

Improved RCI Techniques for Treating $4f^n$ Atoms and Ions: Application to Gd IV Energies

Donald R. Beck and Eric Domeier

Abstract: Relativistic Configuration Interaction results for energy levels and Landé g -values of Gd IV $4f^7$ $J=7/2$ and Gd IV $4f^65d$ $J=5/2, 7/2, 9/2$; and energies of 51 new levels are presented. The average error between adjacent energy levels in $4f^7$ is 4.5%. Significant improvements in computational efficiency and accuracy for the difficult to treat $4f^7$ and $4f^65d$ states are introduced, including: use of *ab initio* determined shifts of diagonal matrix elements (ME) for $4f^6$ parents, neglecting off-diagonal MEs between quadruple (triple) excitations, and a more systematic treatment of radial convergence.

PACS No.: 31.15.am, 31.15.vj

1. Introduction

This article is dedicated to Prof. Walter Johnson in appreciation of a lifetime of significant contributions to atomic physics. His work with Desiderio [1] on QED effects in many electron atoms still nearly represents state-of-the-art for heavy atoms possessing more than 1 open shell electron 37 years after it first appeared. I also had the pleasure of having one of his Ph.D. students as a postdoc who, using Relativistic Many Body Perturbation Theory, resolved problems with the electron affinity of Yb [2] and Kr I f -values [3].

Atoms and ions with $4f^n$ configurations are of tremendous complexity for the *ab initio* computationalist, because a large N- and 1- electron basis set is required, the high angular momentum ($l=3$) involved and the associated slow convergence of the expansions. In addition, relativistic effects must be included from the start. Historically, the most successful treatments of these species have been by use of semi-empirical methods [4].

The *ab initio* method discussed here – Relativistic Configuration Interaction (RCI) – has been successfully applied [5] to Fe II, and there are good reasons to believe that most properties of $(d+s)^n$ states lying below the first ionization potential (IP) can be well accounted for via RCI by a sufficiently diligent practitioner. Thus it seems appropriate to turn our attention to $4f^n$ states as the next group of states to offer a major challenge to the *ab initio* computationalist interested in complex systems. These species are of considerable technological importance in condensed matter (high temperature superconductivity, radioactive waste, lasers), plasmas (advanced lighting sources), atomic clocks, etc. It may be noted that $4f^n$ ionic energy levels are often little changed by their surrounding solid state environment. Our specific interest in Gd IV arose from its role in PbF_2 :Gd scintillators [6], and as a possible means of studying the electron electric dipole moment [7].

Donald R. Beck and Eric Domeier, Physics Department
Michigan Technological University
Houghton, MI 49931

2. Methodology

The RCI methodology we employ has been described in detail up to 2006 [5], so we only give a brief summary up to that time. The Hamiltonian used is the Dirac-Breit with the uniform charge distribution nuclear model. Wavefunctions are eigenstates of J^2 , J_z , and parity, and are separated into a reference [e.g. $4f^n$] and a correlation part [e.g. selected single and double excitations from the reference part]. Each N-electron basis function is a linear combination of Slater determinants whose elements are spinors. The radial parts of the reference spinors are determined by solving the Dirac-Hartree-Fock equations numerically [8]. Correlation radial functions associated with unfilled (in the reference) subshells (virtually) are represented by relativistic screened (Z^*) hydrogenic functions (RSH), whose Z^* is determined during diagonalization of the energy matrix (at which time, the Breit operator is also added). Use of RSH prevents collapse of virtuals into the positron sea.

2.1. What are the limitations?

Our approach to RCI is to use a very efficient basis set, and have typical CPU times of less than 1 day. For the PC in hand [AMD 2.4GHz CPU] and the code we've developed [5, 9], this means matrices of order 20 000 or less, 1M determinants (dets) or less, and 75M coefficients or less.

An efficient basis set produces wavefunctions that can be used to readily calculate other properties (e.g. f -values, including non-orthonormality effects), and properties that can be readily analyzed to determine what the important correlation effects are.

Our RCI program [9] is determinantal based with the matrix element structure explicitly constructed. This allows its reuse for determining Z^* 's, for adding new basis functions (existing structure is reused), etc. Structure construction CPU costs are $\sim 70\%$ of the total, mainly arising from the distribution of coefficient products arising from a pair of determinants to individual matrix element structures. Thus the total number of coefficients, and to a lesser extent, the total number of determinants accounts for most of the CPU cost.

