

Ab Initio Energy Levels, Oscillator Strengths, and Landé g Values for $J = 0, 1$ States of Zr III and Nb IV

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Abstract

Relativistic Configuration Interaction calculations are reported for Zr III and Nb IV $J = 0 \rightarrow J = 1$ transitions between $4d^2 + 5s^2$ and $4d(4f+5f+5p+6p+7p)+5s5p$ levels. Gauge agreements average 3%. Landé g -values are obtained, and the $5s^2$ level in Nb IV is repositioned.

1. Introduction

We have been interested in properties of transition metal (TM) atoms since the early 1990's [1] both because of their technological importance, for example as impurities in plasma fusion devices, and because of the theoretical challenge they pose, due to the necessity of simultaneously including both correlation and relativistic effects. Just treating correlation effects on their own is quite a challenge which arises from the complexities present with open d shell electrons (rare earths with their open f-shell electrons are even worse, of course). Each configuration can have very many basis functions (J^2 , J_z eigenstates) associated with it (up to several thousand) which are expressible as linear combinations of (perhaps) tens of thousands of Slater determinants.

The frequent near degeneracy of nd and $(n+1)s$ electrons and the differing relativistic effects for them (> 0.1 eV [2]) means that relativistic effects must be included from the first, and that a multi-reference $(d+s)^N$ zeroth order function must be used, at least for neutral and lightly ionized species. This notation is short hand for the 3 configurations: $(nd)^N$, $(nd)^{N-1}(n+1)s$ and $(nd)^{N-2}(n+1)s^2$. A relativistic formalism is additionally complicated compared to a non-relativistic one, because there are fewer good quantum numbers (L^2 and S^2 are "lost") leading to an increase in wavefunction size.

Complexity of the calculation increases strongly with N . The present situation — from the viewpoint of a Relativistic Configuration Interaction (RCI) methodology — is that TM atoms and ions with $N < 5$ can be treated adequately in most circumstances. For example, for $N = 2, 3$ average energy errors of 2-300 cm^{-1} and electric dipole f -value ($f > .01$) length and velocity gauge agreements of 5% are achievable. Similar accuracies for $N = 4$ are also sometimes achievable [3,4]. To date, our largest calculation is for lifetimes in Tc I [5], where we were only able to achieve average energy errors of 1500 cm^{-1} , and average gauge agreements of 19%. The difficulty can be partially understood by realizing that the correlation configurations formed by exciting 2 $(d+s)$ valence electrons in the $(d+s)^N$ reference to 2 f electrons (a very important effect) creates 653 basis functions ($J = 7/2$) for $(d+s)^4p$ and 4248 basis basis functions ($J = 7/2$) for $(d+s)^6p$ [5]. I.E. in crude terms, the size of the problem has increased 6.5 times in going from $N = 5$ to $N = 7$. It is also worthwhile to note that for correlation, $N = p$ and $N = 10 - p$ problems are not of equivalent sizes — the latter can be much greater ($p < 5$). A simple example is given by $p = 2$. Here, double excitation out of $(d+s)^2$ leaves no open subshell electrons, whereas double excitation out of $(d+s)^8$ leaves 6 open subshell electrons.

In the work reported here on Zr III and Nb IV, we are dealing with the simpler case of $N = 2$. Zr III has been observed by astrophysicists in the B-type star chi Lupi [6] and the spectrum has been recently revised by Reader and Acquista (RA) [7], who also produced some semi-empirical wavefunctions which were used to obtain oscillator strengths, and percentage composition for the levels. There are also two other semi-empirical predictions of f -values for some of the levels [8,9], and there is some significant variation among the results.

An interesting feature of the RA work was its relocation of the $5s^2 \ ^1S_0$ and $5s5p \ ^1P_1$ levels, and the substantial configuration interaction (semi-empirical) for some of the levels, between the $4d5p$ and $5s5p$ (and $4d6p$ and $4d4f$) configurations. Many of the $J = 1$ levels of these configurations are closely spaced (1-2000 cm^{-1}) making them a challenge to the

computationalist.

For Nb IV there is also fairly recent experimental work on the spectrum [10], but more levels—including $5s^2 \ ^1S_0$ — are uncertain, and no (semi-empirical) f -values are available there, although a limited number of results are available elsewhere [11,12].

This work has the goal to provide a thorough *ab initio* relativistic-correlation study of Zr III and Nb IV $J = 0, 1$ levels which produces energy level positions, f -values, level compositions, and Landé g -values. Questions to be answered include: given the near degeneracy, just how accurately can we determine the properties? Since so much of the Zr III and Nb IV spectrum is known [7,10], just how many eigenvalues can we accurately extract from a single RCI energy matrix, and what strategy is needed to maximize this number? Answers to this question have a bearing on the TM data demands of the opacity project [3]. For Zr III (and by implication, Nb IV) we accurately extracted 17 levels from the $J = 1$ RCI matrix. In principle, perhaps another 6-12 additional levels could have been extracted. For the more complicated (higher N) Fe ions, for example, one can not be as optimistic.

2. Methodology

To construct the reference functions, Φ , we start with the Dirac-Coulomb Hamiltonian, H_{DC} . Each Φ is constructed to be an eigenstate of J^2, J_z , parity, and have a unique non-relativistic manifold. A manifold consists of all relativistic configurations reducing to the same non-relativistic configuration in the $c \rightarrow \infty$ limit. The Φ 's are expressed as linear combinations of Slater determinants, whose elements are spinors. The spinors are expressed as products of unknown radial functions and the spin-angular functions of the Dirac hydrogen atom. Usually there is more than one Φ per manifold, so there are coefficients as well as radial functions to be determined by application of the energy variational principle. The resulting integro-differential Dirac-(Hartree)Fock equations are solved using Desclaux's algorithm [13].

