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Multireference relativistic configuration-interaction calculations for $(d+s)^n$ transition-metal atomic states: Application to Zr II hyperfine structure

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Our relativistic configuration-interaction (RCI) methodology has been extended to multireference cases, and improved to permit the construction of angular-momentum functions of arbitrary size, and to minimize the number of vectors needed with each configuration. We report RCI calculations on the fine (fs) and hyperfine (hfs) structure for the $(d+s)^3$ $J=0.5$ and 1.5 levels of Zr II. The average fs error is 0.075 eV, and 17% for hfs, when compared to available experiment. These results indicate that it is possible to correctly position all levels of $(d+s)^n$ configurations in the transition-metal atoms.

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I. INTRODUCTION

Transition-metal atoms are technologically important due to their role in catalysis, as deep level traps in semiconductors, and as impurities in plasma fusion devices. Properties of the $(d+s)^n$ states of the transition-metal atoms are not very will understood theoretically—errors of 1 eV in the position of d^n energies are frequent in nonrelativistic many-body treatments [1,2], independent-particle hyperfine structure (hfs), relativistic and nonrelativistic, can have the wrong sign [2–4], and nonrelativistic many-body hfs can exhibit large errors [5].

Because differential relativistic effects on energy differences can be as large [6] as several tenths of an eV, and can be of the same order as the observed [7] differences, relativistic effects must be introduced into any comprehensive theoretical treatment from the start. Since it is well known that inclusion of many-body effects is also essential for accurate results, one needs to apply a general open shell relativistic many-body theory.

Due to the strong interactions among the various $(d+s)^n$ configurations, the methodology will have to be a multireference one. The presence of open d subshell electrons also means it must be capable of dealing with large numbers (several hundreds) of n-electron angular-momentum functions associated with a single "nonrelativistic manifold" of relativistic configurations. Depending on the theory chosen, it may also be necessary to handle the possible few thousands of determinants associated with some of these manifolds. Additionally, as we shall see, in representing many-body effects, one needs orbital symmetries at least through $l=4$, and has to include some shallow core-valence and shallow core-core many-body effects. These requirements are very substantial demands to place on any of the existing *ab initio* many-body approaches [8–13]. In our own case, we have had to make several improvements in our relativistic configuration-interaction (RCI) method [14–17], which we now report.

In order to carry out our calculations, we have made three substantial improvements in the RCI methodology. (1) A relativistic variant of the Bartlett-Condon-Beck procedure (BCB) [18] is introduced. This allows rapid formation of n-electron J^2 and J_z eigenfunctions for basis sets consisting of several thousand determinants, by splitting configurations into two or more parts during construction. (2) We generalize our relativistic REDUCE procedure [15] to apply to multireference function cases, and also specialize it to allow greater efficiencies when many-body effects are largely nonrelativistic, as they are for Zr II. By rotating the, up to several hundred, n-electron eigenvectors associated with a single nonrelativistic manifold, one can create a new manifold, such that only ≈10% of the new eigenvectors interact with the multireference zeroth-order function. (3) The large-order multiroot diagonalization algorithm of Weber, Lacroix, and Wanner [19] is introduced to deal with the RCI matrices which are typically of order ≈1000 and from which ten or more roots are desired. We also note an improvement of a factor of 5 in the efficiency of the original diagonalizer [20]. We discuss all these improvements in Sec. II.

To illustrate the method, we carry out extensive calculations (see Sec. III) on the fine (fs) and hyperfine structure (hfs) of 15 $(4d+5s)^3$ levels of Zr II having $J=0.5$ or 1.5. All calculated fs and hfs results are in excellent agreement with available experimental results [7,21,22]. Because this is the first time such accuracies (0.075 eV fs; 17% for hfs) have been simultaneously achieved for all $(d+s)^n$ fs and hfs, and much work is still to be done [1,2] on these species, we provide a detailed listing of the individual configurational contributions.