To constrain the order of the matrix, we need to develop well converged N- and 1- electron basis sets. For the former, we employ REDUCE [5, 9], which rotates the original basis set for a correlation excitation [e.g. $4f^2 \rightarrow v h^2$] to maximize the number of zero interactions with the reference functions [e.g. the

50 $4f^7$ $J=7/2$ vectors]. Rotated $4f^5vh^2$ $J=7/2$ vectors yielding zero interactions are then discarded. REDUCE yields nearly 10 fold reductions in basis set size (See Table 1) with little energy loss (differentially, well below 100 cm^{-1}), but each of the survivors uses the full set of dets, and that increases the CPU cost of constructing the surviving structure. Additionally, prior to the improvement in REDUCE discussed below, CPU times for each REDUCE calculation (and there could be dozens of them) could be several hours on an AMD 2.4 GHz CPU for Gd IV.

To develop the 1-electron virtual radials (RSH), a series of “ 2×2 ” separated RCI calculations are done. For example, $4f^7+4f^5vh^2$ is done separately to determine $Z^*(vh)$, and to see how many RSHs are needed ($l=5$) to achieve convergence. These runs are also used to determine whether a specific excitation (e.g. $4f^2 \rightarrow vh^2$) should be included in the final combined run.

Table 1 lists the correlation included in the final combined run for E(6G)-E(8S). This excitation energy is displayed as it exhibits the greatest energy change between the separate and combined runs. The largest changes occur for $4d^2 \rightarrow 4f^2$, $4d^2 \rightarrow vf^2+vd^2+vg^2$, $4d \rightarrow vg$. The triple and quadruple excitations we chose to explore (e.g. see Table 1) were formed from products of these single and pair excitations. The table also indicates the size (difficulty level) of the computational problem.

2.2. Computational Efficiencies Introduced Recently

While some of these may appear to be technical details, they can be implemented by other scientists employing RCI methods.

1. Implementation of bit-packed REDUCE. Savings factor: $3 \times$

Allows speedy (1 linear vs a quadratic search) comparison of two dets to determine how they are related. The number of dets increases dramatically with l (see Table 1). Previously implemented in the RCI code.

The set of rotated [REDUCE] vectors can be further decreased by using a more limited reference set (rather than the full set as we do now). For example for $4f^7$ $J=7/2$, there are 50 vectors. If we were only interested in the bottom 10 energy levels, we could use the bottom 10 Dirac-Fock (DF) [8] vectors as references, decreasing the number of REDUCE survivors (for ALL correlation configurations) an additional 5 fold. We have successfully demonstrated this for a few calculations. Should this prove too restrictive, the $4f^7$ portion of a limited RCI calculation could replace the 10 DF references.

2. Setting matrix elements $\langle Q|H|Q' \rangle$, $\langle T|H|T' \rangle$, $\langle Q|H|T \rangle=0$ when $Q \neq Q'$, $T \neq T'$. Savings factor: $5 \times$ [e.g. 10 hrs to 2 hrs].

The same strategy was used in treatment of Breit operator introduced earlier [5]. When necessary, triple and quadruple excitations are split to allow their accommodation by the RCI program [9]. Triple (T)/quadruple (Q) excitations formed from the product of an important single (S)/double (D) excitation and an important double excitation are likely to be the most important second order effects. The $4d^74f^9vg$ triple excitation, formed from

the $4d \rightarrow vg$ single excitation (from the $4f^7$ reference) and the $4d^2 \rightarrow 4f^2$ double excitation is such an example. This triple is too large to be included directly; specifically it has too many (57 million) coefficients (see Table 1). To gauge its impact, we do a series of smaller calculations with the 4 configurations: $4d^{10}4f^7$, $4d^84f^9$, $4d^94f^7vg$ and $4d^74f^9vg$ (Ti), where (Ti) indicates that we have included only a portion of the T eigenvectors in each of the i calculations. In this case, the effect of the triple excitations for each of the calculations on the $^6G-^8S$ energy difference was no more than a few cm^{-1} , so this T is a little consequence.

Philosophy: These matrix elements (ME) are of higher order [beyond 4th in energy] and are consistently dropped, because 4th order is incomplete. However, diagonal elements such as $\langle T|H|T \rangle$ are retained, in case second order energy denominators such as $H_{D,D} - H_{D',D'}$ are small

3. A more systematic treatment of radial and angular convergence of pair correlation, using published [10, 11] results for closed shell systems.

