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Relativistic-configuration-interaction results for the hyperfine-structure constants of ^{133}Cs II and ^{137}Ba III $5p^5(5d+6s+6p)$ levels

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Relativistic configuration interaction hyperfine constants (HFC) have been obtained for all $5p^5(5d+6s+6p)$ ^{133}Cs II levels. The 22 magnetic dipole constants, A, agree with experiment to 12% or better for all but three levels. Many of the odd $J=1,2$ levels, which include these three, exhibit large many body effects. Our values for the quadrupole HFS constants are considerably smaller than the few highly uncertain experimental values, which we believe need remeasurement. There are also significant many body results present in the lowest ^{137}Ba III odd parity $J=1,2$ levels; here, there are no experimental results available. We have found certain excitations from the $4d$ subshell to be important; we ascribe this to the presence of an open $5p$ subshell. [S1050-2947(96)04611-2]

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I. INTRODUCTION

This work is a continuation of our study of the hyperfine structure of transition metal positive ions, using a relativistic configuration interaction (RCI) methodology which we have been extending, as needed, during the study. Earlier work had been on the two electron states of Sc II, Y II, and La II [1,2]; the three electron states of Zr II [3,4] and the four electron states of Nb II [5]. Our focus has been on $(d+s)^n$ states as these can exhibit significant d^n, $d^{n-1}s$, and $d^{n-2}s^2$ mixing, resulting in hyperfine structure (HFS) constants which can have incorrect signs, if these interactions are not properly included. This has been found to require the inclusion of relativistic effects, which can change the relative positions of ''d'' and ''s'' levels from one to a few tenths of an eV [6]. Calculational errors for energy differences for the more recent results range from about 450 cm^{-1} [Nb II] on the average to 320 cm^{-1} [La II]. However, often the topmost level in the $(d+s)^n$ manifold has twice or more this error. The work on La II suggested that this is due to second order (in Ψ) electrostatic effects, which occur because the correlation added to the manifolds of interest ''pulls them away'' from their nearby Rydberg series members. In the La II work, we partially compensated for this by artifically adding this correlation energy back into the diagonal matrix elements for these higher Rydberg series members. Ultimately, this must be included properly by introducing triple and quadruple excitations into our wave functions.

Our original interest in Cs II and Ba III HFS was stimulated by remarks made by Berry [7] that the quadrupole constants of Cs II should be remeasured, and both dipole and quadrupole constants for Ba III should be measured. Although these species appear simpler than the ones previously studied, as there is only one electron outside of a ''core,'' which has allowed us to report results for all J's of these manifolds for Cs II, a substantial computational challenge remains. This is due to the prescence of the ubiquitous, strong $(5d+6s)$ mixing characteristic of our earlier transition metal positive ion studies. Initially we did our usual ''first order'' study, involving single and pair excitations from electrons in $5s$, $5p$, $5d$, and $6s$ subshells. This was found to give errors close to 500 cm^{-1} for some of the Ba III energy differences, and over 5000 cm^{-1} for the topmost Ba III $J=1$ level, which were not significantly improved by performing selected triple and quadruple excitations from $5p$, $5d$, and $6s$ electrons. Instead, we ultimately found the corrections to be associated with excitations involving the $4d$ subshell, of which $4d\rightarrow vg$; $4d5d\rightarrow 5pvf$; and $4d5p\rightarrow(5d+6s)vf$ are the most important. Since all of these involve directly, or indirectly, the $5p$ subshell, and they are seemingly absent [2] in La II, which has a closed $5p$ subshell, we ascribe their importance to the presence of the open $5p$ shell.

In Sec. II we briefly review the methodology employed, in Secs. III and IV we present our results, including an analysis of the important contributors to energy differences and HFS constants, and in Sec. V we draw our conclusions.

II. METHODOLOGY

We begin by generating zeroth order wave functions by doing Dirac-Fock (DF) calculations with the program of Desclaux [8]. Specifically, for the $J=1,2$ odd parity calculations, we generate separate DF solutions for the two closest $5p^55d$ and $5p^56s$ states. A common orthonormal radial set is formed by taking the $1s,\ldots,5d$ radials from the first calculation, and the $6s$ from the second calculation, and forcing the latter to be orthogonal to the $1s,\ldots,5s$ radials already present. Further variation of these radial functions with level are accounted for during the RCI stage, through single excitations. The structure necessary to correct the average energy for the DF calculations is provided by our RCI program [9]. While we do have the ability to include the effects of the Breit operator in both the DF and RCI matrices, we normally do not do so, due to the extra computational expense involved (calculations can be four times longer). To check the effect of its absence, we insert the Breit operator during an RCI calculation which involves just the DF configurations. For Ba III $J=1$ odd parity states, the average absolute effect on energy differences is 130 cm^{-1}; the maximum effect is 278 cm^{-1}.

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Our calculations are inherently multireference ones; for $J=1,2$ odd parity cases, the five levels of interest are all treated on an equal footing. Corrections to zeroth order, DF solutions, are generated by creating an RCI wave function which has a first order form. In this case, we initially make single and double excitations from all reference levels (<6) into existing open subshells, or into unocuppied subshells. We call the latter virtual subshells, and the radial portion of their spinors is represented by a relativistic screened (Z^*) hydrogen function, RSHF, whose screening constant, Z^*, is determined during the energy variational procedure. This choice has several advantages: (1) a single function is capable of representing a major part (often 90%) of a (discrete and continuous) Rydberg series, (2) it avoids the problem of variational collapse into negative energy space by coupling the major and minor components, and (3) it provides a simple means of changing the function during the energy variation iteration process. Its suitability for HFS calculation can be judged by the rate of convergence of the HFS constants and the past and present agreement with experiment. To date, both criteria have been well satisfied. The angular part of the virtual spinors is the same as their corresponding hydrogen counterparts.