II. THEORY

To generate the fs wave functions, as a Hamiltonian we use the one-electron Dirac Hamiltonians and the two-electron electrostatic interaction [14]. Two-electron relativistic effects are treated using the Breit operator [14] and first-order perturbation theory. Formally, the wave function is split up into a perturbation theory hierarchy; within each order, the wave function is calculated using the energy variational principle. For reasons of efficiency, all n- and one-electron functions must be orthonormal. A zeroth-order function must be as accurate as possible (to reduce the importance of higher-order corrections), yet be capable of being generated with ease for a great variety of cases. The (multiconfigurational) Dirac-Fock approximation, as implemented by the computer program of Desclaux [23], is our choice to do this. Since we must deal with up to ten ($J=1.5$) levels simultaneously, we have a multireference (multiple zeroth-order functions) situation, i.e., no unique way of generating a multiconfiguration Dirac-Fock (MCDF) solution. Because our initial interest was in $(4d)^3\,{}^2P$ hfs, we chose to generate the $1s\ldots 4d_{3/2}, 4d_{5/2}$ spinors from a MCDF calculation for this level; the $5s$ spinor was obtained from a MCDF calculation on the nearby $4d^2 5s\,{}^4P$ level, followed by reorthogonalization to the $1s$-$4s$ spinors of $(4d)^3$. Now it is well known [24] that the $4d$ (and to a lesser extent $5s, 4p, 4s, \ldots$) spinors of $4d^3$, $4d^2 5s$, and $4d5s^2$ can differ substantially. Due to the requirements of orthonormality, this difference must be accounted for in higher perturbation theory orders. Principally, this is done in first order through the presence of symmetry preserving (e.g., $4d_j \rightarrow d_j$) single excitations from $4d^2 5s$ and $4d5s^2$ which we call "Brillouin excitations"; for the core (e.g., $4p_j \rightarrow p_j$), these are restricted to the single core coupling $J_c=0$. Such excitations vanish according to Brillouin's theorem [25], when a fully self-consistent set of MCDF spinors are used.

By definition, many-body effects first appear in a first-order wave function, which is formed from the zeroth-order function through single and double excitation into unoccupied spinors. Our nonrelativistic CI work [26] suggests these spinors should have their radial parts represented as simple analytic functions of a single parameter (Z^*), to be adjusted (iterated) during the CI process. To avoid variational collapse into the positron sea, we must properly "connect" the major and minor component radial spaces; we do this by using [15] relativistic screened (Z^*) hydrogenic functions. We have found restricting the principle quantum number, $n_p = l+1$ (l of the major component) to be most effective [27].

Formally, the second-order function can be generated by single and double excitations from the first-order function. This brings in configurations which are triple, quadruple, or higher excitations from all of the zeroth-order functions. In this work, we find only a few such excitations, from the valence ($4d$, $5s$) space, to be important.

In order to minimize the size of the CI matrix, we use n-electron functions which are eigenstates of J^2, J_z, and parity; each also has a common configurational "manifold," i.e., all relativistic configurations present in the function approach the same nonrelativistic function as $v \rightarrow c$. Formerly, we have been producing these functions, which can include restricting subgroups of electrons to specific values of J, by direct diagonalization (e.g., 26). However, the present problem and many future problems can require obtaining several hundred eigenvalues of a matrix of order several thousand—a time-consuming process. Instead, here we introduce a relativistic variant of the BCB method [18] to remove this bottleneck.

In the BCB method the configurational manifold is split into two (or more) parts. Because of the Pauli principle, all spinors "associated" with the same nonrelativistic subshell must be in the same part. For each part, eigenstates of J^2 and $J_z = +J$ are created by diagonalization methods [26]; if these are nonunique, a labeling subscript, n_1 (n_2) is used. Due to the split, these diagonalizations occur very efficiently; if not, a further split is used. Eigenvectors for other values of J_z are generated, for each part, by applying the step-down operator, J_-. This maintains the proper relative phase. The set of eigenvectors for the original manifold is constructed according to the formula

$$|n_1 n_2 J M_J\rangle = \sqrt{2J+1} \sum_{M_{J_1}, M_{J_2}} \begin{bmatrix} J_1 & J_2 & J \\ M_{J_1} & M_{J_2} & -M_J \end{bmatrix} \times |X_I(n_1 J_1 M_{J_1})\rangle \times |X_{II}(n_2 J_2 M_{J_2})\rangle \ . \tag{1}$$

This procedure is an order of magnitude more efficient than direct diagonalization for matrices of order 200; the efficiency gain for problems of order 2000 is even greater (construction times on a Sparc 10 workstation are no more than a few seconds). To illustrate, in one case, part 1 was $(4p_{3/2})^3 4d_{3/2} 4d_{5/2}$ and part 2 was $vd_{5/2} vf_{7/2}$, where v indicates a virtual function. The final assembled product has 430 determinants and 52 eigenvectors for $J=1.5$.

