

# Improved RCI techniques for Atomic $4f^n$ Excitation Energies and Polarizabilities

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**Abstract.** We propose an efficient method by which previously computationally expensive, but moderately important, pair correlation effects can be incorporated into  $f^n$  excitation energies. Application is to Gd IV. Secondly, we extend two methods of obtaining static and tensor dipole polarizabilities and apply them to the Ni II ground state. The first uses the sum over  $f$ -values approach, and the second is variational.

## 1. Calculation of Excitation Energies for Lanthanides and Actinides

Our long term computational interest has been to develop (when necessary) and apply the relativistic configuration interaction (RCI) method to predict properties of complicated atoms and ions – specifically, for transition metals, lanthanides and actinides.

Triply ionized lanthanide and actinide ions appear as impurities in condensed matter systems where they can serve as centers of lasing activity [1], play a role in MRI medicine as endohedral metallofullerenes (e.g.  $Gd_3N-C_{80}$ ) [2], appear as important constituents of high temperature super-conductors, etc. There also has been interest in the free Gd IV ion as a possible means of detecting an electron electric dipole moment [3].

Experimentally, only a few of the low lying excitation energies within the  $f^n$  configuration are generally known [4, 5] from measurements made in the condensed phase. Dipole transition energies  $f^n - f^{n-1}d$  are generally not known experimentally, as the d levels in the solid are not very well localized [5]. It also may be noted that most prevalent charge state of the lanthanide/actinide ion in the solid is  $3^+$  [5].

Computationally, these excitation energies are also difficult to obtain [6]. The calculations require the use of a relativistic Hamiltonian (Dirac-Breit) and a correlated wavefunction having at least a first order form, i.e. one that includes all the differentially important single and double subshell excitations from a set of reference functions. At present, a reasonable *ab initio* accuracy goal for excitations within  $f^n$  would be to position all levels to  $\sim 1000 \text{ cm}^{-1}$  relative to the ground state. Our recent Gd IV [6] achieved  $1257 \text{ cm}^{-1}$ , and we improve this to  $838 \text{ cm}^{-1}$  here, accompanied by a drop in calculation time of 67%.

Two points need to be made about this accuracy ( $1000 \text{ cm}^{-1}$ ): (1) It is still a challenge to obtain this for some of the transition metals, and more importantly, (2) that for many properties, such as  $f$ -values, the important figure of merit is the average error in the position of adjacent energy levels [7], which usually is more accurately determined.

These errors can be reduced, after a good *ab initio* relativistic-correlation calculation is done (we use the Relativistic Configuration Interaction (RCI) method) if the experimental spectrum is thoroughly known, as it is for the transition metals, by shifting the appropriate diagonal matrix elements a “small” amount (generally) [7] to improve the agreement with the observed spectrum.

But for the lanthanides, the spectrum is too incomplete to take this approach. So, we need some *ab initio* way of obtaining these shifts (which represent correlation we are not able to include in RCI due to the complexities encountered). On the other hand, what is excluded in the initial RCI calculation must be small enough to be well represented by a shift in the diagonal matrix elements. If one only shifts the reference matrix elements, then the shifts are to account for missing first order correlation effects.

Our approach is a relativistic variant of a procedure introduced in 1969 [8] and which was not widely used after that. Non-relativistically, it was shown that dynamical (i.e. bi-virtual) pair correlation (e.g.  $4f^2 \rightarrow vg^2$  in Gd IV) contributions to the correlation energy from subshells  $a$  and  $b$ , could be written:

$$E_{vv'}(C_2; LS) = \sum_{ls} \beta_{C_2; LS}(n_a l_a, n_b l_b; ls) \epsilon(n_a l_a, n_b l_b; ls) \quad (1)$$

where  $C_2 = (n_a l_a)^{q_a} (n_b l_b)^{q_b}$ , i.e. the “ $a, b$  subshell portion” of the reference configuration.

The angular factors,  $\beta$ , can be obtained from eqn. (A.2) of the Appendix which appeared previously [8, 9]. The radial pair energies,  $\epsilon$ , are independent of  $q_a, q_b$  and  $L, S$ .

Simple expressions for the  $\beta$ 's are given [9] in two important cases, included in table 1, viz (i) for interactions between a closed subshell  $a$  and a subshell  $b$  having occupancy  $q_b$  ( $a \neq b$ ); (ii) if the subshell  $a$  has a single hole ( $b = a$ ); (iii)  $q_a + q_b = 2$ .