To introduce correlation effects, we apply perturbation theory to suggest what additional manifolds are needed in the wavefunction. To first order, correlation effects would be restricted to either single or double excitation from the appropriate outer subshells of each of the reference functions. The correlation manifolds almost always need additional radial functions. In the RCI methodology these are known as virtuals, and we represent them with Relativistic Screened Hydrogenic (RSH) functions with a single parameter, Z^* , the effective charge. Such a choice avoids problems with variational collapse into the positron sea (the major and minor components are simultaneously determined by choosing Z^*), and produces radial expansions as rapidly convergent as one can expect from a single particle expansion (90% with one term, with a total of 2-3 terms per symmetry (κ)/per shell adequate). These virtuals represent the compact portion of an entire Rydberg and continuum series.

In perturbation theory, the second order energy is given by:

$$\frac{|H_{0,i}|^2}{|H_{0,0} - H_{i,i}|} \quad (1)$$

Clearly while small denominators (near degeneracy) need careful treatment, the more usual concern is to maximize the numerator. This is best done by using virtuals which have a very similar value of $\langle r \rangle$ as the reference radials they are replacing. This gives us an estimate

for each Z^* . Fine tuning of the estimated Z^* is made during the diagonalization of the RCI matrix, which also yields all the coefficients of the correlation basis functions (these are also eigenstates of J^2, J_z and parity).

Initially, our main interest was in the $5s^2$ $J = 0$ and $5s5p$ $J = 1$ levels of Zr III and Nb IV, and we chose as our reference for $J = 0$ the $3\ 4d^2+5s^2$ and for $J = 1$, the $5\ 4d5p+5s5p$ basis functions. I.E. We included basis functions to represent all levels below the levels of interest. For low N ($N = 2$ here), the precise source of the radial functions is not critical, as the RCI process can adjust for most deficiencies through the use of symmetry preserving single excitations. Initially, the $1s \cdots 4d$ $J = 0$ radials were generated from $4d^2\ ^3P_0$ and the $5s$ radial extracted from $5s^2$, and reorthogonalized to the existing $1s, 2s, 3s, 4s$ radials (our methodology is an orthogonal one). For $J = 1$, $1s \cdots 4d$ were generated from $4d5p\ ^3D_1$ and $5s$ and $5p$ from $5s5p\ ^3P_1$, with re-orthogonalization. More details of the methodology up to this point can be found in our work on the $(5d+6s)^2$ $J = 2$ levels of La II [14].

It was clear from our early calculations (also indicated by RA[7]) that second order effects were going to be important with this choice of references. Since a second order wavefunction is much larger than a first order one, some systematic *a priori* way of picking out just which are the differentially important second order effects is important (only these are included). Roughly, these will be large correlation corrections for the differentially large nearly degenerate first order effects. Correlation contributions may be approximately assigned to each manifold using intermediate normalization, whereby the reference function(s), but not the total wavefunction is normalized. In this instance, each correlation wavefunction χ_i contributes

$$e_i = \frac{C_i}{C_0} H_{i,0} \quad (2)$$

to the correlation energy. To present the results in a usable form, we collect all the e_i contributions belonging to the same manifold, and compress all virtual radials of the same symmetry into a single term. These results are presented in Table I for Zr III $J = 1$, in units of 10 meV, referred to the ground state $4d5p\ ^3D_1$.

From this table, we may observe that the differentially large nearly degenerate contributions include $4d_{vf}$ and $4d_{vp}$ (as well as $5p_{vd}$). In RA terms, these would principally be associated with the $4d4f$ and $4d6p$ configurations. Large excitations like $4p^2 \rightarrow 4d^2$, included in $4d5p$ and $5s5p$ (see Table I) would then also need to be included for $4d_{vf}$ and $4d_{vp}$ in order to maintain the near degeneracy (as correlation is added) of the relevant levels. Viewed from a reference of $4d5p + 5s5p$ these $4p^2 \rightarrow 4d^2$ excitations are second order.

A more systematic way to deal with this missing correlation, in the current instance, is to enlarge the reference space. The enlarged basis includes $4d4f$ and $4d6p$ (as they are important for $5s5p$) and additional functions for each of the additional levels we wish to extract from the RCI matrix. In the present instance, we have chosen to obtain results for the $4d5f$ and $4d7p$ levels as well (6 additional). It is quite important that the reference decision be made very early in the project stage, so as to avoid any extensive inclusion of second order effects (which are harder to identify).

As part of this project, a new short algorithm was written [15] which analyzes what are the important (a threshold of .01 eV was necessary) excitations for one of the atom's

wavefunctions (here 4d5p $J = 1$), and then it checks to see that the equivalent excitations are present in all the other references {4d(6p+7p+4f+5f), 5s5p}. This was very effective in reducing user time (hand checks were previously done), while improving accuracy.

Our current RCI matrix size is limited to 20 000, in order to maintain all the non-zero elements (30-40% of the total) in memory. It should be noted that most of the RCI cpu time is spent in assembling the matrix, and not diagonalizing it. Larger matrices could be retained on disk, with little additional cost, with the diagonalizer algorithm in use [16]. But we prefer smaller matrices, because this permits us to retain some physical intuition concerning wavefunction composition, and the effect of different correlation manifolds on atomic properties. Obviously, this requires some care in ensuring that nothing important is missed.

However, even in the present “simple” cases ($N = 2$) and just allowing single and double excitations from the 4s and 4p core subshells, a matrix of order $\sim 40\,000$ would be needed for $J = 1$. A prime illustration of why is to consider the $4p^2 \rightarrow 4dvg$ excitation from the 4d4f basis functions. There are 1128 basis functions associated with this configuration (and 4 times this number as we have 4d5f to consider, and a second virtual g). The most differentially important excitations from the core are $4p \rightarrow f$ and the $4p^2 \rightarrow 4d^2$ exclusion effects, as is common [17] for transition metal states with differing d/s occupations.