Key arguments: Non-relativistic (NR) bi-virtual pair correlation is approximately expressible as a linear combination of group factors (β 's) and radial pair energies (ϵ 's). These ϵ 's are roughly independent for nearby Z 's & N 's [12, 13]. The β 's can be determined from “standard” angular momentum theory [12].

Jankowski *et al* [10] have the $4f^2$ ϵ 's for Yb I $4f^{14}$, computed at 2nd order, decomposed by angular type. For the NR closed shell case the $\beta = (2S + 1)(2L + 1)$.

Assuming NR, for $4f^7$ we compute the β 's for the $4f^2$ (1S , 3P , 1D , 3F , 1G , 3H and 1I) pairs. This assumes the $4f^7$ levels are pure LS (which is not very accurate, except for the lowest levels) However, one can choose to work with a pure LS basis during the convergence assessment part of the RCI process.

We then use the [10] ϵ 's for Yb I with the $4f^7$ β 's to predict each angular pair contribution [i.e. $4f^2 \rightarrow vlv'l'$] to energy differences (dE). (Contributions are assigned using intermediate normalization). We then compare this prediction to what was achieved in a partial RCI calculation on Gd IV $4f^7$ for this excitation [$4f^2 \rightarrow vlv'l'$]. If there is a significant difference (say $> 50 \text{ cm}^{-1}$), we add an additional radial function (RSH) to vl (and/or) vl' and optimize their Z^* 's during this partial RCI stage. Once this stabilizes, this excitation is considered complete. Angular convergence is determined by seeing when the prediction (using Jankowski *et al* [8] ϵ 's) drops below a few tens of cm^{-1} .

Usually there is good agreement between Jankowski [10] and what we achieve. However, in a few low l cases of importance, e.g. $4f^2 \rightarrow vd^2$, our values differ considerably, even where we have used 3 virtuals. This seems ascribable to the different order of calculations done. Jankowski's is pure 2nd order; ours (matrix diagonalization) includes higher orders. It is just such excitations that show the greatest change between the separate (Table 1) and combined (final) RCI calculations.

4. Use of *ab initio* determined relative shifts for $4f^6(L_p, S_p)5d$ diagonal matrix elements.

The $4f^65d$ levels are even more complicated than $4f^7$, due to the excitation of one electron out of $4f$ into a new subshell [e.g. $4f^7$ $J=7/2$ has 50 vectors; $4f^65d$ $J=7/2$ has 371 vectors]

While the bottom few levels mainly have $4f^6$ coupled to 7F (see Tables 3-5), levels “soon” acquire significant contributions from 5X , especially 5D and 5G . These have substantially different correlation contributions from $4f^2 \rightarrow vlv'l'$ excitations than does 7F . At this development stage it seems unlikely that one can include these differences in a fully *ab initio* manner.

From Table 1, we can anticipate that the most important contributions to dE for $4f^6$ will come from $4f^2 \rightarrow vf^2+vg^2$ and $4d^2 \rightarrow 4f^2$ (an exclusion effect). We have included these in (separate) RCI calculations for Gd V $4f^6$, where the references are constrained to be LS functions. The correlation energy from these Gd V $4f^6$ calculations is then used as a relative shift for the Gd IV $4f^65d$ calculations with an improvement of up to 3500 cm^{-1} in the position of the upper (non 7F) levels. Technical note: in the cases of multiple $4f^6$ LS parents, an average shift is used. It is also assumed that the shift is independent of J . Both these assumptions can be removed (tailoring the shifts to individual references) in the future.

3. Results and Conclusions

3.1. $4f^7$ Levels

In Table 2, we give the energy differences (relative to 8S) and the Landé g -values for the lowest 19 $4f^7$ $J=7/2$ levels. The upper 9 levels and all the Landé g -values have been previously unavailable. The levels labelled “mix” are so impure that any LS label is not useful. For example, the level at 55267 cm^{-1} is 23% 6G , 23% 4D , 11% 2F , with the other pieces < 10%. These labels are determined from the reference part of the wavefunction only. Landé g -values, on the other hand, are determined using the entire wavefunction. Our energy level results are on average 2132 cm^{-1} higher than observation [14]. As might be expected, the semi-empirical “Cowan” values [7] show a better average agreement (1153 cm^{-1}), and the small, older RCI values [7] have a worse (4275 cm^{-1}) agreement on average.