In the present application, as many as 300 eigenvectors can arise from a single manifold: if all these were kept throughout, the CI matrix would be of order 3000 for Zr II, and considerably larger for more complicated species (e.g., higher n). By creating and applying a multireference, specialized version of the first-order algorithm [15] REDUCE, the number of eigenvectors per manifold can be reduced as much as tenfold.

The energy matrix element between a reference function Φ and a relativistic configurational function X, in first order, may be written formally as

$$\langle \Phi | H | X(i) \rangle = \sum_{j=1}^{m} \alpha_j^i R^{k_j}(a_j b_j ; c_j d_j) \ , \tag{2}$$

where the R^k are radial integrals and the α's are constants determined by angular-momentum theory. The index i permits p eigenvectors for the relativistic configurations; in many cases, $p \approx 3m$. Thus we can create a new basis $X'(i) = \sum_{j=1}^{p} b_j^i X(j)$, such that the first $p-m$ X' have a zero matrix element with Φ. Consistent with a first-order approximation, these can be discarded, leaving m X'.

For the multireference function case, we carry this out for each of the Φ (up to ten, here). Since a given X may have a nonzero matrix element with more than one Φ, a set of nonorthogonal X' may result. This situation is resolved by simply reorthogonalizing the final set of X'. At this stage, the original set of X has been reduced to a

TABLE I. REDUCE applied to $4p^4 4d^5$ for $J=1.5$. The first number gives the number of eigenvectors associated with the $4p^4 4d^5$ configuration, and the second number gives the number of different radial integrals in the matrix element $\langle \Phi | H | X \rangle$. Both numbers depend on "origin," i.e., on Φ.

Correlation function X (occupancy)				Reference function Φ									
$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	$4d^3_{3/2}$		$4d^3_{5/2}$		$4d^2_{3/2}4d_{5/2}$		$4d_{3/2}4d^2_{5/2}(0)$[a]		$4d_{3/2}4d^2_{5/2}(2)$[a]	
2	2	4	1	1	2			1	2				
2	2	3	2	9	2^b			9	2^b	9	2^b	9	2^b
2	2	2	3			15	2^b	15	2^b	15	2^b	15	2^b
2	2	1	4			9	2			9	2	9	2
2	2	0	5			1	2						
1	3	4	1	2	2			2	1				
1	3	3	2	12	1			12	2	12	1	12	1
1	3	2	3			21	1	21	1	21	2	21	2
1	3	1	4			12	2			12	1	12	1
1	3	0	5			2	1						
0	4	3	2	2	1					2	1	2	1
0	4	2	3			3	1	3	1				
0	4	1	4							2	1	2	1
Relativistic total				26	8	62	11	63	11	82	12	82	12
Nonrelativistic total				7	2	8	2	9	2	10	2	10	2

[a] The number in parentheses indicates the J for $4d^2_{5/2}$.

[b] Due to linear dependence, only one eigenvector survives.

set about $\frac{1}{3}$ its size.

Table I illustrates an application of REDUCE for the $(4p)^4(4d)^5$ manifold with $J=1.5$. Since this configuration interacts only with the $(4d)^3$ reference functions, just the five of them are shown. The application of REDUCE has decreased the original 91 eigenvectors [equal to the total number of eigenvectors from each of the 14 $(4p)^4(4d)^5$ relativistic configurations, counted once only] to 44.

While the reduction is considerable, the CI matrices are still quite large (order ≈ 2000 for Zr II). A further gain can be made by realizing that Zr II is still substantially a nonrelativistic system, insofar as many-body effects are concerned. Practically, we make use of this by assuming that the radial integrals are independent of j. In the above case, this means that instead of 20 radial integrals, there are only two. When the REDUCE process is applied to each reference function separately, the 44 parents become only ten.