The energy matrix size can be substantially lowered by employing a formally first order procedure which we call REDUCE [17]. Its essence is to rotate the full basis set for the correlation manifold to maximize the number of zero energy matrix elements the rotated basis makes with the reference functions (the Φ 's). Such rotated basis functions are then discarded. To formulate the problem mathematically, the spin-angular integrations are performed for each of the matrix elements, such that each matrix element is expressed as a linear combination of a small number of radial integrals, which become the independent variables of the procedure. For the rotated basis, the coefficient of each radial integral must vanish for as many functions as possible, subject to the condition that the basis remains orthonormal. This is expressible as a set of n (n is the number of radial integrals) homogeneous equations in M unknowns (M is the # of basis functions; $M \gg n$). This underdetermined problem is solved very well (stable, accurate, and efficient) by the Singular Value Decomposition (SVD) procedure of Press *et al* [18]. The size reduction can be very great — for the $4p^2 \rightarrow 4dvg$ case cited above, the # of surviving basis functions is only 6 for the 3 4dnf references. There is of course some energy loss, but for this illustration it is only 40cm^{-1} (out of 1008cm^{-1}) which is quite tolerable. Errors in an early study on Zr II [17], which has $N = 3$, didn't exceed 200cm^{-1} . To be cautious, we normally apply REDUCE to correlation manifolds which make only small to moderate contributions to the correlation energy. For example, the $4p^2 \rightarrow 4d^2$ excitations are represented by the full basis set, not by REDUCE vectors.

Once the wavefunctions are obtained, Landé g -values and f -values may be obtained. Since the $J = 0$ and $J = 1$ wavefunctions are found separately, they are not orthonormal. We have developed methods of including such effects quite efficiently [~ 2.0 hrs on a 1 GHZ Blade 2000] based on the corresponding orbital method of King *et al* [19]. A more detailed

discussion may be found in references [5,20].

3. Results

3.1. Zr III Energies and Landé g -values

In Table II, the energies of the Zr III $J = 1$ $4d(5p+6p+7p+4f+5f)+5s5p$ and the $J = 0$ $4d^2+5s^2$ levels are given. RCI matrix sizes for $J = 1$ were 19 149 (with much use of REDUCE) and 3557 (no REDUCE) for $J = 0$. The longest calculation time, on a 1 GHz Blade 2000, was ~ 6.2 hrs for Zr III $J = 1$ with the Breit operator “turned on”. The wavefunctions were constructed by single and double excitations from the 4s, 4p and valence electrons from all references (17 for $J = 1$, 3 for $J = 0$). Initially, we had also included the excitations from 3d electrons which potentially [21] might have made significant contributions to the f -values, but they were removed (i.e. the 3d shell was closed). There were two reasons for this closure: (1) the 3d excitations had little effect on the f -values (as expected the velocity gauge was affected most),

(2) their inclusion—initially for the lower levels only—upset the energy balances in the upper levels, which would have had to have been properly compensated by including analogous 3d excitations for these levels as well, thus greatly complicating the calculation. The magnetic portion of the Breit operator has been included. Its main effect is to raise the $5s5p$ ($5s^2$) levels relative to the others $\sim 150\text{cm}^{-1}$ per 5s electron.

A useful assessment of the energy errors is to calculate the average error between adjacent levels, both absolutely (in cm^{-1}) and as a %. This gives some indication of how accurately the basis functions are “mixed together”. Correct mixing can be crucial to some properties like hyperfine structure [1] where different nearly degenerate basis functions can yield very different property results. For Zr III $J = 1$, using semi-empirical estimates where no experiment is available [7], we have an average energy error of 212 cm^{-1} . Absolutely, this is quite small for such calculations [17]. The % error, on the other hand is 9.9%; it’s considerably larger because many of the upper levels are closely spaced ($1\text{-}2000 \text{ cm}^{-1}$), and a 10% error there can be $1\text{-}200 \text{ cm}^{-1}$.

Perhaps it is a bit disappointing to see an error of 460cm^{-1} for the $5s5p$ 1P , 3P splitting (also seen in Nb IV), but it is helpful to realize that at the Dirac-Fock level this error is $\sim 7000\text{cm}^{-1}$ due to the large exchange integral. From Table I, it can be seen that the configurations $5pvd$, $4dvf$, $4dvp$, $4p^54d5p^2$ and $4p^54d5s^2$ are differentially much more important for $5s5p$ 1P than for $5s5p$ 3P . Furthermore, there is a loss of $\sim 500 \text{ cm}^{-1}$ of the energy contributions in $4dvp$ and $5pvd$ when 4p (and 4s) is opened. One can hypothesize that $4dvp$ and $5pvd$ are missing some double and/or single excitations (which would be second order effects to the reference space). Indeed, $5pvd$ is missing about $\sim 0.3 \text{ eV}$ in such excitations. To simulate the effect of these, we shifted the $5pvd$ diagonal matrix elements by this amount, but this had little effect on the position of $5s5p$ 1P (a shift of $\sim 1.5\text{eV}$ was needed, but there is no way to justify such a large shift).

It can also be useful to compute errors in energy differences relative to a fixed reference, say $4d5p$ 3D in the $J = 1$ case. Here we note that errors for the groups of $4d6p$, $4d7p$ and $4d5f$ levels are all $\sim 1000 \text{ cm}^{-1}$, which may suggest some missing core-4d correlation effects as the cause.

In setting up Table II (and throughout), we have used the RCI labels for 4d7p 1P and 4d4f 3D which reverse those of Reader and Acquista [7]. These levels are very close (300 cm^{-1}) and it is not difficult to believe the improved RCI results could interchange the configurational labels. Table II also contains Landé g -values. For pure LS levels, $g(^1P_1)=1.000$, $g(^3P_1)=1.500$, $g(^3D_1)=0.500$ (we have not included the anomalous g -value QED correction, which produces a smaller error than missing correlation contributions). Some RCI g -values deviate by more than 10% from pure LS values, but there seems to be at least rough agreement with the semi-empirical wavefunction compositions [7]. RCI g -values also support exchanging the terms of the levels at 91230 and 91603 cm^{-1} . The loss of "LS purity" will show up in the f -values, and is also a function of how accurately nearly degenerate levels are located, as well as the relativistic Hamiltonian used.

