table V. The average error [10] for 8 energy differences is .030 eV ($\sim 200 \text{ cm}^{-1}$). One new level is predicted, and 3 of the A's show large differences (sign or order of magnitude) between the DF and RCI results. Most of our tables also contain predictions for the electric quadrupole constant, B, divided by the quadrupole moment, Q. One can either extract B, if Q is known [15], or if a measurement of B is available, as in Zr II [11], a determination of Q may be made.

In Table VI, we present our results for the Ta III member of this sequence. Since we were unable to find any experiment work on energy levels, our results constitute predictions for the relative positions of 9 levels. In this case, there are 5 A's exhibiting substantial differences between DF and RCI results.

Table VII contains our results for the W IV member of this sequence. Again, there appears to be no available experiment, so 9 new levels are predicted. Three A's exhibit

sign changes between the DF and RCI value. Studies in the Zr II and Hf II sequences were terminated once we reached species of lesser technological interest (in our judgement); dramatic differences between at least a few RCI and DF A values are likely to persist beyond the ions reported here.

C. Results for La I

La I has been well studied experimentally, for both energy differences [16] and hfs constants [17]. In addition to reporting results for $J=3/2$, we also did calculations for $J=7/2$ and $9/2$ as the 2G hfs constants (B's), exhibit some substantial second order (from A) contributions.

In Table VIII our results for $J=3/2$ are presented and compared to experiment. For 8 energy differences, the average error is only .028 eV (227 cm^{-1}), and one new level is predicted. The largest errors are associated with the uppermost levels, which may suggest the presence of significant second order electrostatic effects (see Discussion section). The average error for the 6 measured A's is 10.3% ,with the maximum error 19.0% . While there are no sign changes (DF vs RCI) in these bottom 6 A's, the top 2 of them show large differences, and for 2 of the unmeasured A's there are sign changes. For the 6 B's, the average error is 32%, and the RCI values represent at best only a marginal improvement over DF values. For the smallest measured B (-6.00), we estimate a 12.4% correction from second order hfs effects (see below).

The average energy difference errors for $J=7/2$ and $J=9/2$, shown in Table IX, are 0.17 eV and 0.13 eV respectively (1350 cm^{-1} and 1020 cm^{-1}). This is indicative that the basis set of Table I, so useful for $J=3/2$, needs improvement for these J's. Our more accurate studies on La II [9], Nb II [18], and Cs II [19] contain suggestions of what might be added. Comparing the A's, on the other hand, with observation [17] yields an average error of 11% for $J=7/2$ and 14% for $J=9/2$, which is comparable to our $J=3/2$ accuracy.

Both Tables VIII and IX contain results for B's, the electric quadrupole constants; those for the $5d^2 6s \ ^2G$'s involve large second order hfs effects which we discuss in the next section.

D. Electric Quadrupole Constants for La I $J=7/2, 9/2$

When $|\frac{B}{A}| \ll 1$ and fs splittings are small, second order contributions from A may be important; experiment measures net hfs, not individual poles (M1, E2). Lower order poles (M1) must be treated in high enough order so errors are smaller than those desired in the pole of interest. Based on the experimental work [17], the 4 levels with the largest discrepancies [B_{obs} vs $B_{\text{corrected}}$] in La I are shown in Table X. Only the last two are of interest here, as we don't work on $J=5/2$. In Table X, the B_{obs} values are deduced from experiment without any second order corrections as determined semi-empirically by fitting experiment [17]. This does not produce an entirely satisfactory fit to the directly observed frequencies [17].

The second order correction may be expressed as in [17] as

$$\frac{|\langle \ ^2G_{7/2}, F | H(M1) | \ ^2G_{9/2}, F \rangle|^2}{E(^2G_{7/2}) - E(^2G_{9/2})}$$

where $H(M1)$ is the relativistic magnetic dipole operator, and the denominator is the fine structure (fs) difference. In ref [17] this was initially evaluated at MCDF level, but that yielded too small corrections. Here we show that the RCI second order contribution is adequate to explain observation without having to introduce extra semi-empirically determined parameters.