Even for such simple reference configurations, configurations in the first order RCI wave function can have a few hundred vectors associated with them. This can mean that we might rapidly approach the 7000 limit we have placed on the order of the RCI matrix. As in the past, we used the REDUCE procedure [e.g., [4]] to cut the number of vectors for such configurations by about one order of magnitude in this case; gains are correspondingly larger for more complicated states [5]. The essence of the procedure is to make use of the first order formalism while recognizing that the number of independent parameters (radial integrals) in off diagonal matrix elements involving a reference and correlation configuration is much less (normally) than the number of vectors. A linear transformation of the original vectors is done, so that the number of nonzero off diagonal elements is equal to the number of radial integrals. All transformed vectors yielding zero matrix elements are discarded. In the present case, this has been found to generate errors in energy differences no larger than 80 cm^{-1}; average errors are around 45 cm^{-1}. Finally, we note these calculations are the first ones we have done on our Alpha station 250 4/266 which is five times faster than the Sparc 10 we had been using. An additional speed gain of a factor of four, for calculations involving many vectors produced by REDUCE has also been made by ordering the determinants within such vectors by relativistic configuration. During structure evaluation, which constitutes 70–80 % of the computational cost, these sub blocks are pretested to see if there will be any interaction; if not, the determinatal tests are skipped. More details of the methodology can be found in Refs. [2] and [4], and references therein.

III. Cs II RESULTS

For Cs II we report RCI and MCDF results for odd parity $J=1,2,3$ states and even parity $J=1,2$ states. MCDF results are also given for the odd parity $J=4$ and even parity $J=3$ cases. Experimental energy differences as well as HFS constant A's are available [10–12] for all levels. In addition there are a few experimental HFS constant B's available [13] with which our considerably smaller values disagree (see Table I). Hyperfine moments are taken from Refs. [14,15].

The work reported here shows a strong correlation between the accurate determination of the relative position of energy levels (to a few cm^{-1} for the most sensitive) and accurate results for HFS constants. There has been a substantial revision of the Cs II energy levels reported in Moore [16], by Sansonetti and Andrew [10]. In particular, quoting from that work: ‘‘many reported levels, including levels of the low-lying $5p^5(5d+6s)$ configurations, were rejected as being unreal.’’ More details concerning the revisions, including references to the work of others, are given in Sansonetti and Andrew [10].

Final *ab initio* results for energy differences and HFS constants are given in Table I. The average error in RCI energy differences is 350 cm^{-1}; if the uppermost $J=1$ level is ignored, this drops to 193 cm^{-1}. Individual energy contributions for the odd parity $J=1,2$ levels, which are of particular interest due to the strong $5p^5(5d+6s)$ configuration mixing, are reported in Tables II and III. For these particular states, our final RCI matrices are of order 5189 for $J=1$ and 6374 for $J=2$. The virtual radials have the following type and number (given in parentheses): $vs(3)$, $vp(3)$, $vd(3)$, $vf(3)$, and $vg(2)$; as well as $vh(2)$ for the $J=1$ case. The first and third sets of virtuals have $n=\ell+1$, while the second set has $n=\ell+2$.

The energy correlation contributions are calculated using the intermediate normalization $\langle\Phi,\Psi\rangle=1$, where Φ is the MCDF, and Ψ is the RCI wave function. Then the energy contribution for parent χ_i is given by

$$E_i=\frac{c_i}{c_\Phi}\langle\Phi|H|\chi_i\rangle. \tag{1}$$

Here c_i is the RCI configuration weight for the parent χ_i, and c_Φ is the combined weight for all MCDF parents (single manifold). All contributions for parents arising from the same nonrelativistic manifold are added to form a single entry in Tables II and III.

Energy analysis from Tables II and III show the most important contributions to the energy differences (particularly between the $5p^55d$ and $5p^56s$ manifolds) arise from the following excitations: $5p\rightarrow vp$, $5p\rightarrow vf$, $5p5d\rightarrow vfvd$, $5p^2\rightarrow 5d^2$, $5p^2\rightarrow 5dvd$, $5s\rightarrow 5d$, $5s\rightarrow vd$, $5s5p\rightarrow 5dvf$. In addition $5d\rightarrow vd$ is important for the topmost $5d$ root for $J=1$, which is over 7000 cm^{-1} above the experimental value at the MCDF level.

The large interaction between the $5p^55d$ and $5p^56s$ levels in the $J=1,2$ cases leads to a crucial dependence of the HFS constants on the energy differences of these levels. In the $J=2$ case, the gap between the $6s_1$ and $5d_1$ levels in our final results is $\sim$200 cm^{-1} too small (5196 cm^{-1} compared to 5403 cm^{-1} [10,11]). As a result, the errors in the A's for the $6s_1$ and $5d_1$ levels are 7% and 30% at this stage. Here, noticable improvment of these values occurred in previous runs as this energy gap was brought closer to experiment. We therefore manually shifted the $5p^55d$ diagonal elements upwards to explore the effects of this $6s_1$-$5d_1$ gap on our HFS results. Shifting these elements by 356 cm^{-1} brings the separation of interest to 5406 cm^{-1} and produces substantial

TABLE I. ^{133}Cs II energy levels and hyperfine structure.[a]