The average $J = 0$ separation error is 163 cm^{-1} , or 0.7%. Reader and Acquista [7] have also found $J = 0$ levels of 4d5d and 5p² (but not 5s6s). These are much higher ($\sim 61\,000$ cm^{-1}) than 5s². The RCI positions of these levels with the tabulated basis is only fair (10 000 cm^{-1} too high) — but this has no significant impact on the 4d² and 5s² positions or f -value. This was determined by watching how energy differences and f -values changed as the positions of these upper levels improved during the calculation process.

3.2. Zr III f -values

The velocity (Coulomb) and length (Babuskin) gauges are shown in Table III for the 22 f -values > 0.01 . F -values smaller than this are not displayed, as they are not likely to be as reliable. The two gauges agree on average to 3.2% [$\% = 200 \frac{L-V}{L+V}$] which is good for RCI. As is well known, gauge agreement is a necessary but not sufficient condition for accuracy. This was manifested in a minor way during the later stages of calculation when some f -values retained their good gauge agreement, but the values from differing calculations fell (slightly) outside each others ranges.

Table III values include full non-orthonormality effects [19,20], the Breit operator, with 1s...3d subshells closed. We used our "one-pass" f -value algorithm [4,15] which computes all transitions simultaneously for a fixed energy difference, and then scales appropriately the individual f -values with the experimental energy difference [7], when available. This is restricted to "optical" transitions, where the small r expansion of the spherical Bessel function is valid. We also did a calculation for $J = 0$ which included excitations from 3d likely [21] to make the most important contributions to f -values. The effect was to modestly change (2nd digit at most) some of the velocity values. This is consistent with the general expectation that excitations from the core are more likely to change velocity values than length ones. For this reason, we recommend the length values in Table III. The Breit operator affects the length value by $\leq 10\%$; for most transitions $\leq 5\%$.

Two semi-empirical sets of f -values for Zr III obtained using Cowan's program [22] are presented in Table III [7,8] along with a third semi-empirical set [9] based on a relativistic quantum defect method. We also include an *ab initio* result for 5s² \rightarrow 5s5p 1P_0 which has valence correlation and limited core-valence correlation. This value [12] is in good agreement with our results. The semi-empirical methods differ by whether they include core-polarization [9] or not [7,8], and which configurations are included, among other factors. The RCI values seem to be nearly uniformly lower than the semi-empirical ones. For most

transitions, at least one semi-empirical value is in pretty good agreement with the RCI result. An exception is the $4d^2\ ^3P_0 \rightarrow "4d5f"\ ^3D_1$ transition. But this state is so degenerate with $4d7p\ ^1P$ that the RCI levels are reversed. A second exception is $4d^2\ ^1S \rightarrow 4d4f\ ^1P$; here not even the sum over 7 oscillator strengths to nearby levels is conserved [23], which may suggest some incompleteness of the radial space is responsible. We did add additional p & f radial functions in $4d(p+f)$, but this had little impact. It may be noted that FOTOS [21] suggests f^2 configurations be present in the $J = 0$ state, when the $J = 1$ state contains df configurations as it does. No f^2 configurations are present in the semi-empirical work [7,8,9].

3.3. Nb IV Energies and Landé g -values

About 70% of computing time is spent setting up the energy matrix structure, viz: expressing each matrix element as a linear combination of radial integrals [15]. This structure is reused while iterating the virtual Z^* 's, or for a successor calculation which adds in new basis functions. This reuse is quite efficient, and can be valuable for isoelectronic studies, providing only the radial functions need to be changed. One might think that Zr III and Nb IV are sufficiently ionic that this would be the case—but in fact this is not so. The reversal of the relative positions of the $4d4f$ and $4d6p$ [7,10] illustrates this point. Nonetheless, there is a lot of commonality in the basis sets for Zr III and Nb IV, and because of this the equivalent of Table I is not presented for Nb IV.

In Table IV, the energies and Landé g -values for Nb IV $J = 1\ 4d(5p+4f+6p)+5s5p$ and $J = 0\ 4d^2+5s^2$ levels are given. RCI matrix sizes are 19136 for $J = 1$ and 3633 for $J = 0$. REDUCE was not used in either case. The Breit operator is included, and $3d$ is closed for both J 's.

The Nb IV $J = 1$ calculation includes 6 fewer levels ($4d5f+4d7p$) than its Zr III counterpart, simply because it was the first calculation. The average absolute error between adjacent $J = 1$ levels is $300\ \text{cm}^{-1}$ or 6.2%. The $5s5p\ ^1P$ - 3P splitting is in error by $\sim 600\text{cm}^{-1}$, which is a little larger error than in Zr III — perhaps due to a less sophisticated wavefunction — but a great reduction in the Dirac-Fock level error of $\sim 9000\text{cm}^{-1}$.

For $5s^2\ J = 0$, there is a significant discrepancy between the published work of Meinders *et al* [10] and RCI. However, newer experimental work exists [24] which is in good agreement with the RCI result.

3.4. Nb IV f -values

The velocity and length gauge results for 19 Nb IV $J = 0 \rightarrow J = 1$ f -values $> .01$ are shown in Table V. The average gauge agreement is 2.7% — quite good. Agreement for the $4d^2$ transitions (1-2%) is better than for the $5s^2$ ones (6.1%), perhaps suggesting any future improvement should concentrate on the $5s^2$. Table V values include full non-orthonormality, the Breit operator, and the $3d$ subshell closed for both states. As for Zr III, we recommend the length over the velocity values.

We could find only two other papers containing Nb IV f -values; both report on the Nb IV $5s^2 \rightarrow 5s5p\ ^1P, ^3P$ transitions only. The Multi- configurational Dirac-Fock + core polarization (MCDF+CP) calculation yields 1.99 [12] and a relativistic local density calculation [25] yields 2.3287. We think both of these are too high (our value is 1.611, see Table V), because they both use incorrect (theoretical) energy differences. As Migdalek and Stanek [12] illustrate, this transition is quite sensitive to the correct energy difference. In Nb IV, an accurate

energy difference was unknown until this work and that in reference 24.