In the spirit of reference [20], we may write the numerator as

$$W_{JJ'}(\text{MHz}) = (-1)^{I+F-J} \sqrt{I(I+1)(2I+1)J_{>}(J_{>}+1)(2J_{>}+1)} A_{JJ'} \begin{Bmatrix} I & J & F \\ J' & I & 1 \end{Bmatrix}$$

where

$$A_{JJ'} = 13074.7 \frac{\mu_I}{I \sqrt{J_{>}(J_{>}+1)}} \langle JJ | T_Q^{(1)} | J'J' \rangle$$

Here μ_I is the magnetic dipole moment [15], $T_Q^{(1)}$ is the Q^{th} component [$Q = J - J'$] of the relativistic magnetic dipole component and $\{ \}$ is a 6j symbol. The constant factor is a product of c and a factor to convert a.u. to MHz. In evaluating $A_{JJ'}$ we take non-orthonormality effects fully into account [21]. Our RCI result for $A(5d^26s \ ^2G_{7/2}, 5d^26s \ ^2G_{9/2})$ is -504.8 MHz, whereas our MCDF value is +343.7 MHz.

Our RCI results for the electric quadrupole constants, using experimental [15] Q 's are $B[5d^26s \ ^2G_{7/2}] = 112.6$ MHz and $B[5d^26s \ ^2G_{9/2}] = 108.3$ MHz. These results are obtained from the Zr II type bases, with $3p \rightarrow vp$ excitations added. These results are in good agreement with the semi-empirical $B(\text{corrected})$ values [17] which are respectively 111.512 and 127.571 MHz. These values appear in Table IX.

It is useful to look at what is happening in detail which we do in Table XI. By columns, these tables contain (1) the experimental energy differences (transitions between hfs levels), (2) experiment with the magnetic dipole contribution removed, using the observed A [labelled $\Delta E_{\text{expt}} - \delta \langle A_{\text{obs}} \vec{I} \cdot \vec{J} \rangle$], (3) the E2 contribution obtained from our RCI B using first order perturbation theory, B_{RCI} , (4) the second order M1 contribution using our RCI A , labelled $-\delta A^{(2)}$, and (5) a final column summing columns (3) and (4), Σ_{Th} . Experimental/theoretical discrepancies are obtained by comparing columns (2) and (5). It can be seen that the agreement is quite good; and that the second order effects associated with M1 can be an appreciable fraction of the first order E2 effects.

IV. DISCUSSION

A cautious estimate for unmeasured A's might be 20-25% for RCI values, except for those below 50 MHz in magnitude. Errors for these might be 50-100%. These estimates are based, in part, in how A changes as the calculation proceeds. Although we have not emphasized, in detail, the importance of the relative positioning of $d^{n-1}s$ levels in this work, this is more thoroughly explored in the work on La II [9] and Cs II [19].

In general, uppermost levels exhibit large errors in energy positions and hfs constants. This is because these levels are closer in energy to "Rydberg" excited states than the lowest levels. Excitations from the core artificially pull all the $(d + s)^n$ levels away from these Rydberg levels, because they aren't given equivalent core correlation.

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TABLE I. Energy contributions in eV for Zr II $J=3/2$. All signs reversed.