Label	J	Relative energies [b] (cm^{-1})		A (MHz)			B (MHz)/Q(b)		
		Expt. [c]	RCI [d]	Expt. [c]	DF [e]	RCI [e]	Expt. [f]	DF [e]	RCI [e]
$5d_3(\frac{1}{2})[\frac{3}{2}]$	1	31335	33908	−1291	−1260	−1157		−144	−176
$5d_2(\frac{3}{2})[\frac{3}{2}]$	1	15731	16028	336	−428	243		558	474
			16023 [g]			300 [g]			466 [h]
$6s_2(\frac{1}{2})[\frac{1}{2}]$	1	14961	15229	5022	5464	4622		−352	−175
			15254 [g]			4566 [g]			−167 [h]
$6s_1(\frac{3}{2})[\frac{3}{2}]$	1	3040	3275	293	185	275		−1243	−814
$5d_1(\frac{3}{2})[\frac{1}{2}]$	1	0	0	20.1	9.50	35.5		352	228
$5d_4(\frac{1}{2})[\frac{3}{2}]$	2	20919	20851	−1002	−850	−878		1020	989
$5d_3(\frac{1}{2})[\frac{5}{2}]$	2	19296	19134	1820	1675	1620		1269	1228
$5d_2(\frac{3}{2})[\frac{5}{2}]$	2	8274	8415	670	639	640		−814	−762
$5d_1(\frac{3}{2})[\frac{3}{2}]$	2	5403	5196	145	−8.27	189	−2700	724	72.5
			5406 [g]			157 [g]			129 [h]
$6s_1(\frac{3}{2})[\frac{3}{2}]$	2	0	0	1648	1650	1539		−2615	−1970
						1571 [g]			−2027 [h]
$5d_3(\frac{1}{2})[\frac{5}{2}]$	3	15695	15305	1136	1152	1056		414	370
$5d_2(\frac{3}{2})[\frac{5}{2}]$	3	4549	4484	293	352	319		601	546
$5d_1(\frac{3}{2})[\frac{7}{2}]$	3	0	0	610	585	595		−2517	−2380
$5d_1(\frac{3}{2})[\frac{7}{2}]$	4	0	0	375	402		14000	−2391	
$6p_4(\frac{1}{2})[\frac{1}{2}]$	1	16834	16725	−1514	−1477	−1425		231	236
$6p_3(\frac{1}{2})[\frac{3}{2}]$	1	15037	14596	4068	3807	3713		80.8	79.0
$6p_2(\frac{3}{2})[\frac{3}{2}]$	1	3471	3426	786	818	801	5400	−118	−135
$6p_1(\frac{3}{2})[\frac{1}{2}]$	1	0	0	858	748	809		−433	−404
$6p_3(\frac{1}{2})[\frac{3}{2}]$	2	15305	15205	1928	1814	1760		405	458
$6p_2(\frac{3}{2})[\frac{3}{2}]$	2	2676	2851	591	569	579		−314	−325
$6p_1(\frac{3}{2})[\frac{5}{2}]$	2	0	0	969	897	938		−2539	−2395
$6p_1(\frac{3}{2})[\frac{5}{2}]$	3	0	0	589	554		−14000	−2454	

[a] $\mu=2.578$, $I=7/2$, $Q=-0.00376$ from Refs. [14,15].

[b] Relative to the lowest energy of same J. In cm^{-1}.

[c] Reference [10].

[d] Unshifted RCI result.

[e] DF = Dirac Fock result as obtained from RCI coefficients. RCI is recommended value unless otherwise noted.

[f] Reference [13]. The uncertainties are as large as the values.

[g] Shifted result (see text).

[h] Shifted result (see text). Recommended.

improvements in the HFS, dropping the errors in A to 5% and 8% respectively. All values are reported in Table I.

There is a similar, and even stronger, interaction between the $6s_2$ and $5d_2$ levels of the $J=1$ case. Here the experimental energy difference is 770 cm^{-1} [10,11] compared to our RCI difference of 799 cm^{-1}. Of particular interest is the HFS of the $5d_2$ level, where the unshifted RCI A value has an error of 28%. The effect of this energy difference on the HFS is such that during successive improvements of the energy spectrum, a reduction of this gap produced an increase in this HFS A of approximately 1 MHz/cm^{-1}. With such an acute dependence of HFS on a small change in energy, the virtuals vh and vh', though having relatively small effect on energy contributions (see Table II), were quite effective in minimizing the error in this energy gap. Similar to the $J=2$ case the diagonal elements corresponding to the $5p^5 6s$ levels were manually shifted up by 42 cm^{-1} producing the desired $6s_2$-$5d_2$ energy difference of 769 cm^{-1} and reducing the error in the $5d_2$ A to 11%.

IV. Ba III RESULTS

For Ba III we report results only for the odd parity $J=1,2$ states. These were selected because they exhibit the largest correlation effects in Cs II. Experimental energy differences are available [17], but HFS constants A and B are not.

Our final fully *ab initio* results for energy differences and HFS constants are given in Table IV, and contributions to energy differences are given in Tables V and VI. Our final RCI matrices are of order 4453 for the $J=1$ and 2977 for the $J=2$ matrices. The virtual radial set has the following composition, with number of each type given in parentheses: $vs(6)$, $vp(3)$, $vd(4)$, $vf(3)$, $vg(2)$ and $vh(1)$. As usual, most virtuals have $n=\ell+1$; the remainder $n=\ell+2$. It was found necessary to introduce large Z^*vf ($Z^*=18.6$) and vg ($Z^*=22.3$) for the $4d$ excitations.

Absolute errors in energy differences average 306 cm^{-1}. Of particular interest is that the current theory reverses the experimental labeling of the second and third

TABLE II. Energy contributions (-eV) to Cs II $5p^5(5d+6s)$ $J=1$.[a]