Achieving < 1000 cm^{-1} dE accuracy by RCI has recently become [15] a reasonable goal, and perhaps a similar limit can be attained in the next few years for $4f^n$ levels too. Rather large average errors in energy differences relative to the ground state seem somewhat characteristic of RCI, in some measure – perhaps because the reference radial space is created by solving the Dirac-Hartree-Fock equations for the lowest energy level (8S , here). The more important concern in energy difference accuracy is how well one does in positioning adjacent energy levels of the same symmetry, as this determines how accurate the mixing of the basis functions is [5]. Using this measure, our RCI results for the average difference in adjacent energy levels is 698 cm^{-1} or 4.5%. This low percentage suggests the mixing of basis functions is likely to be fairly good. It also suggests there is little near degeneracy among the bottom 5 $4f^7$ energy levels, as is obvious by inspection.

3.2. $4f^65d$ $J=9/2, 7/2, 5/2$ Levels

Our calculations included the following single excitations: $5d \rightarrow vd+vg$, $4f \rightarrow vf$, $4p+5p \rightarrow 4f$ and $5s \rightarrow 5d$. Calculation times were ~ 4.0 hrs for the final combined runs. The contribution from $5p \rightarrow 4f$ was differentially quite significant and should be included in all future calculations. We also examined correlation associated with the $4f, 5d$ pair, but this was differentially insignificant. The lowest 9-10 energy levels have $4f^6$ mainly coupled to 7F , and our RCI results are in close agreement with the semi-empirical Cowan-type results [7], except for the ${}^{6,8}P$ levels which exhibit big changes from $5p \rightarrow 4f$.

Above these “ 7F ” levels, $4f^6$ is next coupled (mainly) as 5D or 5G . These couplings have a substantially different correlation energy than 7F [$\sim 0.4 \text{ eV}$]. Direct inclusion of $4f^2$ pair correlation (e.g. $4f^2 \rightarrow vg^2$) in a RCI combined run is computationally too expensive at present, so we’ve resorted to *ab initio* determined shifts of $4f^6$ (S_p, L_p) $5d$ diagonal matrix elements. Table 1 suggests that the differentially most important $4f^2$ pair correlation comes from the excitations $4f^2 \rightarrow vf^2+vg^2$; the important $4d^2 \rightarrow 4f^2$ “exclusion” effect also must be included. These excitations have been included in a series of Gd V $4f^6$ (S_p, L_p) calculations, from which we extract the shifts. If there is more than one level for fixed (S_p, L_p, J_p), an average value was created. In the future, this averaging could be removed if necessary (it works well here).

We then return to Gd IV $4f^65d$, where we use reference basis functions $4f^6$ (S_p, L_p) $5d$ and introduce the appropriate shift (relative to 7F , to avoid having to introduce equivalent shifts in differentially important excitations already present, such as $5p \rightarrow 4f$).

With these shifts we agree with all the available [7] Cowan-type dE’s for $4f^65d$ to within a few hundred cm^{-1} , except for some of the ${}^{6,8}P$ levels (where we should be more accurate). In Tables 3-5 we include previously unavailable Landé g -values, obtained using the entire combined wavefunction.

We label each of the energy levels with the $4f^6$ parent (some levels have 2 significant parents) and an LS label for all 7 electrons. Both of these are obtained solely from the reference part of the wavefunctions. Due to RCI restrictions [9] (< 1000 dets in a reference function), LS reference functions were constructed independently, and their overlap with the RCI reference functions were then obtained. For many levels, LS labels are of little utility. For a few (“mix”) there is no value in specifying LS at all. For meaningful LS labels, there is good consistency with pure LS Landé g -values [4]. The few experimental energies available [9] for $4f^65d$ involve sextet electric dipole transitions. The 10 observed $4f^65d$ levels thus lay in the middle of our $4f^65d$ energy levels [the octets are lower] and comparing them with our RCI values is difficult in the absence of measured Landé g -values. Our comparison is based on LS labels only-despite their imperfection.

4. Remaining Difficulties

1. Excitation energies for $4f^7 \rightarrow 4f^65d$ transitions. Normally, we would extract these from experiment – but for Gd IV the correspondence of the few observed energy levels to computed levels is difficult because the lower even octet levels are missing, and there are no observed g -values.

On the other hand, there are difficulties in carrying out *ab initio* calculations – because the “active” 4f electron’s radial may be “core-like”. This would seem to mean that in addition to the necessity of including 4f² pair correlation, 4d4f (and perhaps other) pair correlation may be necessary.