We have made two general tests of the validity of this assumption. First, we have examined the radial integrals directly to see how they do vary with j; variations of $\pm 5\%$ around an average value seem typical. For unoccupied spinors, two points need to be emphasized: (1) the Z^* for vl_j for $vl_{(j+1)}$ need to be "kept close" during the iterating process (2) vl_j and $vl_{(j+1)}$ must have a common overall phase convention. We accomplish this by requiring that the major components be positive at the origin. Both requirements arise because as $v \rightarrow c$, we need $vl_j \rightarrow vl_{(j+1)}$ in order to implement this form ("nonrela-

TABLE II. Testing REDUCE on $(d+s)^3+4p^4 4d^5$ for Zr II $J=\frac{3}{2}$. Energies (in a.u.); differences (in cm^{-1}): add -3596 a.u. to get total energy. 0.01 a.u. $=2195\ \text{cm}^{-1}=0.2721$ eV. A and B hfs constants differ in fourth significant figure.

Root No.	Full	REDUCE	Error	Nonrelativistic REDUCE	Error
1	−0.765 387 53	−0.765 377 57	2.0	−0.765 360 28	6.0
2	−0.786 971 89	−0.786 967 66	0.9	−0.786 963 24	2.0
3	−0.822 125 25	−0.822 119 50	1.0	−0.822 110 63	3.0
4	−0.837 932 95	−0.837 924 26	2.0	−0.837 915 44	4.0
5	−0.864 656 49	−0.864 656	0.1	−0.864 656 27	0.05
6	−0.883 503 6	−0.883 471 10	7.0	−0.883 458 93	10.0
7	−0.891 281 66	−0.891 271 78	2.0	−0.891 259 84	5.0
8	−0.898 164 4	−0.898 152 79	3.0	−0.898 141 67	5.0
9	−0.910 067 87	−0.910 067 59	0.06	−0.910 067 24	0.06
10	−0.923 003 42	−0.922 798 61	1.0	−0.922 987 65	1.0
Average			1.9		3.8

tivistic") of REDUCE. Second, in Table II we compare all three methods for a small CI calculation involving the ten $(4d+5s)^3$ reference functions and the $(4p)^4(4d)^5$ manifold. The differences between the methods are very small—only a few cm^{-1} at most. While differences for other manifolds are sometimes of an order of 100 cm^{-1}, this is still well below the average absolute error of our final results (see Sec. III).

With these improvements, our final CI matrices are order 1000 ($J=1.5$) and 850 ($J=0.5$). This is well above the order of 350 permitted by our RCI algorithm [28] which used a standard [29] multiroot diagonalizer. To carry out the Zr II calculations, we have introduced the large-order multiroot diagonalizer of Weber, Lacroix, and Wanner [19], and made the appropriate dimensionality changes in our program [20]. Improvements in efficiency and tests of the Weber-Lacroix-Wanner [10] diagonalizer are discussed elsewhere [20].

III. CALCULATIONS

To keep the size of the energy matrix modest, the set of unoccupied spinors must be optimized in a careful manner, i.e., in "layers." Valence ($4d$, $5s$) shell many-body effects are, as a class, one of the largest contributors to energy differences due to near degeneracies with valence MCDF spinors; valence virtual spinors are also sensitive to orthogonalization order. That is, if they are forced to be orthogonalized to core-virtual spinors, it is difficult to regain the portions of one-electron integrals "lost" to orthogonalization [30].

Consequently, we treat valence many-body effects first. As usual [16], good estimates can be obtained for the virtual Z^* by adjusting them to yield the same $\langle r \rangle$ as the MCDF spinors they are replacing ($4d$, $5s$ in the valence space). While formally the virtual orbital symmetries (major component) would be expected [31] to have $l \leq 6$, we find it is sufficient to have $l \leq 4$ here. Calculation begins by constructing all single and double valence excitations, from each of the reference functions, into the virtual spinors (one of each symmetry, to begin). The valence virtual Z^* are then iterated until the $4d^3\,{}^2P$ root of the energy matrix is minimized.