Basis member	Levels $5d_3$	$5d_2$	$6s_2$	$6s_1$	$5d_1$
$4d^{10}5s^25p^5vs$	0.017	0.002	0.016	0.028	0.008
$4d^{10}5s^25p^5vd$	1.437	0.150	0.010	0.010	0.008
$4d^{10}5s^25p^4vp5d$	0.099	0.051	0.274	0.284	0.013
$4d^{10}5s^25p^4vf5d$	0.466	0.601	0.048	0.067	0.440
$4d^{10}5s^25p^4vh5d$	0.021	0.012	0.000	0.000	0.002
$4d^{10}5s^25p^4vp6s$	0.009	0.010	0.069	0.070	0.002
$4d^{10}5s^25p^4vf6s$	0.026	0.017	0.199	0.191	-0.002
$4d^{10}5s^25p^4vpvs$	0.007	0.009	0.046	0.043	0.006
$4d^{10}5s^25p^4vpvd$	0.064	0.105	0.095	0.093	0.096
$4d^{10}5s^25p^4vfvs$	0.019	0.010	0.000	0.000	0.002
$4d^{10}5s^25p^4vfvd$	0.152	0.164	0.023	0.024	0.139
$4d^{10}5s^25p^4vfvg$	0.092	0.084	0.011	0.013	0.064
$4d^{10}5s^25p^4vhvg$	0.022	0.021	0.004	0.005	0.014
$4d^{10}5s^25p^35d^3$	0.791	0.453	0.000	0.000	0.430
$4d^{10}5s^25p^35d^26s$	0.005	0.003	0.559	0.539	0.009
$4d^{10}5s^25p^35d^2vs$	0.011	0.010	0.000	0.000	0.014
$4d^{10}5s^25p^35d^2vd$	0.718	0.575	0.000	0.000	0.562
$4d^{10}5s^25p^35d^2vg$	0.069	0.061	0.000	0.000	0.063
$4d^{10}5s^25p^35d6svs$	0.004	0.005	0.012	0.010	0.005
$4d^{10}5s^25p^35d6svd$	0.006	0.007	0.646	0.645	0.006
$4d^{10}5s^25p^35d6svg$	0.000	0.000	0.072	0.071	0.000
$4d^{10}5svd5p^55d$	0.223	0.221	0.016	0.017	0.217
$4d^{10}5svg5p^55d$	0.018	0.022	0.000	0.000	0.023
$4d^{10}5svd5p^56s$	0.008	0.009	0.232	0.218	0.005
$4d^{10}5s5p^55d^2$	0.233	0.305	0.006	0.005	0.270
$4d^{10}5s5p^55d6s$	0.008	0.008	0.274	0.253	0.006
$4d^{10}5s5p^4vp5d^2$	0.053	0.047	0.000	0.000	0.047
$4d^{10}5s5p^4vf5d^2$	0.197	0.185	0.000	0.000	0.190
$4d^{10}5s5p^4vp5d6s$	0.043	0.043	0.049	0.049	0.043
$4d^{10}5s5p^4vf5d6s$	0.000	0.000	0.213	0.212	0.000
$4d^{10}5s5p^4vp6s^2$	0.000	0.000	0.020	0.019	0.000
$4d^{10}5s5p^5vsvd$	0.009	0.013	0.000	0.000	0.013
$4d^{10}5s5p^5vdvg$	0.013	0.017	0.000	0.000	0.018
$4d^{10}5s5p^5vpvf$	0.007	0.010	0.000	0.000	0.011
$4d^9vd5s^25p^55d$	0.024	0.020	0.000	0.000	0.017
$4d^9vd5s^25p^56s$	0.000	0.000	0.017	0.012	0.000
$4d^9vg5s^25p^55d$	0.011	0.019	0.000	0.000	0.011
$4d^9vg5s^25p^56s$	0.000	0.000	0.014	0.013	0.000
$4d^95s^25p^4vf5d^2$	0.217	0.166	0.000	0.000	0.162
$4d^95s^25p^4vf5d6s$	0.003	0.004	0.179	0.181	0.003
$4d^95s^25p^6vf$	0.052	0.008	0.000	0.001	0.006
$4d^95s^25p^55d^2$	0.012	0.011	0.000	0.000	0.008
$4d^95s^25p^55d6s$	0.001	0.001	0.015	0.011	0.000
Total	5.206	3.474	3.129	2.981	3.138

[a] Only contributions that exceed 0.01 eV for at least one level are shown. Configurations present in the RCI Ψ but not shown in the table are $4d^{10}5s^25p^4vpvg$, $4d^{10}5s^25p^4vhvd$, $4d^{10}5s^25p^35d6s^2$, $4d^{10}5s^25p^36s^2vs$, $4d^{10}5s^25p^36s^2vd$, $4d^{10}5svs5p^55d$, $4d^{10}5svs5p^56s$, $4d^{10}5s5p^56s^2$, $4d^{10}5s5p^5vs^2$, $4d^{10}5s5p^5vp^2$, $4d^{10}5s5p^5vd^2$, $4d^{10}5s5p^5vd^2$, $4d^{10}5s5p^5vf^2$, $4d^{10}5s5p^5vg^2$, $4d^{10}5s5p^5vfvh$, $4d^95s^25p^4vf6s^2$, and $4d^95s^25p^56s^2$.

$J=1$ states, and that the A's for these states are very sensitive to their positioning relative to one another (see the discussion below on shifts).

The energy analysis (Tables V and VI) shows us that the most important contributions to energy differences arise from the following excitations: $5p\rightarrow vf$, $5p^2\rightarrow 5d^2$, $5d\rightarrow vd$ (top root, $J=1$), then $5p\rightarrow vp$, $5p5d\rightarrow vdvf$, $5s\rightarrow 5d$, $5s5d\rightarrow 5p(vp+vf)$ (top root, $J=1$), $5p^2\rightarrow 5dvd$ (top root, $J=1$). Contributions to the top root, $J=1$, differ because its $5d$ radial differs substantially from

TABLE III. Energy contributions (-eV) to Cs II $5p^5(5d+6s)$ $J=2$.[a]