Newly developed relationships for average  $\beta$ 's between hole and electron configurations (same  $LS$ ) for  $d^n, f^n, d^m p, f^m p, f^m d$  are presented in table 1. At present, all other  $\beta$ 's must be obtained by explicitly evaluating eqn. (A.2).

The key to the utility of the method comes from the remaining part – how one can simply obtain the  $\epsilon$ 's. If this could only be done on the original system (e.g. Gd IV) then little computational effort would be saved (but an important analysis tool would have been created – see below). However, it was noted in the original study [8], that these  $\epsilon$ 's only had a weak dependence on  $N$  (the number of electrons) and  $Z$ . When this is valid, then the calculations for them could be done on a much simpler system – such as Yb I  $4f^{14}$  treated by Jankowski *et al* [10], and the  $\epsilon$ 's extracted using the  $\beta$ 's for Yb I. These could then be inserted back in the Gd IV problem, using its  $\beta$ 's.

So we are left with two major questions: (1) how transferable are the  $\epsilon$ 's for the lanthanide/actinides? (2) how do we make this non-relativistic method relativistic?

**Table 1.** Dynamical pair energy angular factors ( $\beta$ )

Explicit $\beta$ Values ( $g(l, s) = (2l + 1)(2s + 1)$ ) <sup>a</sup>	
(1)	$n^{a1^a}$ closed ( $q_a = 4l_a + 2$ ) $\beta = q_b g(l, s)/(4l_b + 2)$
(2)	$n^{a1^a}$ with one hole $\beta = 2l_a g(l, s)/(2l_a + 1)$
(3)	$q_a + q_b = 2$ $\beta = \delta_{S,s} \delta_{L,l}$
Relationship between average <sup>b</sup> angular factors ( $\beta$ ) between hole and electron configurations (same $LS$ )	
(4)	$\beta_{d^{10-n}:LS}(d^2 : ls) = \beta_{d^n:LS}(d^2 : ls) + (C_n/5)g(l, s)$ , where $C_n = 5 - n$
(5)	$\beta_{f^{14-n}:LS}(f^2 : ls) = \beta_{f^n:LS}(f^2 : ls) + (D_n/7)g(l, s)$ , where $D_n = 7 - n$
(6)	$\beta_{f^{13}d:LS}(fd : ls) = \beta_{fd^9:LS}(fd : ls) + g(l, s)/35$
(7)	$\beta_{f^{13}p:LS}(fp : ls) = \beta_{fp^5:LS}(fp : ls) + (2/21)g(l, s)$
(8)	$\beta_{d^9p:LS}(dp : ls) = \beta_{dp^5:LS}(dp : ls) + g(l, s)/15$

<sup>a</sup>  $s = 0, 1$ .  $|l_a - l_b| \leq l \leq l_a + l_b$  for two subshells ( $a, b$ );  $0 \leq l \leq 2l_a$  and  $s + l = \text{even}$  for one subshell  $a$ .

<sup>b</sup> Configurations  $d^m$  and  $f^m$ :  $m \geq 3$  may have more than one  $LS$  eigenvector (e.g.  $d^3$  has two  $^2D$ 's). Only average hole-electron  $\beta$ 's are given above. If more accuracy is desired, eqn. (A.2) must be evaluated for each case.

Approximate  $LS$  eigenstates are generated from the relativistic reference space by setting the minor component of the radial function to zero, and assuming the major component is independent of  $j$ . The  $L^2$  and  $S^2$  matrices are then simultaneously diagonalized for this basis. Since all possible “ $LS$ ” functions are kept, we are still spanning the reference space. The equations of Appendix A are then evaluated.

What about “transferability” of the  $\epsilon$ ? This is the main question. For Gd IV, the RCI  $\epsilon(4f^2)$ 's are in good agreement with the (non-relativistic)  $\epsilon$ 's of Yb I [10] except in the case of  $4f^2 \rightarrow vf^2$  so we retain this excitation in the RCI wavefunction. This seems to be a “characteristic” difference (e.g. true for Tb IV as well).

To make a more complete transferability test, we sought a more completely measured Lanthanide spectrum. These are quite rare, but the Pr III levels are complete [4]. Retaining the  $4f^2$   $\epsilon$ 's from Yb I [10], but calculating the “nearby” [4]  $4f^2 \rightarrow 5d^2$  pair correlation using RCI, our average error relative to the ground state was  $910 \text{ cm}^{-1}$ .