We have preferred for a long time to use experimental energy differences for f -value evaluation, when they are available. Getting the transition matrix element accurately and calculating the energy differences accurately are two different (and somewhat unrelated) challenges to the computationalist. A trivial illustration is a calculation where $1s^2$ pair correlation was included for $J = 0$ but not for $J = 1$. This would have negligible impact on the transition matrix element, but substantial impact (>1.0 eV) on the computed energy difference. It is only for “simple” systems like alkali isoelectronic sequences calculated with Relativistic Many Body Perturbation theory that — at this time — we may expect to see both accurate transition matrix elements and energy differences produced from the same calculation. If, as can occur infrequently, the experimental energy differences are wrong, then one would see a lack of gauge agreement in what would be presumably an accurate calculation of the transition matrix element. In that case, a rigorous theoretical investigation of energies would be recommended.

4. Summary

In this work, we have produced what should be a more accurate set of f -values for Zr III $J = 0 \rightarrow J = 1$ transitions, and the first comprehensive set of f -values for many of the analogous transitions in Nb IV. For Nb IV, the position of $5s^2 J = 0$ (relative to $4d^2 \ ^3P_0$) has been corrected, and Landé g -values have been given for both sets of $J = 1$ levels.

We have also made progress in systematizing the treatment of multi-level cases (up to 17 for Zr III, $J = 1$) pointing out the importance is making a proper initial decision about the reference space, and then making sure that equivalent correlation excitations appear in all reference functions.

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Table I. *Zr III* $J = 1$ Correlation Contributions Relative to $4d5p\ ^3D_1$ in units of 10 meV^*

	4d5f			4d7p			4d4f			4d6p			5s5p		4d5p	
	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	¹ P	³ P
$4s^2\ 4p^6\ 4d\ 5p$	1	0	1	0	0	0	4	0	1	0	0	2	0	0	0	0
$4s^2\ 4p^6\ 5s\ 5p$	3	0	0	0	0	0	12	1	0	2	0	0	0	0	0	0
$4s^2\ 4p^6\ 4d\ vf$	4	4	4	15	0	1	4	4	4	-13	-3	-1	-24	1	-2	1
$4s^2\ 4p^6\ 4d\ vp$	11	4	-16	2	2	2	11	5	5	2	2	2	-8	2	1	1
$4s^2\ 4p^6\ 5p\ vs$	0	0	0	0	0	0	0	0	0	-1	0	0	0	0	0	0
$4s^2\ 4p^6\ 5p\ vd$	-2	0	-1	0	0	0	-7	0	-2	0	0	0	-37	-5	0	0
$4s^2\ 4p^6\ 5s\ vp$	-2	0	1	0	0	0	0	0	0	-1	0	0	1	-20	-4	-3
$4s^2\ 4p^6\ vp\ vd$	0	0	0	0	0	0	0	0	0	0	0	0	-2	0	-1	-1
$4s^2\ 4p^6\ vd\ vf$	0	0	0	2	2	3	-1	0	2	1	1	2	-4	3	-5	-3
$4s^2\ 4p^6\ vf\ vg$	-2	-1	-1	0	0	0	-5	-3	-3	0	0	0	-2	0	0	0
$4s^2\ 4p^5\ 4d\ 5p^2$	4	4	4	4	4	4	4	4	4	4	4	4	-30	-14	1	1
$4s^2\ 4p^5\ 4d\ 5p\ vp$	13	13	13	10	10	10	13	13	13	10	10	10	-9	-7	1	1
$4s^2\ 4p^5\ 4d\ 5p\ vf$	62	62	62	64	64	64	62	61	61	64	64	64	57	61	0	-4
$4s^2\ 4p^5\ 5s\ 5p\ vp$	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0
$4s^2\ 4p^5\ 4d^3$	0	-2	-1	0	1	1	0	-3	-4	1	1	1	1	1	0	0
$4s^2\ 4p^5\ 4d\ 5s^2$	0	0	0	0	0	0	0	0	0	0	0	0	-17	0	-2	0
$4s^2\ 4p^5\ 4d^2\ 5s$	12	12	12	10	10	10	12	12	12	9	9	8	8	9	4	3
$4s^2\ 4p^5\ 4d^2\ vs$	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0	0
$4s^2\ 4p^5\ 4d^2\ vd$	15	14	14	13	13	13	13	13	12	11	11	10	15	15	4	2
$4s^2\ 4p^5\ 4d\ 5s\ vd$	1	1	1	1	1	1	1	1	1	1	1	1	-12	-15	-1	0
$4s^2\ 4p^5\ 5s^2\ vd$	0	0	0	0	0	0	0	0	0	0	0	0	-2	0	0	0
$4s^2\ 4p^5\ 5p^2\ vs$	0	0	0	0	0	0	0	0	0	0	0	0	-1	-1	0	0
$4s^2\ 4p^5\ 5p^2\ vd$	3	3	3	3	3	3	3	3	3	3	3	3	0	2	0	0
$4s^2\ 4p^5\ 5p\ vs\ vp$	0	0	0	0	0	0	0	0	0	0	0	0	-1	-1	0	0
$4s^2\ 4p^5\ 5p\ vp\ vd$	10	10	10	6	7	7	10	10	10	6	6	6	5	5	0	0
$4s^2\ 4p^5\ 5p\ vd\ vf$	10	10	10	14	14	14	10	10	10	14	14	14	9	9	0	0
$4s^2\ 4p^5\ 5p\ vf\ vg$	11	11	11	11	11	11	11	11	11	11	11	11	9	10	0	0
$4s^2\ 4p^5\ vp\ vd\ vf$	-10	-10	-10	-13	-13	-13	-10	-10	-10	-13	-13	-14	0	0	0	0
$4s^2\ 4p^5\ vd\ vf^2$	-13	-13	-13	0	0	0	-14	-14	-14	0	0	0	0	0	0	0
$4s^2\ 4p^5\ vf^2\ vg$	-9	-9	-9	0	0	0	-10	-10	-10	0	0	0	0	0	0	0
$4s^2\ 4p^5\ 4d\ vp\ vf$	-8	-7	-6	-67	-66	-65	-7	-7	-8	-64	-66	-64	0	0	0	0
$4s^2\ 4p^5\ 4d\ vf^2$	-65	-65	-65	1	0	1	-64	-65	-65	0	0	0	1	1	0	0
$4s^2\ 4p^5\ 4d^2\ vg$	0	-1	-1	0	0	0	-1	-3	-3	0	0	0	0	0	0	0
$4s^2\ 4p^5\ 4d\ vp^2$	1	1	1	-7	-8	-8	1	1	1	-8	-9	-9	1	1	0	0
$4s^2\ 4p^5\ vp^2\ vd$	0	0	0	-10	-10	-10	0	0	0	-9	-10	-10	0	0	0	0
$4s^2\ 4p^5\ vp\ vf\ vg$	0	0	0	-9	-10	-10	0	0	0	-9	-9	-10	0	0	0	0
$4s^2\ 4p^5\ 5s\ vp^2$	0	0	0	0	0	0	0	0	0	0	0	0	-1	-1	0	0
$4s^2\ 4p^4\ 4d^3\ 5p$	141	141	141	141	141	141	141	141	141	141	141	141	132	139	5	1
$4s^2\ 4p^4\ 4d^2\ 5s\ 5p$	0	0	0	0	0	0	0	0	0	0	0	0	-159	-171	-9	-3
$4s^2\ 4p^4\ 4d^2\ 5p\ vd$	89	89	89	89	89	89	89	89	89	89	89	89	84	88	4	1