Basis member	Levels $5d_4$	$5d_3$	$5d_2$	$5d_1$	$6s_1$
$4d^{10}5s^25p^5vd$	0.033	0.024	0.018	0.046	−0.002
$4d^{10}5s^25p^5vg$	0.001	0.027	0.023	0.000	0.000
$4d^{10}5s^25p^4vp5d$	0.050	0.062	0.070	0.054	0.219
$4d^{10}5s^25p^4vf5d$	0.584	0.548	0.535	0.493	0.013
$4d^{10}5s^25p^4vp6s$	0.009	0.004	0.004	0.011	0.013
$4d^{10}5s^25p^4vf6s$	0.010	0.016	0.015	0.007	0.182
$4d^{10}5s^25p^4vpvs$	0.009	0.005	0.005	0.008	0.050
$4d^{10}5s^25p^4vpvd$	0.104	0.109	0.107	0.099	0.108
$4d^{10}5s^25p^4vfvs$	0.011	0.016	0.016	0.004	0.000
$4d^{10}5s^25p^4vfvd$	0.168	0.145	0.149	0.155	0.025
$4d^{10}5s^25p^4vfvg$	0.078	0.062	0.064	0.071	0.010
$4d^{10}5s^25p^35d^3$	0.346	0.376	0.356	0.343	0.000
$4d^{10}5s^25p^35d^26s$	0.006	0.006	0.005	0.004	0.451
$4d^{10}5s^25p^35d^2vs$	0.019	0.017	0.016	0.022	0.000
$4d^{10}5s^25p^35d^2vd$	0.537	0.552	0.548	0.535	0.000
$4d^{10}5s^25p^35d^2vg$	0.056	0.060	0.058	0.056	0.000
$4d^{10}5s^25p^35d6svs$	0.005	0.005	0.005	0.004	0.020
$4d^{10}5s^25p^35d6svd$	0.005	0.005	0.005	0.006	0.624
$4d^{10}5s^25p^35d6svg$	0.000	0.000	0.000	0.000	0.065
$4d^{10}5svd5p^55d$	0.264	0.267	0.245	0.246	0.011
$4d^{10}5svg5p^55d$	0.020	0.018	0.018	0.022	0.000
$4d^{10}5svd5p^56s$	0.010	0.010	0.010	0.017	0.218
$4d^{10}5s5p^55d^2$	0.275	0.205	0.205	0.239	0.010
$4d^{10}5s5p^55d6s$	0.022	0.022	0.024	0.031	0.210
$4d^{10}5s5p^4vp5d^2$	0.034	0.034	0.034	0.033	0.000
$4d^{10}5s5p^4vf5d^2$	0.175	0.186	0.184	0.178	0.000
$4d^{10}5s5p^4vp5d6s$	0.041	0.041	0.041	0.041	0.039
$4d^{10}5s5p^4vf5d6s$	0.000	0.000	0.000	0.000	0.202
$4d^{10}5s5p^4vp6s^2$	0.000	0.000	0.000	0.000	0.021
$4d^{10}5s5p^6vp$	0.001	0.000	0.000	-0.004	0.045
$4d^{10}5s5p^6vf$	0.002	0.063	0.051	0.000	0.000
$4d^{10}5s5p^5vsvd$	0.014	0.014	0.014	0.014	0.000
$4d^{10}5s5p^5vdvg$	0.017	0.016	0.017	0.018	0.000
$4d^{10}5s5p^5vpvf$	0.010	0.010	0.010	0.010	0.000
$4d^9vd5s^25p^55d$	0.026	0.026	0.022	0.020	0.000
$4d^9vd5s^25p^56s$	0.000	0.000	0.000	0.000	0.016
$4d^9vg5s^25p^55d$	0.024	0.023	0.022	0.017	0.000
$4d^9vg5s^25p^56s$	0.000	0.000	0.000	0.001	0.017
$4d^95s^25p^4vf5d^2$	0.527	0.528	0.530	0.529	0.000
$4d^95s^25p^4vf5d6s$	0.023	0.023	0.025	0.026	0.595
$4d^95s^25p^4vf6s^2$	0.000	0.000	0.000	0.000	0.011
$4d^95s^25p^55d^2$	0.012	0.012	0.010	0.008	0.000
$4d^95s^25p^55d6s$	0.001	0.001	0.001	0.000	0.010
Total	3.553	3.563	3.490	3.220	3.393

[a]Only contributions that exceed 0.01 eV for at least one level are shown. Configurations present in the RCI Ψ but not shown in the table are $4d^{10}5s^25p^5vs$, $4d^{10}5s^25p^4vpvg$, $4d^{10}5s^25p^35d6s^2$, $4d^{10}5s^25p^36s^2vs$, $4d^{10}5s^25p^36s^2vd$, $4d^{10}5svs5p^55d$, $4d^{10}5svs5p^56s$, $4d^{10}5svg5p^56s$, $4d^{10}5s5p^56s^2$, $4d^{10}5s5p^5vs^2$, $4d^{10}5s5p^5vp^2$, $4d^{10}5s5p^5vd^2$, $4d^{10}5s5p^5vf^2$, $4d^{10}5s5p^5vg^2$, $4d^95s^25p^6vf$, and $4d^95s^25p^56s^2$.

the other $5d$ levels, as determined by separate MCDF calculations (and confirmed by the importance of $5d \rightarrow vd$), so that exclusion effects are the smallest of the $5d$ levels. This seems to have little impact on the relative effect of triple and quadruple excitations, however (see below). Important contributions to energy differences from opening the $4d$ subshells come from $4d5p \rightarrow 5dvf$. Additionally, the excitation $4d5d \rightarrow 5pvf$ is crucial for the top root for $J=1$. Selected triple and quadruple excitations were chosen for exploration by forming them from products of the most important single

TABLE IV. ^{137}Ba III energy levels and hyperfine structure.[a]

Label[b]	J	Relative energies[b] (cm^{-1})		A (MHz)		B (MHz)/Q(b)	
		Expt.[c]	RCI[d]	DF[e]	RCI[e]	DF[e]	RCI[e]
$5d_3(\frac{1}{2})[\frac{3}{2}]$	1	45459	46098	-1253	-1175	-181	-205
$6s_2(\frac{1}{2})[\frac{1}{2}]$	1	35624	35438	5938	6186	-402	-404
$6s_1(\frac{3}{2})[\frac{3}{2}]$	1[f]	19926	20270	-497	-285	743	85.2
			20339[g]		-248[h]		-46.0[h]
$5d_2(\frac{3}{2})[\frac{3}{2}]$	1[f]	18487	18773	222	-7.4	-1233	-516
			18900[g]		-44.2[h]		-384[h]
$5d_1(\frac{3}{2})[\frac{1}{2}]$	1	0	0	82.5	109	467	450
$5d_4(\frac{1}{2})[\frac{3}{2}]$	2	21526	21723	-872	-906	1329	1274
$5d_3(\frac{1}{2})[\frac{5}{2}]$	2	18753	18732	1835	1803	1759	1748
$6s_1(\frac{3}{2})[\frac{5}{2}]$	2	14152	13877	1999	2068	-3320	-3033
$5d_2(\frac{3}{2})[\frac{5}{2}]$	2	4947	5175	736	729	-1015	-972
$5d_1(\frac{3}{2})[\frac{3}{2}]$	2	0	0	-4.5	26.9	781	634
					36.1[h]		

[a] $\mu=0.9357$, $I=3/2$, $Q=0.2456$ from Refs. [14,15]. To a good approximation $A(^{135}\text{Ba})=0.8939\,A(^{137}\text{Ba})$ and B/Q for both isotopes are the same (see text).