In the next layer, we explore whether the valence space is sufficiently saturated. First, we insert the most important core single excitations, i.e., $4p_j \rightarrow vp_{j'}, vf_{j''}$ using the just determined virtual spinors. This produces a more realistic energy matrix. It should be noted that both the "Brillouin" core coupling ($J_c=0$) and the hfs couplings ($J_c=1$ for magnetic dipole [17] and $J_c=2$ for the electric quadrupole) associated with the core single excitations are not part of the REDUCE process, as they contribute to both fs and hfs, so that portions of them may not be eliminated on the basis of fs alone. Triply excited valence configurations are also added now. A second set of valence virtual spinors is added, with $n_p=l_p+2$ (to avoid possible degeneracy effects) along with "cross" configurations such as those created by $4d^2 \rightarrow vp_j vp_{j'}$ which are missing in the first layer. The second set has its Z^* iterated; we find that the valence space is then saturated. In the next layer, we add the next important class of single excitations from the core, $4s \rightarrow 4d + vd$, $4s \rightarrow vs$ and add the second valence virtual set and a third set of "core" virtual spinors ($n_p=l+1$), to all core excited configurations, and determine those Z^* by energy minimization. This completes selection of the virtual spinors (adding an additional set of virtual spinors had little effect). We display the final results in Table III for $J=1.5$ (the $J=0.5$ virtual spinors are quite similar).

At this stage, errors in some of the energy differences were found to be an unacceptably large several tenths of an eV. It seemed that the missing configurations responsible for this error would be associated with shallow-core ($4p$ and $4s$) excitations, such as $4p4d \rightarrow$ and $4p5s \rightarrow$. Excitations into $vp_j vd_{j'}$ and $vd_j vf_{j'}$ were tried for both pairs but found to be an order of magnitude too small; excitations $4p^2 \rightarrow$ were next considered. Since these excitations have the same occupation numbers in *all* reference configurations, one expects them to be only *differentially* significant when they are excited into already partially occupied subshells, viz., $4d$ or $5s$. The candidates are $4p^2 + 4d^2 + 4dvd + 4dvs + 5s^2 + 5svs + 5svd$. Of these, the first is expected to be absolutely and differentially largest [it follows from the $l^2 \rightarrow (l+1)^2$ maximum rule [26] and has the largest exclusion effects]. Insertion of these in fact reduces the discrepancy in ΔE to an average error of 0.075 eV for energy differences. The $4p^2 \rightarrow 4dvd$ excitations were also examined but found to have a modest effect.

Perturbation theory can be used [26] to analyze the CI result—in particular to assign, to first order, a specific energy contribution to each basis function. Let $\Psi = \Phi + \sum_i c_i X_i$ where Ψ is the CI eigenvector, Φ is the zeroth-order function, and X_i are the many-body basis functions. With the normalization conditions $\langle \Phi | \Phi \rangle = \langle \Phi | \Psi \rangle = 1$, we have $E = \langle \Phi | H | \Psi \rangle = E_\Phi + \sum_i c_i \langle \Phi | H | X_i \rangle$. The quantity $c_i \langle \Phi | H | X_i \rangle$ can be identified as the (first-order) correlation energy associated with basis function X_i, and is displayed in Table IV for $J=1.5$.

Contributions are grouped by nonrelativistic manifolds, as both a matter of convenience, and because many-body effects are substantially nonrelativistic in this system (e.g., manifold contributions exhibit only a moderate J dependence). Contributions have been ob-

TABLE III. Parameters (n, Z^*) of the Zr II $J=\frac{3}{2}$ virtual basis. Prior to orthogonalization, the radial functions are relativistic screened (Z^*) hydrogenic functions with principle quantum number n.

$s_{1/2}$	(1,0.815), (2,1.79), (1,1.40)
$p_{1/2}$	(2,1.96), (3,3.55), (2,6.66)
$p_{3/2}$	(2,1.96), (3,3.55), (2,6.26)
$d_{3/2}$	(3,2.94), (4,4.45), (3,15.214)
$d_{5/2}$	(3,2.94), (4,4.84), (3,15.214)
$f_{5/2}$	(4,7.12), (5,9.78)
$f_{7/2}$	(4,7.12), (5,9.78)
$g_{7/2}$	(5,10.89)
$g_{9/2}$	(5,10.89)