Table I. *Continued*

	4d5f			4d7p			4d4f			4d6p			5s5p		4d5p	
	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	³ D	¹ P	³ P	¹ P	³ P
4s ² 4p ⁴ 4d 5s 5p vd	1	1	1	1	1	1	1	1	1	1	1	1	-93	-99	-5	-2
4s ² 4p ⁴ 4d 5s 5p vg	0	0	0	0	0	0	0	0	0	0	0	0	-12	-13	0	0
4s ² 4p ⁴ 4d ³ vf	-144	-144	-144	0	0	0	-144	-144	-143	0	0	0	0	0	0	0
4s ² 4p ⁴ 4d ² vd vf	-90	-90	-90	0	0	0	-90	-90	-90	0	0	0	0	0	0	0
4s ² 4p ⁴ 4d ² vf vg	-12	-12	-12	0	0	0	-12	-12	-12	0	0	0	0	0	0	0
4s ² 4p ⁴ 4d ³ vp	0	0	0	-144	-144	-144	0	0	0	-145	-144	-143	0	0	0	0
4s ² 4p ⁴ 4d ² vp vd	0	0	0	-89	-89	-89	0	0	0	-87	-85	-85	0	0	0	0
4s ² 4p ⁴ 4d 5s vd vf	0	0	0	0	0	0	0	-1	-1	0	0	0	0	0	0	0
4s ² 4p ⁴ 4d ² vp vg	0	0	0	-12	-12	-12	0	0	0	-12	-12	-12	0	0	0	0
4s ² 4p ⁴ 4d ² 5p vg	12	12	12	12	12	12	12	12	12	12	12	12	11	12	0	0
4s 4p ⁶ 4d ² 5p	2	2	2	2	2	2	2	2	2	2	2	2	1	1	-1	-2
4s 4p ⁶ 4d 5s 5p	2	2	2	2	2	2	2	2	2	2	2	2	1	2	0	0
4s 4p ⁶ 4d 5p vs	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0
4s 4p ⁶ 4d 5p vd	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	0	0
4s 4p ⁶ 4d 5p vg	4	4	4	4	4	4	4	4	4	4	4	4	4	4	0	0
4s 4p ⁶ 5s 5p vd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0
4s 4p ⁶ 5p vf ²	0	0	0	1	1	1	0	0	0	1	1	1	0	0	0	0
4s 4p ⁶ 5p vs vd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0
4s 4p ⁶ 5p vd vg	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0
4s 4p ⁶ 4d ² vp	0	0	0	-3	-3	-2	0	0	0	-3	-3	-2	0	0	0	0
4s 4p ⁶ 4d 5s vp	0	0	0	-1	-1	-1	0	0	0	-1	-1	-1	0	0	0	0
4s 4p ⁶ 4d 5s vf	-1	-1	-1	0	0	0	-1	-1	-1	0	0	0	0	0	0	0
4s 4p ⁶ 4d ² vf	-2	-3	-3	0	0	0	-3	-3	-3	0	0	0	0	0	0	0
4s 4p ⁶ 4d vs vf	-1	-1	-1	0	0	0	-1	-1	-1	0	0	0	0	0	0	0
4s 4p ⁶ 4d vd vf	0	0	0	0	0	0	-1	-1	-1	0	0	0	0	0	0	0
4s 4p ⁶ 4d vf vg	-3	-3	-3	0	0	0	-3	-4	-4	0	0	0	0	0	0	0
4s 4p ⁶ vs vd vf	0	0	0	0	0	0	0	0	-1	0	0	0	0	0	0	0
4s 4p ⁶ vd vf vg	0	0	0	0	0	0	-1	-1	-1	0	0	0	0	0	0	0
4s 4p ⁶ 4d vp vg	0	0	0	-3	-3	-3	0	0	0	-3	-3	-3	0	0	0	0
4s 4p ⁶ 4d vs vp	0	0	0	-1	-1	-1	0	0	0	-1	-1	-1	0	0	0	0

* A positive # signifies that the state is raised relative to 4d5p ³D₁.
Contributions from virtuals of the same symmetry are collected together.