[b] Relative to the lowest energy of same J. In cm^{-1}.

[c] Reference [17].

[d] Unshifted RCI result.

[e] DF = Dirac Fock result as obtained from RCI coefficients. RCI is recommended value unless otherwise noted.

[f] RCI labels are flipped (see text) compared to experiment.

[g] Shifted result (see text).

[h] Shifted result (see text). Recommended.

and pair excitations. We investigated $5p^3 \rightarrow 5d^2vf$, $5s5p^2 \rightarrow 5d^3$, and $5p^4 \rightarrow 5d^4 + 5d^3vd$. None of these was important enough to keep in the final wave function. Additionally, we also tried including the following pair excitations: $5s^2 \rightarrow 5pvp + 5d^2 + 6s^2 + 6svs + 5dvd$; $5p^2 \rightarrow vd^2 + vf^2$; $5s(5d+6s) \rightarrow vp^2 + vd^2 + vsvd + vpvf$; $5s5p \rightarrow vdvf$; $4d5s \rightarrow 5p(vp+vf) + 5dvd + 5d6s$; $4d^2 \rightarrow 5d^2 + 5dvd + 5p(vp+vf)$; $4p(5d+6s) \rightarrow 5p(vs+vd)$; $4p^2 \rightarrow 5d^2 + 5d6s$; $4p \rightarrow 5p$; $4d5d \rightarrow vf^2 + vpvf$. All choices were made either because the absolute energy contributions were thought large, or because exclusion effects might be important. None of these had a large enough impact on energy differences to retain in the final wave function.

For the fully *ab initio* results, the $J=1$ $5d_1$ and $6s_1$ levels are separated by 1502 cm^{-1}, while the experimental energy difference is 1439 cm^{-1} [17]. The *ab initio* levels are only about 63% pure, with most of the remaining contribution coming from the other configuration ($5p^55d$ or $5p^56s$). The close spacing of these two levels results in the correlated values of A and B being very different from the Dirac-Fock results (which are obtained throughout this work from coefficients generated during the RCI process). This great change means we should inquire as to what further modification would occur if the *ab initio* energy difference had been 1439 cm^{-1}. We estimate this effect by manually shifting the $5p^56s$ diagonal matrix elements upwards by 237 cm^{-1}, which is roughly four times our error. A difference of this sort should not be unexpected as the process of diagonalizing two nearly degenerate vectors is not a linear one. The change in the HFS constants (*ab initio* to shifted; see Table III) is dramatic in the case of B for the upper of the two levels, where a sign change is observed. The purity of the two levels is also decreased to 57%, demonstrating the increased interaction.

It is easy to understand the source of the large changes observed; it is because the DF values for the two levels are both large, and of opposite sign. The more difficult questions are which of the two values (*ab initio* or shifted) is more reliable, and how reliable is it? We believe the shifted value is the more reliable one, based on our observation that when shifting two different *ab initio* results (an earlier calculation with an energy difference of 1590 cm^{-1}), the two shifted results are nearly identical. This still leaves open questions like: are there important core polarization effects which are missing? The largest included effect, for B, are the $5p \rightarrow vp$ excitations. We added and iterated a third vp ($Z^* \sim 12.0$) with little effect. We then included $4s \rightarrow s$ ($J=1{,}2$) and $4s \rightarrow d$, $4p \rightarrow p$ ($J=1$). The $4s \rightarrow s$ was the largest of these, lowering the $5d_2$ A 171 MHz and changing the sign of the small $6s_1$ A ($-41 \rightarrow 45$ MHz) in $J=2$. For $J=1$, the only significant effect was to double the small $5d_1$ A. The effect of $4s \rightarrow d$ was small for $J=1$; consequently it was not tried for $J=1$. For $J=1$, the significant effect of $4p \rightarrow p$ was to reduce the A for $6s_1$ by a factor of 1.7 and reduce the B for $5d_2$ by a factor of 1.3.

In La II [2] we found that shifting Rydberg series basis functions, here represented by $5p^5vs$ and $5p^5vd$, could have an important effect on lowering the top root of the manifolds of interest. With no shift, our sixth and seventh roots for $J=1$ are located at 100 842 and 101 184 cm^{-1}, whereas the experimental values [17] are at 82 852 and 84 269 cm^{-1} for $5p^56d$ and $5p^57s$, respectively. To adjust these roots to their experimental positions, we shift the diagonal matrix elements for $5p^5vd$ and $5p^5vs$ 17 886 and 16 789 cm^{-1} re-

TABLE V. Energy contributions (-eV) to Ba III $5p^5(5d+6s)$ $J=1$.[a]