Now the ionization potential of Gd IV is known [2] to be ~ 44.0 eV. It seems reasonable that if we can account for this accurately, we should also be able to account for the 4f⁷ \rightarrow 4f⁶5d excitation energies. The Dirac-Fock IP is about 1.23 eV higher than experiment [4]. We can estimate the 4f² pair correlation by computing the angular factors [12] and using published [10] radial pair energies. With this addition the IP is 0.11 eV too low. This is $\sim 1\%$ of the excitation energies, and suggests this method is adequate to determine reasonably accurate excitation energies.

2. However, for spectra where there are near degeneracies of the same symmetry (parity, J) involving Rydberg series and core-like perturbers such as Mo VI 4p⁶*nf* and 4p⁵4d² $J=5/2$ [16] and Yb I 4f¹⁴6s*np* and 4f¹³5d²6s [4, 17] there remain considerable difficulties in performing a completely *ab initio* treatment. Placement of the perturber relative to the series is critical in determining the proper mixing of the basis functions into the wavefunction, and this mixing is strong (of the Symmetric-Exchange of Symmetry or SEOS [18] type) as it involves $d^2 \leftrightarrow pf$. These calculations may well require extensive accurate treatment of core-valence and core-core correlation.
3. A third incompletely resolved issue is how to include triple and quadruple excitations for 4f^{*n*} states in a more systematic manner. While we have made some progress in this area, much more needs to be done – in principle. Fortunately in the present instance (likely due to the rather high ionicity) these contributions seem very moderate.

5. Acknowledgements

Support from the National Science Foundation, grant No. PHY-0097111 is gratefully acknowledged.

References

1. A. M. Desiderio and W. R. Johnson, Phys. Rev. A **3**, 1267 (1971)
2. E. N. Avgouostoglou and D. R. Beck, Phys. Rev. A **55**, 4143 (1997)
3. E. N. Avgouostoglou and D. R. Beck, Phys. Rev. A **57**, 4286 (1998)
4. W. C. Martin, R. Zalubas, and L. Hagan, Atomic Energy Levels—the Rare Earth Elements, NSRDS-NBS60, U. S. GPO. Washington, DC (1978)
5. D. R. Beck, Phys. Scr. **71**, 447 (2005)
6. Huitian Jiang, private communication. Related work may be found in: H. Jiang *et al.*, J. Phys. Cond. Matt. **16**, 3081 (2004).
7. V. A. Dzuba, O. P. Sushkov, W. R. Johnson, and U. I. Safronova, Phys. Rev. A **66**, 032105 (2002)
8. J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975)
9. Program RCI, D. R. Beck, unpublished (1978-present). Restrictions: Matrix order < 20K, # of dets < 750K, # cofs < 75M
Program REDUCE, D. R. Beck, unpublished (1987-present)
10. K. Jankowski, P. Malinowski, A. Sokolowski, I. Lindgren, and A. -M. Martensson-Pendrill, Int. J. Quant. Chem. XXVII, 665 (1985)
11. D. Datta and D. R. Beck, Phys. Rev. A **47**, 173 (1993)
12. D. R. Beck and C. A. Nicolaides in *Excited States in Quantum Chemistry*, C. A. Nicolaides and D. R. Beck, editors, D. Reidel, Dordrecht (1978) p.105ff
13. I Oksuz and O. Sinanoglu, Phys. Rev. **181**, 54 (1969)
14. J. F. Kielkopf and H. M. Crosswhite, J. Opt. Soc. Am. **60**, 347 (1970)
15. D. R. Beck, J. Phys. B. **40**, 651 (2007)
16. L. Pan and D. R. Beck, Phys. Scr. **73**, 607 (2006)
17. D. R. Beck and E. Domeier, unpublished (2007)
18. D. R. Beck and C. A. Nicolaides, Int. J. Quant. Chem. Symp. **8**, 17 (1974)

Table 1. N-electron Basis Sets and Major Energy Contributions (in eV) for Gd IV $4f^7 6G - 8S J=7/2$