tained using the largest of $4d^3$, $4d^25s$, or $4d5s^2$ manifold as the zeroth-order function, the others are listed in Table IV as the first entry. The "Brillouin excitations" ($4d \rightarrow vd, 4p \rightarrow vp$) are next largest, particularly for $4d^25s$ and $4d5s^2$ as might be expected, based on how the MCDF radial set was constructed. Following these closely are $4p \rightarrow vf$, $4d^2 \rightarrow vf^2$ and $4p^2 \rightarrow 4d^2$. All other manifolds individually differentially contribute ≤ 0.3 eV. Contributions from triple excitations (mainly $vdvp^2+vd^3$) are not shown, as they are a higher-order effect. The largest triple coefficients are 0.03–0.05. Eigenvectors have been carefully screened; only those contributing significantly to ΔE or hfs have been retained. The $J=\frac{3}{2}$ final CI matrix has ≈ 1000 eigenvectors while $J=\frac{1}{2}$ has ≈ 850.

Our fine-structure results are compared with experiment [7,21] for $J=\frac{3}{2}$ in Table V and for $J=\frac{1}{2}$ in Table VI. For $J=\frac{3}{2}$, we confirm Kiess's [21] corrections to Moore [7] that the level at 17 614.00 cm^{-1} is spurious,

TABLE IV. Energy contributions in eV for Zr II $J=1.5$. All signs are reversed.

Basis	Roots									
	$4d^3$	$4d^25s$ $+4d^3$	$4d^3$ $+4d5s^2$	$4d5s^2$ $+4d^3$	$4d^3$	$4d^25s$	$4d^3$ $+4d^25s$	$4d^25s$	$4d^3$	$4d^25s$
	^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
$4dvs^2$	0.010	0.000	0.003	0.013	0.000	0.000	0.000	0.000	0.000	0.000
$4dvp^2$	0.269	0.304	0.166	0.473	0.056	0.005	0.003	0.040	0.022	0.005
$4dvd^2$	0.339	0.011	0.228	0.002	0.192	0.002	0.216	−0.003	0.161	0.001
$4dvf^2$	0.571	0.054	0.395	0.010	0.351	0.000	0.338	−0.010	0.244	0.001
$4dvg^2$	0.069	0.008	0.044	0.000	0.021	0.000	0.021	−0.002	0.014	0.000
$4dvsvd$	0.000	0.061	0.006	0.000	0.000	0.047	0.000	0.044	0.000	0.048
$4dvpvf$	0.090	0.383	0.102	0.000	0.019	0.196	−0.031	0.214	0.041	0.192
$4d^2vs$	0.000	0.004	0.009	0.000	0.000	0.027	0.048	0.018	0.001	0.022
$4d^2vd$	0.024	0.063	0.066	0.036	0.091	0.016	0.075	0.006	0.084	0.004
$4d^2vg$	0.068	0.086	0.051	0.000	0.034	0.003	0.039	0.003	0.014	0.009
$5svp^2$	0.000	0.014	0.000	0.097	0.000	0.034	0.000	0.009	0.000	0.000
$5svd^2$	0.000	0.050	0.000	0.002	0.000	0.062	0.000	0.062	0.000	0.037
$5svf^2$	0.000	0.164	0.000	0.016	0.000	0.172	0.000	0.127	0.000	0.058
$5svg^2$	0.000	0.019	0.000	0.003	0.000	0.020	0.000	0.013	0.000	0.005
$5svsvd$	0.000	0.000	0.000	0.033	0.000	0.000	0.000	0.003	0.000	0.000
$5svpvf$	0.000	0.000	0.000	0.227	0.000	0.000	0.000	−0.006	0.000	0.014
$4d5svs$	0.004	0.000	−0.002	0.162	0.000	0.000	0.001	0.035	0.001	0.000
$4d5svd$	0.000	0.561	0.010	0.047	0.000	0.316	−0.017	0.364	0.000	0.295
$4d5svg$	0.012	0.000	−0.001	0.032	0.000	0.000	0.000	0.028	0.000	0.015
$5s^2vd$	0.000	0.000	0.000	0.434	0.000	0.000	0.000	−0.010	0.000	0.000
$4p^5vf4d^3$	0.911	0.034	1.003	0.000	1.109	0.021	1.010	0.021	1.166	0.020
$4p^5vf4d^25s$	0.022	0.853	0.020	0.054	0.020	0.852	0.023	0.805	0.019	0.899
$4p^5vf4d5s^2$	0.000	0.007	0.000	0.505	0.000	0.006	0.000	0.007	0.000	0.006
$4p^5vp4d^3$	0.012	0.040	0.016	0.000	0.030	0.042	0.021	0.056	0.035	0.084
$4p^5vp4d^25s$	0.000	0.067	0.002	0.092	0.004	0.067	0.004	0.081	0.005	0.079
$4p^5vp4d5s^2$	0.000	0.000	0.000	0.334	0.000	0.000	0.000	0.001	0.000	0.004
$4svd4d^3$	0.049	0.014	0.036	0.000	0.042	0.005	0.032	0.002	0.022	0.006
$4svd4d^25s$	0.025	0.056	0.034	0.015	0.026	0.041	0.001	0.020	0.026	0.018
$4svd4d5s^2$	0.000	0.009	0.000	0.020	0.000	0.006	0.000	0.000	0.000	0.005
$4p^44d^5$	0.746	0.000	0.630	0.000	0.576	0.000	0.621	0.000	0.505	0.000
$4p^44d^45s$	0.000	0.757	0.001	0.000	0.000	0.754	−0.002	0.749	0.000	0.680
$4p^44d^35s^2$	0.005	0.000	0.002	0.876	0.001	0.000	0.001	−0.001	0.001	0.000
$4p^54d^2vdvf$	0.062	0.011	0.070	0.000	0.070	0.012	0.074	0.012	0.075	0.012
$4p^54d5svdvf$	0.000	0.054	0.000	0.024	0.000	0.054	0.000	0.053	0.000	0.055
$4p^55s^2vdvf$	0.000	0.000	0.000	0.029	0.000	0.000	0.000	0.000	0.000	0.000
$4svs4d^3$	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.003	0.000
$4svs4d^25s$	0.000	0.017	0.000	0.000	0.000	0.015	0.000	0.015	0.000	0.012
$4svs4d5s^2$	0.000	0.000	0.000	0.056	0.000	0.000	0.000	0.000	0.000	0.000
$4s4d^35s$	0.001	0.062	0.004	0.004	0.005	0.061	0.004	0.045	0.006	0.016
$4s4d^25s^2$	0.000	0.000	0.000	0.017	0.000	0.008	0.000	0.010	0.000	0.007
$4s4d^4$	0.041	−0.005	0.063	0.000	0.057	0.002	0.042	0.003	0.016	0.002
$4p^5vpvd5s^2$	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 V. Fine and hyperfine structure of Zr II $J=\frac{3}{2}$ $(d+s)^3$ states.