Basis	Roots									
	$4d^3$	$4d^25s$	$4d^3 +$	$4d5s^2$	$4d^3$	$4d^25s$	$4d^3 +$	$4d^25s$	$4d^3$	$4d^25s$
	2D	2P	2D	2D	4P	4P	2P	2D	4F	4F
$(4d + 5s)^3$	-0.195	-1.041	-0.385	-0.140	0.010	0.002	0.993	0.738	0.014	0.008
$4d vp^2$	0.269	0.304	0.166	0.473	0.056	0.005	0.003	0.040	0.022	0.005
$4d vd^2$	0.339	0.011	0.228	0.002	0.192	0.002	0.216	-0.003	0.161	0.001
$4d vf^2$	0.571	0.054	0.395	0.010	0.351	0.000	0.338	-0.010	0.244	0.001
$4d vg^2$	0.069	0.008	0.044	0.000	0.021	0.000	0.021	-0.002	0.014	0.000
$4d vs vd$	0.000	0.061	0.006	0.000	0.000	0.047	0.000	0.044	0.000	0.048
$4d vp vf$	0.090	0.383	0.102	0.000	0.019	0.196	-0.031	0.214	0.041	0.192
$4d^2 vs$	0.000	0.004	0.009	0.000	0.000	0.027	0.048	0.018	0.001	0.022
$4d^2 vd$	0.024	0.063	0.066	0.036	0.091	0.016	0.075	0.006	0.084	0.004
$4d^2 vg$	0.068	0.086	0.051	0.000	0.034	0.003	0.039	0.003	0.014	0.009
$5s vp^2$	0.000	0.014	0.000	0.097	0.000	0.034	0.000	0.009	0.000	0.000
$5s vd^2$	0.000	0.050	0.000	0.002	0.000	0.062	0.000	0.062	0.000	0.037
$5s vf^2$	0.000	0.164	0.000	0.016	0.000	0.172	0.000	0.127	0.000	0.058
$5s vs vd$	0.000	0.000	0.000	0.033	0.000	0.000	0.000	0.003	0.000	0.000
$5s vp vf$	0.000	0.000	0.000	0.227	0.000	0.000	0.000	-0.006	0.000	0.014
$4d 5s vs$	0.004	0.000	-0.002	0.162	0.000	0.000	0.001	0.035	0.001	0.000
$4d 5s vd$	0.000	0.561	0.010	0.047	0.000	0.316	-0.017	0.364	0.000	0.295
$4d 5s vg$	0.012	0.000	-0.001	0.032	0.000	0.000	0.000	0.028	0.000	0.015
$5s^2 vd$	0.000	0.000	0.000	0.434	0.000	0.000	0.000	-0.010	0.000	0.000
$4p^5 vf 4d^3$	0.911	0.034	1.003	0.000	1.109	0.021	1.010	0.021	1.166	0.020
$4p^5 vf 4d^2 5s$	0.022	0.853	0.020	0.054	0.020	0.852	0.023	0.805	0.019	0.899
$4p^5 vf 4d 5s^2$	0.000	0.007	0.000	0.505	0.000	0.006	0.000	0.007	0.000	0.006
$4p^5 vp 4d^3$	0.012	0.040	0.016	0.000	0.030	0.042	0.021	0.056	0.035	0.084
$4p^5 vp 4d^2 5s$	0.000	0.067	0.002	0.092	0.004	0.067	0.004	0.081	0.005	0.079
$4p^5 vp 4d 5s^2$	0.000	0.000	0.000	0.334	0.000	0.000	0.000	0.001	0.000	0.004
$4s vd 4d^3$	0.049	0.014	0.036	0.000	0.042	0.005	0.032	0.002	0.022	0.006
$4s vd 4d^2 5s$	0.025	0.056	0.034	0.015	0.026	0.041	0.001	0.020	0.026	0.018
$4p^4 4d^5$	0.746	0.000	0.630	0.000	0.576	0.000	0.621	0.000	0.505	0.000
$4p^4 4d^4 5s$	0.000	0.757	0.001	0.000	0.000	0.754	-0.002	0.749	0.000	0.680
$4p^4 4d^3 5s^2$	0.005	0.000	0.002	0.876	0.001	0.000	0.001	-0.001	0.001	0.000
$4p^5 4d^2 vd vf$	0.062	0.011	0.070	0.000	0.070	0.012	0.074	0.012	0.075	0.012
$4p^5 4d 5s vd vf$	0.000	0.054	0.000	0.024	0.000	0.054	0.000	0.053	0.000	0.055
$4p^5 5s^2 vd vf$	0.000	0.000	0.000	0.029	0.000	0.000	0.000	0.000	0.000	0.000
$4s vs 4d 5s^2$	0.000	0.000	0.000	0.056	0.000	0.000	0.000	0.000	0.000	0.000
$4s 4d^3 5s$	0.001	0.062	0.004	0.004	0.005	0.061	0.004	0.045	0.006	0.016
$4s 4d^4$	0.041	-0.005	0.063	0.000	0.057	0.002	0.042	0.003	0.016	0.002
$4p^5 vp vd 5s^2$	0.000	0.000	0.000	0.040	0.000	0.000	0.000	0.000	0.000	0.000
Total	3.136	2.721	2.576	3.516	2.718	2.846	3.520	3.553	2.473	2.623

TABLE II. Fine and hyperfine structure of Zr II $J=3/2$ $(d + s)^3$ states.