Basis member	Levels $5d_3$	$6s_2$	$6s_1$	$5d_2$	$5d_1$
$4d^{10}5s^25p^5vd$	1.215	0.011	0.104	0.000	0.002
$4d^{10}5s^25p^4vp5d$	0.046	0.341	0.102	0.354	0.101
$4d^{10}5s^25p^4vf5d$	0.655	0.049	0.786	0.044	0.571
$4d^{10}5s^25p^4vh5d$	0.035	0.000	0.017	0.000	0.003
$4d^{10}5s^25p^4vp6s$	0.008	0.027	0.009	0.029	0.005
$4d^{10}5s^25p^4vf6s$	0.021	0.220	0.005	0.206	0.001
$4d^{10}5s^25p^4vpvs$	0.007	0.054	0.007	0.052	0.006
$4d^{10}5s^25p^4vpvd$	0.070	0.067	0.093	0.070	0.085
$4d^{10}5s^25p^4vfvd$	0.140	0.039	0.132	0.044	0.114
$4d^{10}5s^25p^4vfvg$	0.121	0.011	0.100	0.011	0.075
$4d^{10}5s^25p^4vhvg$	0.028	0.001	0.023	0.001	0.016
$4d^{10}5s^25p^35d^3$	1.115	0.000	0.602	0.000	0.592
$4d^{10}5s^25p^35d^26s$	0.005	0.770	0.006	0.745	0.005
$4d^{10}5s^25p^35d^2vs$	0.010	0.000	0.009	0.000	0.012
$4d^{10}5s^25p^35d^2vd$	0.582	0.000	0.464	0.000	0.457
$4d^{10}5s^25p^35d^2vg$	0.089	0.000	0.078	0.000	0.080
$4d^{10}5s^25p^35d6svs$	0.004	0.010	0.004	0.009	0.004
$4d^{10}5s^25p^35d6svd$	0.006	0.532	0.006	0.532	0.006
$4d^{10}5s^25p^35d6svg$	0.000	0.092	0.000	0.091	0.000
$4d^{10}5svs5p55d$	0.008	0.000	0.013	0.000	0.014
$4d^{10}5svd5p55d$	0.163	0.021	0.168	0.019	0.164
$4d^{10}5svg5p55d$	0.029	0.000	0.035	0.000	0.035
$4d^{10}5svd5p56s$	0.009	0.168	0.016	0.152	0.010
$4d^{10}5s5p^55d^2$	0.253	0.008	0.375	0.011	0.334
$4d^{10}5s5p^55d6s$	0.014	0.329	0.020	0.298	0.015
$4d^{10}5s5p^5vsvd$	0.012	0.000	0.017	0.000	0.019
$4d^{10}5s5p^5vdvg$	0.012	0.000	0.014	0.000	0.015
$4d^{10}5s5p^4vp5d^2$	0.046	0.000	0.041	0.000	0.044
$4d^{10}5s5p^4vf5d^2$	0.280	0.000	0.262	0.000	0.270
$4d^{10}5s5p^4vp5d6s$	0.042	0.049	0.043	0.048	0.042
$4d^{10}5s5p^4vf5d6s$	0.000	0.304	0.000	0.304	0.000
$4d^{10}5s5p^4vp6s^2$	0.000	0.020	0.000	0.019	0.000
$4d^{10}5s5p^6vp$	0.103	0.040	0.008	0.027	0.009
$4d^9vd5s^25p^55d$	0.027	0.000	0.027	0.000	0.022
$4d^9vd5s^25p^56s$	0.000	0.014	0.000	0.010	0.000
$4d^9vg5s^25p^55d$	0.026	0.000	0.053	0.000	0.027
$4d^9vg5s^25p^56s$	0.000	0.034	0.000	0.033	0.000
$4d^95s^25p^4vf5d^2$	1.214	0.000	0.913	0.000	0.893
$4d^95s^25p^4vf5d6s$	0.027	1.002	0.026	1.018	0.031
$4d^95s^25p^4vf6s^2$	0.000	0.016	0.000	0.018	0.000
$4d^95s^25p^6vf$	0.408	0.010	0.015	0.018	0.010
$4d^95s^25p^55d^2$	0.018	0.000	0.016	0.000	0.011
$4d^95s^25p^55d6s$	0.001	0.019	0.001	0.014	0.000
Total	6.900	4.262	4.570	4.231	4.156

[a] Only contributions that exceed 0.01 eV for at least one level are shown. Configurations present in the RCI Ψ but not shown in the table are $4d^{10}5s^25p^5vs$, $4d^{10}5s^25p^4vpvg$, $4d^{10}5s^25p^4vfvs$, $4d^{10}5s^25p^4vhvd$, $4d^{10}5s^25p^35d6s^2$, $4d^{10}5s^25p^36s^2vs$, $4d^{10}5s^25p^36s^2vd$, $4d^{10}5svs5p56s$, $4d^{10}5svg5p56s$, $4d^{10}5s5p^56s^2$, $4d^{10}5s5p^5vd^2$, $4d^{10}5s5p^5vpvf$, and $4d^95s^25p^56s^2$; as well as the energetically small $4s\rightarrow s+d$ and $4p\rightarrow p$ excitations, which are important for HFS constants (see text).

spectively. This shift is supposed to, crudely, reflect the idea that by correlating the $5p^5(5d+6s)$ manifolds ($>32\,000$ cm^{-1}), we have, mostly, not done the equivalent for the $6d$ and $7s$ states. There are also corrections necessary, of course, due to the errors the radial virtual sets make in representing the $7s$ and $6d$ DF radial functions. The net effect on the topmost $J=1$ root is move it from being 641 cm^{-1} above the experimental result, to being 794 cm^{-1} below the experimental result. At the same time, however, the values for A and B show little change. On the other hand, when the

TABLE VI. Energy contributions (-eV) to Ba III $5p^5(5d+6s)$ $J=2$.[a]