If transferability of  $\epsilon$  within  $4f^7$  levels of Gd IV is valid, which seems likely, then the above results suggest there is negligible contribution to excitation energies within  $4f^7$  from pair excitations involving the core electrons. I.E. Core-valence pair correlation has little net impact.

On the other hand, positioning of  $f^{n-1}d$  levels relative to  $f^n$  levels will involve the core, in two ways: through  $\epsilon(a, 4f)$  where  $a = 5p, 5s, 4d, 4p, 4s \dots$ , due to the changing  $4f$  occupation, and (ii) through the interaction of the  $5d$  electron with the core. This should be a smaller effect, as the  $5d$  radial is more diffuse than that of the  $4f$ . Sample core-valence dynamical pair correlation is given in table 2 for  $\text{Tm}^- 4f^{14}6s^2$ . These results, although incomplete (only 1 virtual/ $l$  and no contributions from  $1s \dots 3p$ ) when “transferred” to Gd IV, predict that  $4f^7$  has  $\sim -1.183 \text{ eV}$  more correlation than  $4f^6$ .

**Table 2.**  $E_{vv'}$ ( $4f^{14}$ , core) dynamical pair correlation (in -eV) for  $\text{Tm}^- 4f^{14} 6s^2$ 

Core Subshell	Correlation
6s	0.1543
5p	8.2174
5s	1.9489
4d	9.7044
4p	2.3511
5s	0.6288
3d	1.5604

Dzuba and Flambaum [11] have recently discussed some of these core-valence issues in a more formalistic manner.

## 2. Scalar and Tensor Polarizability of the Ni II Ground State

Recent and on-going measurements of high Rydberg states by Lundeen and collaborators [12] have yielded results for dipole polarizabilities of atomic ions, the most recent of which is for the Ni II ground state [13]. Such polarizabilities are of interest in determining the long-range interactions between atomic species, for example.

### 2.1. A “Sum” over $f$ -values Approach

Originally [14] we treated atomic scalar dipole polarizabilities using the well known expression [15] involving  $f$ -values, viz:

$$\alpha = \sum_n \frac{f_{0n}}{(E_n - E_0)^2} + \int_{I_1}^{\infty} \frac{(df/dE)dE}{(E_0 - E)^2} \quad (2)$$

Calculations at the time were non-relativistic, included non-orthonormality effects, but didn’t include the continuum portion of the sum, and used experimental excitation energies, when available. As argued there [14], our results provided a lower bound for the scalar dipole polarizability of ground states. To convert these results (in  $\text{A}^3$ ) to the units used here (a.u.<sup>3</sup>), divide by  $(.52917)^3$ .

Here, we report a fully relativistic variant of the method, which does include the continuum portion of the sum. Neglect of the continuum can lead to a serious underestimate of the polarizability in cases where the lowest Rydberg level is high lying (near the first ionization limit) as in the case for the  $3d \rightarrow f$  excitations in Ni II. On the other hand, the lower lying  $3d \rightarrow p$  Rydberg transitions in Ni II tend to be dominated by the discrete portion. In all cases, however, a careful calculation using equation (2) would include the continuum portion. The contribution from the highest  $n$  Rydberg states has been obtained by linearly extrapolating the continuum result below the ionization limit to “capture” this piece.

To generate a relativistic frozen core continuum spinor, we use a version of the program created by Perger and co-workers [16]. The  $f$ -values are constructed from available formulae [17], using computer programs created by Beck and co-workers [18].

## 2.2. Variational Method

This is a method applied by Vo Ky Lan and co-workers [19] which we found attractive due to its ease of application, use of (non-relativistic) configuration interaction (CI), and uncomplicated extension to a fully relativistic treatment.

One produces a lower bound for the second order energy in the presence of the polarizing field (arising from the potential energy,  $V_1$ ) by maximizing

$$E_2(\Phi_1) = \langle \Phi_1 | H_0 - E_0 | \Phi_1 \rangle + 2 \langle \Phi_1 | V_1 | \Phi_0 \rangle = -\alpha/2 \quad (3)$$

which is eqn. (9) of ref. [19].  $\Phi_0$  is a solution of the unperturbed (no-external field) problem, viz

$$H_0 \Phi_0 = E_0 \Phi_0 \quad (4)$$

Here,  $\Phi_0$  is expanded in a linear combination of relativistic configuration state functions which are eigenstates of  $J^2$ ,  $J_z$ , and parity, and have pre-determined (via no-field RCI calculations) coefficients. For the Ni II ground state, this would include the  $3d^9 \ ^2D_{5/2}$  configuration, and perhaps a limited amount of correlation (see below and [19])