Level ^a		Energy (cm ⁻¹)		A(MHz) ^b		B(MHz)/Q(b) ^b	B(MHz) ^b
Config.	SLJ	Expt. ^a	Theory ^b	Theory ^c	Expt.	Theory ^c	Expt.
4d ³	² D	27 699.96	29 066	-190.0		224.0	
4d ³	² P	20 080.30	20 710	111.5 (-76.0)	109.768	-138.4 (-33.9)	33.716
4d 5s ²	² D	14 298.64	14 996	-114.7		-82.9	
4d ³	² D	13 428.64	14 387	-66.8		165.1	
4d ³	⁴ P	9 742.80	10 072	134.1 (-56.4)	110.177	-133.3 (-156.2)	34.713
4d ² 5s	⁴ P	7 736.02	8 209	-534.6		159.5	
4d ² 5s	² P	6 111.70	6 788	134.3		-132.2	
4d ² 5s	² D	4 248.30	5 084	190.3 (375.1)	199.250	-28.8 (-83.8)	7.706
4d ³	⁴ F	2 572.21	2 950	-298.0		-57.3	
4d ² 5s	⁴ F	0.00	0	273.8		60.5	

^aLabeling of levels is from Moore [10] as corrected by Kiess [12]. Experimental energy is also drawn from these sources.

^bFrom previous work [11].

^cDirac-Fock results are given in parentheses.

TABLE III. Fine and hyperfine structure of Nb III $J=3/2$ ($d + s$)³ states^a.

Config.	Level		Energy (cm ⁻¹)		A(MHz)	B(MHz)/Q(b)
	SLJ		Expt. ^b	Theory ^c	Theory ^d	Theory ^d
4d 5s ²	² D			71 816	937.7 (710.0)	355.9 (326.5)
4d ² 5s	² P			44 448	-1012.2 (-965.6)	-314.5 (-314.8)
4d ² 5s	² D		36 536	37 111	-1355.6 (-1526.7)	-114.0 (-132.3)
4d ² 5s	⁴ P		34 807	35 360	2401.4 (2563.0)	255.7 (251.9)
4d ³	² D			33 870	943.7 (660.3)	371.4 (406.4)
4d ² 5s	⁴ F		25 221	25 061	-1149.3 (-1361.0)	103.2 (100.8)
4d ³	² D			13 602	289.6 (427.4)	-42.78 (-8.66)
4d ³	² P		10 912	11 411	-47.82 (378.8)	-248.5 (-271.2)
4d ³	⁴ P		8 608	8 864	-267.7 (310.4)	-215.8 (-241.2)
4d ³	⁴ F		0.0	0.0	1128.0 (659.4)	-104.3 (-114.9)

^aA=92.90, Z=41, I=9/2, $\mu_I=6.167$.

^bFrom L. Iglesias [13].

^cUses same configurational basis set as Zr II $J=3/2$.

^dDirac-Fock results are given in parentheses.

TABLE IV. Fine and hyperfine structure of Mo IV $J=3/2$ ($d + s$)³ states^a.

Config.	Level SLJ	Energy (cm ⁻¹)		A(MHz)	B(MHz)/Q(b)
		Expt. ^b	Theory ^c	Theory ^d	Theory ^d
4d 5s ²	² D		146 242	-342 (-264)	501 (456)
4d ² 5s	² P	81 052	81 858	423 (387)	-446 (-436)
4d ² 5s	² D	74 009	74 862	493 (510)	-170 (-180)
4d ² 5s	⁴ P	72 163	73 065	-871 (-919)	350 (345)
4d ² 5s	⁴ F	60 893	60 794	447 (511)	143 (138)
4d ³	² D	39 231	41 548	-272 (-247)	524 (559)
4d ³	² D+ ² P	17 107	17 857	-106 (-141)	10.9 (37.6)
4d ³	² P+ ² D	14 176	14 920	-86.0 (-162)	-388 (-419)
4d ³	⁴ P	10 331	10 738	48.7 (-112)	-315 (-340)
4d ³	⁴ F	0.0	0.0	-379 (-246)	-151 (-161)

^aA=95.94, Z=42, I=5/2, $\mu_I=-0.9133$.