Level		Energy (cm^{-1})			
Configuration[a]	*SLJ*	Experiment[b]	Theory	*A* (MHz)	*B* (MHz)/*Q*[(b)]
$4d^3$	^2D	27 699.96	29 097	−190.0	224.0
$4d^25s+4d^3$	^2P	20 080.30	20 671	110.3[c]	−137.4[c]
$4d^3+4d5s^2$	^2D	14 298.64	15 004	−114.7	−82.8
$4d5s^2+4d^3$	^2D	13 428.50	14 329	−66.8	165.1
$4d^3$	^4P	9 742.80	10 103	134.1[c]	−133.3[c]
$4d^25s$	^4P	7 736.02	8 115	−534.6	159.5
$4d^3+4d^25s$	^2P	6 111.70	6 765	134.3	−132.2
$4d^25s$	^2D	4 248.30	5 033	181.5[c]	−28.3[c]
$4d^3$	^4F	2 572.21	2 980	−298.0	−57.3
$4d^25s$	^4F	0.00	0.00	273.8	60.5

[a] See text.

[b] References [7,21].

[c] Experimental and MCDF hfs values available in Ref. [22].

and the location of the upper $4d^3\,^2D$. Our average absolute error is 0.087 eV (705 cm^{-1}). We do reverse [22] the configurational assignments of Moore for the ^2P's—the primary one has a weight of 53%, the secondary (Moore label) of 37%. The configuration labels of the lower $4d^3\,^2D$ and $4d5s^2\,^2D$ are also reversed, but because our accuracy is scarcely larger than the splitting [7], we cannot insist on the reversal. For $J=\frac{1}{2}$, the average absolute error is 0.050 eV and the configurational assignments except for the ^2P's (see above) agree [22] with Moore [7].