Excitation	# Vectors ^a			⁶ G- ⁸ S dE (in eV) ^b		
	Actual	Max	#Dets	#Coefs	Separate	Combined
$4f \rightarrow vf$	466		3.0K	0.2M	0.166	0.163
$4f \rightarrow vh$	508		4.3K	0.3M	0.111	0.104
<hr/>						
$4f^2 \rightarrow vp^2$	415		2.3K	0.1M	0.013	0.008
$4f^2 \rightarrow vd^2$	149(R)	1073	6K	0.6M	0.114	0.059
$4f^2 \rightarrow vf^2$	198(R)	1758	12.K	1.7M	0.202	0.173
$4f^2 \rightarrow vg^2$	199(R)	1921	18.K	2.7M	0.112	0.073
$4f^2 \rightarrow vh^2$	199(R)	1921	24.K	3.6M	0.030	0.014
$4f^2 \rightarrow vpvf$	99(R)	1864	11K	1.1M	0.021	0.012
$4f^2 \rightarrow vdvf$	149(R)	3070	23K	0.8M	0.062	0.046
$4f^2 \rightarrow vfvh$	149(R)	3233	35K	1.3M	0.019	0.010
$4f^2 \rightarrow vgvf$	149(R)	3233	47K	1.8M	0.027	0.016
<hr/>						
$5p \rightarrow 4f$	240		2K	.05M	0.022	0.020
$5p \rightarrow vp$	349(R)	1548	17K	2.9M	-0.047	-0.036
$5p \rightarrow vf$	198(R)	2980	19K	3.7M	0.030	0.021
<hr/>						
$5p^2 \rightarrow 4f^2$	415		2K	0.1M	0.023	0.015
<hr/>						
$5s \rightarrow vs$	188		1K	.05M	-0.015	-0.013
$5s \rightarrow vd$	823		11K	0.5M	0.114	0.110
<hr/>						
$4d \rightarrow vg$	594(R)	5182	77K	11.4M	0.024	0.002
<hr/>						
$4d^2 \rightarrow 4f^2$	1073		13K	0.7M	0.281	0.168
<hr/>						
$4p \rightarrow 4f$	240		2K	.05M	0.135	0.125
$4p \rightarrow vf$	198(R)	2980	19K	3.7M	0.031	0.021
<hr/>						
$4p^2 \rightarrow 4f^2$	415		2K	0.1M	0.031	0.031
<hr/>						
$4s4d \rightarrow 4f^2$	519		3K	1.4M	0.030	0.022
<hr/>						
Totals	8498	36065	327K	57M	1.536	1.164^c
<hr/>						
RCI CPU time (on AMD 2.4 GHz) is ~ 36 hrs (Combined Run)						
<hr/>						
Quads, Trips						
<hr/>						
$4f^4 \rightarrow vf^2vg^2$	26613		283K	374M		
$4d^4 \rightarrow 4f^4$	1021		13.6K	0.6M		
$4d^3 \rightarrow 4f^2vg$	32463		261K	449M		

^a The # of vectors, dets, and coefficients is given for 1 virtual/*l* only. (R) indicates vectors compressed using REDUCE [7]. K = 1000 ; M = 1 000 000

^b dE > 0 means ⁶G is lowered more than ⁸S by correlation.

^c The Dirac-Fock contribution is 7.843 eV.

Table 2. Energy Differences (cm^{-1}) for Gd IV $4f^7$ $J=7/2$ Levels

Label	Landé g	dE(RCI-BC)	dE(RCI-BS)	dE(RCI-Z)	dE(C-Z)	Expt
^8S	1.991	0	0	0	0	0
^6P	1.675	33908	33080	37103	33018	32084
^6I	0.463	37692	38035	38833	36109	35808
^6D	1.585	42618	42035	45120	41877	40599
$^6\text{G F}$	1.190	52317	49197	54061	51626	49526
mix	1.189	55267	55170			
$^6\text{F G}$	1.285	57948	56796			
$^4\text{H D}$	0.960	59022	58147			
^6H	0.882	61384	60048			
mix	1.085	64336	63022			
^4H	0.768	67126	65894			
^4G	0.985	68553	67295			
$^4\text{G F}$	1.037	70042	69561			
mix	1.048	71013	71162			
$^4\text{D F}$	1.247	72696	70679			
$^4\text{G D F}$	1.155	76845	75282			
^4H	0.722	79622	78107			
$^4\text{D G F}$	1.184	81019	80518			
mix	1.051	81106	79406			

Note:

Experimental energies [14] are absolute values.

RCI-Z (C-Z) are RCI (Cowan-type) calculations [7]

RCI-B(C,S)= this work. The S column adds correlation effects missing from the combined (C) run to the $4f^7$ diagonal matrix elements, as obtained from separate RCI calculations. The S column contains the preferred RCI values.