$\Phi_1(J')$  is similarly expanded, but here includes only those configurations connected to the ground state via the dipole operator, i.e. by  $V_1$ . For Ni II, this means inclusion of  $3d \rightarrow vp+vf$  and  $3p \rightarrow 3d$  with  $J'$  limited to  $J' = J - 1, J, J + 1$ . Additional excitations from the core (e.g.  $3p \rightarrow vd$ ;  $3s \rightarrow vp$ ) were found to be small. As with the first method, calculations for different  $J'$  can be done separately. The unknowns in  $\Phi_1$  are of two types: (1) the virtual radial functions, e.g.  $vp, vf$  which as usual [7] we represent as Relativistic Screened Hydrogen (RSH) functions with adjustable effective charges ( $Z^*$ ) and the coefficients ( $b$ ) multiplying the configurational functions in which  $\Phi_1$  is expanded. Operationally, estimates for  $Z^*$  are made, and the resulting linear equations for the  $b$ 's (eqn. (13) of [19]) are solved, from which the scalar polarizability,  $\alpha_{sc}(J, J')$  here, is obtained. Another guess for the  $Z^*$ 's is made, and  $\alpha_{sc}(J, J')$  is recomputed. Characteristically, convergence is rapid.

Calculations need be done for only one set  $M, M'$  for each  $J, J'$  set as there is a simple relationship between the component results, viz:

$$\alpha_{sc}(J, M; J', M') = \left( \begin{array}{ccc} J & 1 & J' \\ -M & M - M' & M' \end{array} \right)^2 |\langle J \| \| J' \rangle|^2 \quad (5)$$

We then sum over  $M, M'$  and divide by 3. We note that an expression for the  $V_1$  matrix element in (3) may be obtained from available results for the nuclear quadrupole matrix element [20]. An equivalent non-relativistic relationship is used in eqn. (19) of ref. [19].

An important question that remains is “how much correlation” needs to be “put into”  $\Phi_0$  and  $\Phi_1$ ? Non-relativistic results for first row atoms and ions [19] don’t provide a definitive answer to this question. However, in the spirit of our “standard” treatment of oscillator strengths [7] and eqn. (1), we think that the transition matrix element  $\langle \Phi_1 | V_1 | \Phi_0 \rangle$  and energy differences ( $E_0$  and  $\langle \Phi_1 | H_0 | \Phi_1 \rangle$ ) can, in the main, be treated separately.

We do this as follows: (1) the ground state radials  $1s \cdots 3d$  are used in both  $\Phi_0$  and  $\Phi_1$  (this avoids the need for the inclusion of non-orthonormality effects), (2) We compute the ionization potential of Ni II using just the  $3d^9 \ ^2D_{5/2}$  and  $3d^8 \ ^3F_4$  relativistic configuration functions and compare it to the observed value [21]. The difference is used to shift  $E_0$ , so that  $\langle \Phi_1 | H_0 | \Phi_1 \rangle - E_0$  matches the observed IP. The key assumption here is that all correlation effects for all  $3d^8 (L, S, J_c) np/\epsilon p$  and  $3d^8 (L, S, J_c) nf/\epsilon f$  states do NOT depend on  $n$  or  $\epsilon$ , but only depend on  $L, S, J_c$ . We allow for “local” shifts by coupling  $3d^8$  to  $L, S, J_c$  when setting up our relativistic configuration state functions used to build  $3d^8 vp/vf (J', M' = +J')$ .

Scalar polarizabilities are “moderately” affected by these shifts (NOT so for tensor polarizabilities – see below), and show little change when using more than one virtual (e.g. adding  $xp, xf$ ) or including a limited amount of correlation directly.