Table II. *Zr III Energy Levels and Landé g -values*

Label($J = 1$)	Energy (in cm^{-1})		
	Expt ^a	RCI ^b	Landé g^b
4d5p ³ D	0	0	.517
4d5p ³ P	4083	3989	1.418
4d5p ¹ P	6501	6635	1.064
5s5p ³ P	24491	24645	1.498
5s5p ¹ P	43147	43761	1.001
4d6p ³ D	62185	63138	.538
4d6p ³ P	(63875)	64951	1.348
4d6p ¹ P	65390	66569	1.109
4d4f ³ D	67725	67926	.620
4d4f ³ P	69071	69622	1.382
4d4f ¹ P	71225	72097	1.001
4d7p ³ D	(88162)	89120	.556
4d7p ³ P	(88899)	89947	1.308
4d5f ³ D ^c	(90173)	91183	.828
4d7p ¹ P ^c	(90472)	91422	1.059
4d5f ³ P	(91458)	92457	1.245
4d5f ¹ P	(92613)	93566	1.003
4d ² ¹ S	15915	15930	
5s ² ¹ S	40443	40148	

^a From reference 7. Experimental, except for entries with () which are obtained semi-empirically. Rounded to the nearest 1 cm^{-1} . All $J = 1$ levels are referenced to 4d5p ³D₁ and all $J = 0$ levels to 4d² ³P₀. Absolute energies of the $J = 1$ levels are generated by adding 55615.87 cm^{-1} to the $J = 1$ levels and 8063.63 cm^{-1} to the $J = 0$ levels.

^b This work. Includes the magnetic part of the Breit operator.

^c These two levels are heavily contaminated with the other basis function, and the RCI and semi-empirical labels are interchanged. The RCI labelling is shown.

Table III. *Zr III* $4d^2 + 5s^2$ $J = 0 \rightarrow 4d(5p + 6p + 7p + 4f + 5f) + 5s5p$ $J = 1$ f -values^a

Transition	RCI				Other Values
	Vel	Len	Avg	Spread	
$5s^2 \ ^1S \rightarrow 4d5f \ ^1P$.048	.048	.048	0.2%	.066 ^b
$5s^2 \ ^1S \rightarrow 4d4f \ ^1P$.181	.196	.188	3.9%	.148 ^b
$5s^2 \ ^1S \rightarrow 5s5p \ ^1P$	1.487	1.722	1.604	7.3%	1.995 ^b , 1.65 ^e
$5s^2 \ ^1S \rightarrow 4d5p \ ^1P$.026	.026	.026	0.5%	
$4d^2 \ ^1S \rightarrow 4d5f \ ^1P$.167	.163	.165	1.4%	.269 ^b , .21 ^c
$4d^2 \ ^1S \rightarrow 4d5f \ ^3D$.024	.022	.023	4.9%	
$4d^2 \ ^1S \rightarrow 4d4f \ ^1P$.373	.377	.375	0.5%	.69 ^b , .92 ^c
$4d^2 \ ^1S \rightarrow 4d6p \ ^1P$.090	.098	.094	4.6%	.126 ^b
$4d^2 \ ^1S \rightarrow 4d6p \ ^3P$.019	.021	.020	5.8%	
$4d^2 \ ^1S \rightarrow 5s5p \ ^1P$.232	.261	.246	5.9%	.186 ^b
$4d^2 \ ^1S \rightarrow 4d5p \ ^1P$.199	.221	.210	5.4%	.234 ^b , .31 ^c , .32 ^d
$4d^2 \ ^1S \rightarrow 4d5p \ ^3P$.021	.024	.022	5.9%	.030 ^b , .040 ^d
$4d^2 \ ^3P \rightarrow 4d5f \ ^1P$.018	.019	.019	2.4%	
$4d^2 \ ^3P \rightarrow 4d5f \ ^3P$.044	.045	.045	1.9%	
$4d^2 \ ^3P \rightarrow 4d5f \ ^3D$.161	.166	.164	1.4%	.316 ^b , .31 ^c
$4d^2 \ ^3P \rightarrow 4d4f \ ^1P$.015	.015	.015	1.4%	.015 ^b
$4d^2 \ ^3P \rightarrow 4d4f \ ^3P$.050	.050	.050	0.4%	.081 ^b
$4d^2 \ ^3P \rightarrow 4d4f \ ^3D$.564	.577	.571	1.1%	.776 ^b , .62 ^c
$4d^2 \ ^3P \rightarrow 4d6p \ ^3D$.011	.011	.011	0.5%	.004 ^b , .002 ^c
$4d^2 \ ^3P \rightarrow 4d5p \ ^1P$.024	.026	.025	3.9%	.040 ^d
$4d^2 \ ^3P \rightarrow 4d5p \ ^3P$.138	.151	.145	4.4%	.166 ^b , .24 ^c , .17 ^d
$4d^2 \ ^3P \rightarrow 4d5p \ ^3D$.054	.061	.058	6.3%	.081 ^b , .080 ^c , .10 ^d

^a Only f -values $> .01$ are listed. Experimental energies are used (when available). The length value is preferred. F -values are assigned to the proper label. I.E. The RCI levels $4d5f \ ^3D$ and $4d7p \ ^1P$ are interchanged compared to the semi-empirical ordering [7]. The larger f -value (from $4d^2 \ ^3P$) is consistently assigned to $4d5f \ ^3D$.

^b Reference 7.

^c Reference 9; core polarization value.

^d Reference 8.

^e Reference 23; Multi-Configurational Dirac-Fock + core polarization.