Basis member	Levels $5d_4$	$5d_3$	$6s_1$	$5d_2$	$5d_1$
$4d^{10}5s^25p^5vd$	0.023	0.007	0.014	0.009	0.005
$4d^{10}5s^25p^5vg$	0.001	0.033	0.000	0.029	0.000
$4d^{10}5s^25p^4vp5d$	0.078	0.088	0.318	0.101	0.076
$4d^{10}5s^25p^4vf5d$	0.777	0.720	0.045	0.701	0.602
$4d^{10}5s^25p^4vh5d$	0.016	0.022	0.000	0.021	0.005
$4d^{10}5s^25p^4vp6s$	0.008	0.003	0.013	0.003	0.005
$4d^{10}5s^25p^4vf6s$	0.009	0.013	0.196	0.013	0.001
$4d^{10}5s^25p^4vpvs$	0.003	0.002	0.029	0.002	0.003
$4d^{10}5s^25p^4vpvd$	0.093	0.095	0.070	0.094	0.084
$4d^{10}5s^25p^4vfvd$	0.124	0.106	0.033	0.110	0.113
$4d^{10}5s^25p^4vfvg$	0.092	0.073	0.010	0.075	0.079
$4d^{10}5s^25p^35d^3$	0.569	0.614	0.000	0.587	0.568
$4d^{10}5s^25p^35d^26s$	0.004	0.004	0.737	0.004	0.006
$4d^{10}5s^25p^35d^2vs$	0.012	0.011	0.000	0.011	0.014
$4d^{10}5s^25p^35d^2vd$	0.447	0.457	0.000	0.460	0.452
$4d^{10}5s^25p^35d^2vg$	0.075	0.081	0.000	0.080	0.077
$4d^{10}5s^25p^35d6svs$	0.002	0.002	0.012	0.002	0.002
$4d^{10}5s^25p^35d6svd$	0.006	0.006	0.527	0.006	0.006
$4d^{10}5s^25p^35d6svg$	0.000	0.000	0.088	0.000	0.000
$4d^{10}5svs5p^55d$	0.014	0.013	0.000	0.014	0.016
$4d^{10}5svd5p^55d$	0.182	0.187	0.021	0.171	0.164
$4d^{10}5svg5p^55d$	0.036	0.032	0.000	0.032	0.037
$4d^{10}5svd5p^56s$	0.012	0.012	0.153	0.011	0.010
$4d^{10}5s5p^55d^2$	0.389	0.299	0.007	0.293	0.339
$4d^{10}5s5p^55d6s$	0.015	0.015	0.298	0.016	0.015
$4d^{10}5s5p^4vp5d^2$	0.043	0.045	0.000	0.044	0.044
$4d^{10}5s5p^4vf5d^2$	0.260	0.276	0.000	0.273	0.264
$4d^{10}5s5p^4vp5d6s$	0.045	0.045	0.049	0.045	0.045
$4d^{10}5s5p^4vf5d6s$	0.000	0.000	0.297	0.000	0.000
$4d^{10}5s5p^4vp6s^2$	0.000	0.000	0.024	0.000	0.000
$4d^{10}5s5p^6vp$	0.000	0.000	0.050	0.000	0.006
$4d^{10}5s5p^6vf$	0.003	0.086	0.000	0.072	0.000
$4d^9vd5s^25p^55d$	0.023	0.023	0.000	0.020	0.018
$4d^9vg5s^25p^55d$	0.050	0.047	0.000	0.046	0.031
$4d^9vg5s^25p^56s$	0.000	0.000	0.033	0.000	0.000
$4d^95s^25p^4vf5d^2$	0.880	0.881	0.000	0.883	0.880
$4d^95s^25p^4vf5d6s$	0.031	0.031	0.992	0.033	0.032
$4d^95s^25p^4vf6s^2$	0.000	0.000	0.014	0.000	0.000
$4d^95s^25p^55d^2$	0.016	0.017	0.000	0.014	0.012
$4d^95s^25p^55d6s$	0.001	0.001	0.014	0.001	0.001
Total	4.334	4.360	4.029	4.291	4.089

[a] Only contributions that exceed 0.01 eV for at least one level are shown. Configurations present in the RCI Ψ but not shown in the table are $4d^{10}5s^25p^5vs$, $4d^{10}5s^25p^4vfvs$, $4d^{10}5s^25p^35d6s^2$, $4d^{10}5s^25p^36s^2vs$, $4d^{10}5s^25p^36s^2vd$, $4d^{10}5svs5p^56s$, $4d^{10}5svg5p^56s$, $4d^{10}5s5p^56s^2$, $4d^9vd5s^25p^56s$, $4d^95s^25p^6vf$, and $4d^95s^25p^56s^2$; as well as the energetically small $4s\rightarrow s+d$ and $4p\rightarrow p$ excitations, which are important for HFS constants (see text).

same process is applied to the $J=2$ matrix, the topmost root moves down only 75 cm^{-1}. This is because this root is $\sim$25 000 cm^{-1} further away from its Rydberg series members ($7s$,$6d$) for $J=2$, than for $J=1$.

Because of the small size of $A(5d_1)$ for $J=2$, we also tried to improve the RCI value. First, we observed that the result was quite sensitive to the $5d_1$-$5d_2$ energy difference, but seemed to change in a linear way. Rather than shift matrix elements, which is inconvenient within a manifold, we did a linear extrapolation to the experimental energy difference, yielding a result of 36.1 MHz which we report as a recommended value in Table IV. This also includes an upward shift of the $5p^56s$ manifold, to produce the correct $5d_1$-$6s_1$ energy difference.

V. CONCLUDING REMARKS

All but three RCI A's for Cs II agree with experiment to 12% or better; 50% of the HFS constants exhibit substantial many body effects. These three are very sensitive to the positions of nearby levels and errors in these HFS constants can be reduced to those of the others by adjusting energy differences to experimental values. For Cs II, the few experimental [13] values of B/Q disagree with our RCI values in magnitude and sometimes sign. We believe the problem lies mainly with the experimental results, as they have uncertainities as large as their values [13], and earlier semiempirical estimates [13] exhibit differences with experiment similar to ours. B's may be determined by multiplying the B/Q values by Q, in barns.

For Ba III, there are no experimental results with which to compare; about 30% of the HFS constants exhibit large many body effects. Error estimates for the unshifted Ba III A's may perhaps be made by analogy with Cs II—$\sim$20% for all but the most sensitive RCI values (see text) and perhaps errors up to 100% for the most sensitive.

There is a considerable similarity between the analogous energy contributions to Cs II (Tables II and III) and Ba III (Tables V and VI), after accounting for the change in the relative positions of the $6s$ and $5d$ levels. We make use of this to check for lack of basis set saturation—virtuals are added to the smaller of the two contributions to see if the difference is real.

We may wonder whether large many body effects will be present in La IV $5p^5(5d+6s)$ $J=1$,2 levels. Examination of the energy levels [18] shows that the two top $J=1$ states, which we label $5d_3$ and $6s_2$, are separated by only 4588 cm^{-1}. We also note that the $5d_3$ and $5d_4$ $J=2$ levels are separated by only 3507 cm^{-1}. If the HFS constants of these two pure ''paired'' levels differ substantially, we would predict many body effects would be large.

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