### 2.3. Tensor Polarizabilities

The formalism of Angel and Sandars [22], in particular eqn. (3.16) and (3.17) is used here. Equation (3.16) gives the expression for the scalar dipole polarizability, which in our terms could be written as:

$$\alpha_{sc}(J) = \sum_{J'} \alpha_{sc}(J, J'), \quad (6)$$

which then allows us to remove the reduced matrix elements in (3.17) from the expression for the tensor dipole polarizability, replacing it with  $\alpha_{sc}(J, J')$  and the angular factors in (3.16). Then, writing

$$\alpha_{ten}(J) = \sum_{J'} \gamma(J, J') \alpha_{sc}(J, J') \quad (7)$$

we have

$$\gamma(J, J') = \sqrt{\frac{30J(2J-1)(2J+1)}{(2J+3)(J+1)}} \left\{ \begin{matrix} J' & J & 1 \\ 2 & 1 & J \end{matrix} \right\} (-1)^{-J-J'} \quad (8)$$

So, the result for  $\alpha_{ten}(J)$  can easily be assembled from the previously computed results for  $\alpha_{sc}(J, J')$ . Due to the cancellation associated with the  $\gamma$  factors, which in the case of Ni II are  $-1 (J' = 3/2)$ ,  $8/7 (J' = 5/2)$  and  $-5/14 (J' = 7/2)$ , the tensor polarizability tends to be much smaller (in magnitude) than the scalar polarizability, and much more sensitive to errors/variations in  $\alpha_{sc}(J, J')$  (see table 3). It may be noted that eqn. (3.16) provides the motivation behind our eqn. (4) above.

Our results for the polarizabilities of the Ni II ground state are given in table 3. It can be seen that the two methods agree very well for the scalar polarizability, but that

**Table 3.** Scalar and Tensor Polarizabilities of Ni II  $3d^9 \ ^2D_{5/2}$  (in a.u.<sup>3</sup>)

Quantity	$f$ -value Result	Variational Result
$\alpha_{sc}(3/2)$	1.6575	1.5727
$\alpha_{sc}(5/2)$	3.0416	3.1671
$\alpha_{sc}(7/2)$	3.0375	3.0383
Scalar	7.7367	7.7782
Tensor	+0.734	+0.962

there is a considerable variation in the tensor result, which at best, suggests a minimal uncertainty in our result (until the experimental value is available).

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## Appendix A.

Given the reference function

$$\Phi = \sum_K c_K \Delta_K(\dots k_a \dots k_b \dots) \quad (\text{A.1})$$

taking into account symmetry considerations, it can be shown [eg. 8] that the bi-virtual symmetry adapted energy in first order has the form:

$$\begin{aligned} E_{vv'} = & \sum_K c_K^2 \sum_{k_a < k_b} \sum_{s,l} T_{k_a k_b;sl}^2 \epsilon(n_a l_a n_b l_b; sl) + \\ & + \sum_{K,L(K \neq L)} c_K c_L (-1)^{m_{KL}} \sum_{sl} T_{k_a k_b;sl} T_{l_a l_b;sl} \epsilon(n_a l_a n_b l_b; sl) \end{aligned} \quad (\text{A.2})$$

where  $k_a, k_b$  are the spin-orbitals belonging to the determinant  $\Delta_K$ , of the subshell  $n_a l_a, n_b l_b$  which have been replaced. The second sum arises from two determinants  $\Delta_K$  and  $\Delta_L$  which differ in only two spin-orbitals ( $k_a, k_b$  of  $\Delta_K$  and  $l_a, l_b$  of  $\Delta_L$ ) and which have their  $N - 2$  common spin-orbitals aligned producing the phase factor  $(-1)^{m_{KL}}$ . These may arise from either the same or different configurations (if  $\Phi$  is multi-configurational), although for simplicity we will now restrict  $\Phi$  to be single configurational.

The factor  $T_{ij;SL}$  is that which linearly combines two electron determinants (all with a common  $M_L$  and  $M_S$ ) such that two electron symmetry eigenstates ( $S, L$ ) are formed. In ref. [8] no explicit formula for  $T$  was given because the few results on  $s^m p^n$  configurations were obtained on a case by case basis.

It turns out that  $T$  is well known, i.e.

$$\begin{aligned} T_{k_a k_b;SL} = & (-1)^{l_a + l_b + M_L + M_S} \sqrt{\frac{(2S+1)(2L+1)}{N}} \times \\ & \times \begin{pmatrix} 1/2 & 1/2 & S \\ m_{s,a} & m_{s,b} & -M_S \end{pmatrix} \begin{pmatrix} l_a & l_b & L \\ m_a & m_b & -M_L \end{pmatrix} \end{aligned} \quad (\text{A.3})$$

where  $N = 2$  if the subshells ( $a$  and  $b$ ) are the same, and is 1 otherwise. The  $()$  are 3j symbols.