^bFrom M. T. Fernandez, I. Cabeza *et al* [14].

^cUses same configurational basis set as Zr II $J=3/2$.

^dDirac-Fock results are given in parentheses.

TABLE V. Fine and hyperfine structure of Hf II $J=3/2$ $(d + s)^3$ states^a.

Config.	Level		Energy (cm^{-1})		A(MHz)	B(MHz)/Q(b)
	SLJ	Expt. ^b	Theory ^c	Theory ^d	Theory ^d	
5d ³	² D		45 798	113.1 (104.0)	476.0 (533.0)	
5d ³	² P	37 324	37 198	-60.0 (48.6)	-99.9 (35.5)	
5d ³	² D	30 594	30 479	77.4 (81.7)	-337.0 (-361.0)	
5d ³	⁴ P	27 285	26 958	-121.1 (43.0)	-290.0 (-308.0)	
5d ³	⁴ F	18 897	18 395	140.8 (107.8)	-162.0 (-182.0)	
5d ² 6s	² P	17 830	17 478	-388.0 (-496.0)	-214.0 (-261.0)	
5d ² 6s	² D	14 359	14 446	-224.0 (-258.0)	-170.0 (-284.0)	
5d ² 6s	⁴ P	12 920	12 815	638.0 (686.0)	320.0 (312.0)	
5d ² 6s	⁴ F	3 644	3 336	-343.0 (-445.0)	193.0 (121.0)	
5d 6s ²	² D	0	0	1.88 (117.3)	342.0 (458.0)	

^aA=178.49, Z=72, I=7/2, $\mu_I=0.61$.

^bFrom C. E. Moore [10].

^cUses same configurational basis set as Zr II $J=3/2$.

^dDirac-Fock results are given in parentheses.

TABLE VI. Fine and hyperfine structure of Ta III $J=3/2$ $(d + s)^3$ states^a.

Config.	Level	SLJ	Energy (cm^{-1})		A(MHz)	B(MHz)/Q(b)
			Expt.	Theory ^b	Theory ^c	Theory ^c
5d ³		² D		42 299	478.9 (606.7)	679.1 (756.7)
5d ² 6s		² P		38 054	-1140.0 (-1917.0)	-347.0 (-581.0)
5d ² 6s + 5d ³		² D		30 834	-18.7 (678.0)	545.0 (687.0)
5d ³ + 5d ² 6s +5d6s ²		² D		24 836	-415.3 (469.3)	-220.7 (-365.5)
5d ² 6s		⁴ P + ² P		19 683	308.6 (357.7)	445.9 (474.0)
5d ³		⁴ P + ² P		16 363	-165.1 (240.4)	-235.3 (-128.0)
5d ³		⁴ P + ² D		13 402	-618.5 (337.0)	-295.2 (-470.0)
5d ³		² P + ⁴ P + ⁴ F		7 814	-134.6 (357.0)	-279.6 (-413.0)
5d ² 6s		⁴ F		5 541	-1961.7 (-2433.1)	110.3 (120.7)
5d ³		⁴ F		0	926.7 (663.2)	-299.4 (-338.0)

^aA=180.95, Z=73, I=7/2, $\mu_I=2.36$.

^bUses same configurational basis set as Zr II $J=3/2$.

^cDirac-Fock results are given in parentheses.

TABLE VII. Fine and hyperfine structure of W IV $J=3/2$ $(d + s)^3$ states^a.

Config.	Level	SLJ	Energy (cm^{-1})		$\Lambda(\text{MHz})$ Theory ^c
			Expt.	Theory ^b	
5d 6s ²		² D		89 111	274.0 (316.0)
5d ² 6s		² P		66 789	-863.0 (-1018.0)
5d ² 6s		² D		53 377	-601.0 (-732.0)
5d ² 6s		⁴ P		48 886	1458.0 (1551.0)
5d ³		² D		47 207	299.0 (282.0)
5d ² 6s		⁴ F		32 565	-1058.0 (-1172.0)
5d ³		² P		26 313	-51.5 (145.0)
5d ³		⁴ P + ² D		19 578	-36.4 (158.0)
5d ³		⁴ P + ² P		11 113	-68.4 (160.0)
5d ³		⁴ F		0	458.0 (309.0)

^a $A=183.85$, $Z=74$, $I=1/2$, $\mu_I=0.117$.