Hyperfine structure

Magnetic-dipole, *A*, and electric-quadrupole, *B*, hyperfine-structure constants were evaluated using the CI wave functions generated above. We use the formalism as expressed by Lindgren and Rosen [32]; for our purposes, we may write *A* as

$$A\,(\text{MHz})=-95.4129\frac{\mu_I}{\alpha IJ}\langle J,M_J=J|T_0^{(1)}|J,M_J=J\rangle\ , \tag{3}$$

where $T^{(1)}$ is a sum of one-electron electronic magnetic dipole operators $t^{(1)}$ and where

$$\langle n\kappa m_j|t_q^{(1)}|n'\kappa' m_j'\rangle=(-1)^{1/2+m_j}\sqrt{(2j+1)(2j'+1)}(\kappa+\kappa')\begin{pmatrix} j & j' & 1\\ -\frac{1}{2} & \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix} j & j' & 1\\ -m_j & m_{j'} & q\end{pmatrix}$$
$$\times\int_0^\infty dr\, r^{-2}[P_{n\kappa}Q_{n'\kappa'}+Q_{n\kappa}P_{n'\kappa'}]\ . \tag{4}$$

The magnetic-dipole moment μ and nuclear spin I are available in Fuller and Cohen [33]. For *B*, we have

$$B\,(\text{MHz})=234.9649\alpha\langle J,M_J=J|T_0^{(2)}|J,M_J=J\rangle Q(\text{barns})\ , \tag{5}$$

TABLE VI. Fine and hyperfine structure of Zr II $J=\frac{1}{2}$ $(d+s)^3$ states.

Level		Energy (cm^{-1})		
Configuration	*SLJ*	Experiment[a]	Theory	*A* (MHz)
$4d^25s$	^2S	19 477.89	20 198.99	−2690.31
$4d^25s+4d^3$	^2P	13 889.16	14 071.72	−150.84[b]
$4d^3$	^4P	3 828.72	3 648.02	337.55[b]
$4d^25s$	^4P	1 788.29	1 355.20	−655.01
$4d^3+4d^25s$	^2P	0.00	0.00	−1046.75

[a] References [7,21].

[b] Experimental and MCDF hfs values available in Ref. [22].

where

$$\langle n\kappa m_j | t_q^{(2)} | n'\kappa' m_j' \rangle = (-1)^{1/2-m_j-j-j'} \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & j' & 2 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} j & j' & 2 \\ -m_j & m_{j'} & q \end{pmatrix} \times \int_0^\infty dr\, r^{-3} [P_{n\kappa} P_{n'\kappa'} + Q_{n\kappa} Q_{n'\kappa'}] \ . \tag{6}$$

The radial integrals are in a.u., the ( ) are Wigner $3j$ symbols.

Tables V and VI contain our relativistic many-body results for A and B of ten $J=\frac{3}{2}$ and five $J=\frac{1}{2}$ levels. Five of these levels have just been measured [22], the calculated results differ, on the average, by only 17%. This is particularly striking when one notes that MCDF values frequently have the wrong sign. By comparing theory and experiment for the B's we have also deduced [22] a quadrupole moment Q for Zr II.

Of the seven new A's and B's of $J=\frac{3}{2}$ new in this work, one might expect all those except the two closely spaced ^2D levels to be accurate to $\approx 20\%$. The two ^2D A's might have twice this error. For $J=\frac{1}{2}$, based on how the A values varied as the basis was developed, we would expect the $^2S_{1/2}$ to be known to $<20\%$ and the $4d^25s\ ^2P$ to have an error perhaps twice as large, with the $4d^25s\ ^4P$ between these two.

Configurations important for hfs include many of those important for fs; in addition $4s, 5s \rightarrow s$ excitations are important. Due to current size restrictions no deep core polarizations were included for $J=\frac{3}{2}$; they were included for $J=\frac{1}{2}$ levels and for $4d^3\ ^2P_{1/2}$, they (mainly $ns \rightarrow vs$) contributed about 14% of the total A.

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