Table IV. *Nb IV Energy Levels and Landé g -values*

Label	Expt ^a	RCI ^b	Landé g^b
$J = 1$			
4d5p ³ D	0	0	.521
4d5p ³ P	5974	5805	1.437
4d5p ¹ P	10125	10211	1.042
5s5p ³ P	59155	58836	1.497
5s5p ¹ P	78529	78814	1.002
4d4f ³ D	87378	87751	0.595
4d4f ³ P	89529	90159	1.406
4d4f ¹ P	(92734)	93753	0.883
4d6p ³ D	93918	94884	0.635
4d6p ³ P	96431	97279	1.473
4d6p ¹ P	100875	102399	1.007
$J = 0$			
4d ² ¹ S	22040 22039 ^c	22165	
5s ² ¹ S	(97735) 107228 ^c	107132	

^a From Reference 10, unless otherwise noted. Entries with () are obtained semi-empirically. Rounded to the nearest cm^{-1} . All $J = 1$ ($J = 0$) levels referenced to 4d5p ³D₁ (4d² ³P₀). Absolute positions of the $J = 1$ levels are found by adding 10125.34 cm^{-1} to the $J = 1$ table entries. For $J = 0$ levels, add 9693.84 cm^{-1} .

^b This work. Includes the magnetic part of the Breit operator.

^c Work of T. Ahmad and J. Reader; J. Reader private communication.

Table V. *Nb IV* $4d^2 + 5s^2$ $J = 0 \rightarrow 4d(5p + 6p + 4f) + 5s5p$ $J = 1$ f -values^a

Transition	Vel	Len	Avg	Spread
$5s^2 \ ^1S \rightarrow 4d6p \ ^1P$.238	.280	.259	8.1%
$5s^2 \ ^1S \rightarrow 4d6p \ ^3P$.029	.021	.020	7.0%
$5s^2 \ ^1S \rightarrow 4d6p \ ^3D$.049	.055	.052	5.3%
$5s^2 \ ^1S \rightarrow 4d4f \ ^1P$.072	.077	.074	3.3%
$5s^2 \ ^1S \rightarrow 5s5p \ ^1P$	1.493	1.611	1.511	6.6%
$4d^2 \ ^1S \rightarrow 4d6p \ ^1P$.322	.302	.312	3.1%
$4d^2 \ ^1S \rightarrow 4d6p \ ^3D$.109	.111	.110	1.0%
$4d^2 \ ^1S \rightarrow 4d4f \ ^1P$.237	.245	.241	1.7%
$4d^2 \ ^1S \rightarrow 5s5p \ ^1P$.241	.259	.250	3.5%
$4d^2 \ ^1S \rightarrow 4d5p \ ^1P$.200	.203	.202	0.7%
$4d^2 \ ^1S \rightarrow 4d5p \ ^3P$.011	.011	.011	1.2%
$4d^2 \ ^3P \rightarrow 4d6p \ ^3P$.034	.037	.036	3.8%
$4d^2 \ ^3P \rightarrow 4d6p \ ^3D$.013	.013	.013	2.4%
$4d^2 \ ^3P \rightarrow 4d4f \ ^1P$.046	.048	.047	1.6%
$4d^2 \ ^3P \rightarrow 4d4f \ ^3P$.069	.070	.069	0.2%
$4d^2 \ ^3P \rightarrow 4d4f \ ^3D$.715	.725	.720	0.7%
$4d^2 \ ^3P \rightarrow 4d5p \ ^1P$.019	.019	.019	0.1%
$4d^2 \ ^3P \rightarrow 4d5p \ ^3P$.166	.168	.167	0.7%
$4d^2 \ ^3P \rightarrow 4d5p \ ^3D$.074	.076	.075	1.0%

^a Only f -values $> .01$ are listed. Experimental Energies are used (ref. 10, except for $5s^2$ where ref. 25 is used). The length value is preferred.

References

1. Beck, D. R., Phys. Rev. A **45**, 5251 (1992).
2. Martin, R. L., and Hay, P. J., J. Chem. Phys. **75**, 4539 (1981).
3. O'Malley, S. M., Beck, D. R., and Oros, D. P., Phys. Rev. A **63**, 032501 (2001).
4. Norquist, P. L., and Beck, D. R., J. Phys. B **34**, 2107 (2001).
5. O'Malley, S. M., and Beck, D. R., Physica Scripta, accepted for publication
6. Leckrone, D. S., Johnsson, S., Wahlgren, G. M., and Adelman, S. J., Physica Scripta T **47**, 149 (1993).
7. Reader, J., and Acquista, N., Physica Scripta **55**, 310 (1997).
8. Redfors, A., Astron. Astrophys. **249**, 589 (1991).

9. Charro, E., Lopez-Ayuso, J. L., and Martin, I., *J. Phys. B* **32**, 4555 (1999).
10. Meinders, E., Meijer, F. G., and Remijn, L., *Physica Scripta* **25**, 527 (1982).
11. Sen, K. D., and Puri, A., *Chem. Phys. Letts.* **156**, 505 (1989).
12. Migdalek, J., and Stanek, M., *Z. Phys. D* **27**, 9 (1993).
13. Desclaux, J. P., *Comput. Phys. Commun.* **9**, 31 (1975).
14. Datta, D., and Beck, D. R., *Phys. Rev. A* **57**, 3622 (1995).
15. All computer algorithms used here were written by the author (DRB) and are unpublished, unless otherwise noted.
16. Weber, J., Lacroix, R., and Wanner, G., *Comput. Chem.* **4**, 55 (1980).
17. Beck, D. R., and Datta, D., *Phys. Rev. A* **48**, 182 (1993).
18. Press, W. H. *et al*, *Numerical Recipes in Fortran 77*, Second Edition, Cambridge Press, New York (1992).
19. King, H. F. *et al*, *J. Chem. Phys.* **47**, 1926 (1967).
20. Beck, D. R., and Cai, Z., *Phys. Rev. A* **41**, 301 (1990).
21. Nicolaides, C. A., and Beck, D. R., *Chem. Phys. Lett.* **36**, 79 (1975).
22. Cowan, R. D., “The Theory of Atomic Structure and Spectra”, Univ. California Press, Berkeley, CA. (1981).
23. Nicolaides, C. A., and Beck, D. R., *Chem. Phys. Letts.* **53**, 87 (1978).
24. Ahmad, T., and Reader, J., unpublished. Reader, J., private communication.
25. Sen, K. D. and Puri, A., *Chem. Phys. Letts.* **156**, 505 (1989).