^bUses same configurational basis set as Zr II $J=3/2$.

^cDirac-Fock results are given in parentheses.

TABLE VIII. Fine and hyperfine structure of $^{139}\text{La I } J=3/2 (d + s)^3$ states.

Config.	Level SLJ	Energy (cm^{-1})		A(MHz)		B(MHz) ^d	
		Expt. ^a	Theory ^b	Theory ^b	Expt. ^c	Theory ^b	Expt. ^c
5d ³	² D		27 680	212.6 (175.1)		36.4 (38.8)	
5d ³	² P	21 037	21 614	-64.0 (81.9)		-14.1 (-1.03)	
5d ³	² D	18 038	18 640	190.2 (145.3)		-24.3 (-23.3)	
5d ³	⁴ P	16 735	16 753	-231.8 (68.1)		-17.7 (-22.8)	
5d ³	⁴ F	12 431	12 361	391.8 (176.15)	445.0	-9.87 (-11.3)	-16.07
5d ² 6s	² P	9 719	9 726	-530.7 (-188.96)	-655.0	-24.2 (-24.0)	-33.54
5d ² 6s	² D	8 446	8 692	-422.9 (-321.39)	-423.0	-4.45 (-16.2)	-6.00 ^e
5d ² 6s	⁴ P	7 491	7 556	842.6 (844.26)	930.0	25.0 (22.9)	34.72
5d ² 6s	⁴ F	2 668	2 436	-414.7 (-398.55)	-480.0	10.7 9.26	16.34
5d 6s ²	² D	0	0	129.7 (111.23)	141.0	29.9 (31.8)	44.78

^aExperimental energy is taken from W. C. Martin *et al* [16].

^bThis work. The values in parentheses are MCDF values taken from same reference as footnote ^c.

^cFrom W. J. Childs and U. Nielsen [17].

^dQ is from P. Raghavan [15].

^eEstimated second order hfs contribution $\sim 12.4\%$ (see text).

TABLE IX. Fine and hyperfine structure of $^{139}\text{La I } J=7/2, 9/2 (d + s)^3$ states.

Config.	Level SLJ	Energy (cm^{-1})		A(MHz)		B(MHz)	
		Expt. ^a	Theory ^b	Theory ^b	Expt. ^c	Theory ^b	Expt. ^c
5d ³	² F _{7/2}	18 449	20 920	50.8 (187.0)		28.5	
5d ³	² G _{7/2}	13 529	15 282	137.7 (182.8)		35.1	
5d ³	⁴ F _{7/2}	9 744	10 121	-18.2 (190.9)	-19	-19.3	-20.9
5d ² 6s	² G _{7/2}	6 466	7 493	-253.7 (-189.7)	-292	113	112
5d ² 6s	² F _{7/2}	4 558	5 659	-170.7 (81.9)	-197	37.5	40.3
5d ² 6s	⁴ F _{7/2}	0	0	411.3 (507.9)	463	17.9	16.1
5d ³	² H _{9/2}	14 194	15 704	104 (125)		47.2	
5d ³	² G _{9/2}	13 019	14 357	69 (131)		34.3	
5d ³	⁴ F _{9/2}	9 626	9 968	-53 (82)	-64	-20.6	-27.4
5d ² 6s	² G _{9/2}	5 798	6 694	471 (432)	560	108	128
5d ² 6s	⁴ F _{9/2}	0	0	440 (451)	490	24.2	31.5

^aExperimental energy is taken from W. C. Martin *et al* [16].

^bThis work; RCI. The values in parentheses are MCDF values.

^cFrom W. J. Childs and U. Nielsen [17]. All B's except those for 5d³ ⁴F are obtained using second order hfs effects.

TABLE X. Experimental [17] results for hfs constants [B's] exhibiting significant second order effects.

Level (cm^{-1})	Label		A (MHz)	B_{obs} (MHz)	$B_{\text{corrected}}$ (MHz)
3 010.002	5d ² 6s	⁴ F _{5/2}	300.563	10.873	7.800
9 183.797	5d ² 6s	² D _{5/2}	876.319	-2.772	-5.404
9 919.821	5d ² 6s	² G _{9/2}	559.812	202.638	127.571
9 960.904	5d ² 6s	² G _{7/2}	-292.267	67.537	111.512

TABLE XI. La I $5d^2 6s^2 G$ electric quadrupole results (MHz) including second order effects ^a.

Transition $F \rightarrow F'$	ΔE_{obs}	$\Delta E_{\text{obs}} - \delta \langle A_{\text{obs}} \vec{I} \cdot \vec{J} \rangle$	B_{RCI}	$-\delta A^{(2)}$	Σ_{Th}
$J=7/2 A_{\text{obs}} = -292.267 \text{ MHz}$					
7-6	-2016.965	28.904	46.44	-12.9	33.5
6-5	-1746.669	6.933	11.13	0	11.13
5-4	-1468.190	-6.855	-11.13	7.80	-3.33
4-3	-1182.851	-13.783	-22.08	11.3	-10.78
3-2	-891.992	-15.191	-24.37	11.4	-13.0
2-1	-596.977	-12.443	-20.3	9.05	-11.3
1-0	-299.185	-6.918	-10.4	4.95	-5.44
$J=9/2 A_{\text{obs}} = 559.812 \text{ MHz}$					
8-7	4555.752	77.256	43.04	31.6	76.64
7-6	3943.948	25.264	14.07	12.9	27.0
6-5	3349.169	-9.703	-5.29	0	-5.29
5-4	2768.920	-30.14	-16.84	-7.80	-24.64
4-3	2200.726	-38.522	-21.5	-11.3	-32.8

^aEntries are explained in text. Column 2 constitutes the experimental prediction and the last column constitutes the theoretical prediction.

Bibliography

- [1] D. R. Beck, Phys. Rev. A **45**, 1399 (1992)
- [2] R. L. Martin and P. J. Hay, J. Chem. Phys. **75**, 4539 (1981)
- [3] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975)
- [4] J. Weber, R. Lacroix, and G. Wanner, Comput. Chem. **4**, 55 (1980)
- [5] K. Dinov and D. R. Beck, Bull. Am. Phys. Soc. **38**, 1097 (1993)
- [6] A. Bunge, J. Chem. Phys. **53**, 20 (1970)
- [7] D. R. Beck and D. Datta, Phys. Rev. A **48**, 182 (1993)
- [8] e.g. K. Jankowski, P. Malinowski, and M. Polasik, J. Chem. Phys. **76**, 448 (1982)
- [9] D. Datta and D. R. Beck, Phys. Rev. A **52**, 3622 (1995)
- [10] C. E. Moore, Atomic Energy Levels, Volumes II, 1952 and Volume III, 1958, Circular National Bureau of Standards 467, US GPO, Washington, DC
- [11] L. Young, C. A. Kurtz, D. R. Beck and D. Datta, Phys. Rev. A **48**, 173 (1993)
- [12] C. C. Kiess, J. Opt. Soc. Am. **43**, 1024 (1953)
- [13] L. Iglesias, J. Opt. Soc. Am. **45**, 856 (1955)
- [14] M. T. Fernandez, I. Cabeza *et al*, Phys. Scr. **35**, 819 (1987)
- [15] P. Raghavan, At. Data Nucl. Data Tables **42**, 189 (1989)
- [16] W. C. Martin, R. Zalubas, L. Hagan, Atomic Energy Levels-the Rare Earths, NSRDS-NBS60, USGPO, Washington, DC 1978
- [17] W. J. Childs and U. Nielsen, Phys. Rev. A **37**, 6 (1988)
- [18] L. Young, S. Hasegawa, C. Kurtz, D. Datta, and D. R. Beck, Phys. Rev. A **51**, 3534 (1995)
- [19] S. M. O'Malley and D. R. Beck, Phys. Rev. A **54**, 3894 (1996)
- [20] K. T. Cheng, J. E. Hardis, E. J. Dehm, and D. R. Beck, Phys. Rev. A **30**, 698 (1984)
- [21] Program RHFSOD, D. R. Beck, unpublished