Table 3. Energy Differences (cm^{-1}) for Gd IV $4f^6 5d$ $J=9/2$ Levels

Label	Landé g	dE(RCI-B)	dE(RCI-Z)	dE(C-Z)	Expt
(⁷ F) ⁸ H	1.209	0	0	0	
(⁷ F) ⁸ D	1.686	4396	5383	4330	
(⁷ F) ⁸ F G	1.483	6439	6996	6317	
(⁷ F) ⁸ G F	1.596	7078	7679	6862	
(⁷ F) ⁸ P	1.646	7141	13497	8173	
(⁷ F) ⁶ H	1.083	11041	14939	11052	
(⁷ F) ⁶ F D	1.462	15608	20299	15528	114214
(⁷ F) ⁶ D F G	1.480	18063	23189	17704	117229
(⁷ F) ⁶ G F	1.304	20176	25017	19378	120220
(⁵ D) ⁶ G	1.284	25990	29801	25734	
(⁵ G) ⁶ I	0.890	29431			
(⁵ D) ⁶ F	1.326	29804			
(⁵ G) ⁶ K	1.381	32360			
(⁵ G) ⁶ G H F	1.227	33614			
(⁵ G D) ⁶ F H G	1.390	34343			
(⁵ H) ⁶ K ⁴ I	0.612	34980			
(⁵ G D) ⁶ D F	1.404	35490			
(⁵ G D)mix	1.119	35627			
(⁵ G) ⁶ G I H	1.225	35801			
(⁵ G L) ⁶ D F	0.833	36719			
(⁵ F G) ⁶ I ⁴ I	1.071	37638			
(⁵ G F)mix	1.010	38820			
(⁵ L)mix	0.629	39031			

Notes:

1. Labels are given as $4f^6(XX) 5d YY$ as determined from the reference part of the wavefunction. Landé g -values are from full wavefunction. Uses 322 out of 377 P (no ¹H). Shift+Breit included.
2. Experimental energies [14] are absolute values.

Table 4. Energy Differences (cm^{-1}) for Gd IV $4f^6 5d$ $J=7/2$ Levels

Label	Landé	dE(RCI-B)	dE(RCI-Z)	dE(C-Z)	Expt
$(^1F)^8H$	1.048	0	0	0	
$(^7F)^8D$	1.792	4178	5295	4199	
$(^7F)^8F G$	1.512	6280	6848	6140	
$(^7F)^8P$	1.866	6856	7883	6954	
$(^7F)^8G F$	1.493	7117	13026	8063	
$(^7F)^6P$	1.729	9417	14454	9906	109005
$(^7F)^6H$	0.841	11314	15323	11348	
$(^7F)^6F D$	1.449	15514	20248	15499	113129
$(^7F)^6D F$	1.475	18109	23632	18050	116230
$(^7F)^6G$	1.192	20248	25495	20073	119292
$(^5D)^6G$	1.174	24222	27669	23965	
$(^5D)^6F D$	1.392	28158			
$(^5G)^6I$	0.465	30061			
$(^5D)^6D F$	1.489	31347			
$(^5D)^4G F$	1.151	33542			
$(^5G)\text{mix}$	1.220	33933			
$(^5G)\text{mix}$	1.079	34640			
$(^5DG)\text{mix}$	1.427	35547			
$(^5G)\text{mix}$	1.104	36015			
$(^5DG)\text{mix}$	1.438	36597			
$(^5GD)^6D^4D$	1.485	37116			
$(^5FG)\text{mix}$	1.073	38221			
$(^5DG)\text{mix}$	1.264	38740			

Notes:

1. Labels are given as $4f^6(XX) 5d YY$ as determined from the reference part of the wavefunction. Landé g -values are from the entire wavefunctions. Uses 367 out of 377P. Shift+Breit included.
2. Experimental energies [14] are absolute values.
3. RCI-Z (C-Z) are RCI (Cowan-type) calculations [7]. RCI-B = this work

Table 5. Energy Differences (cm^{-1}) for Gd IV $4f^6 5d$ $J=5/2$ Levels

Label	Landé g	dE(RCI-B)	dE(RCI-Z)	dE(C-Z)	Expt
$(^1F)^8H$	0.693	0	0	0	
$(^7F)^8D^6P$	1.994	3481	4734	3487	
$(^7F)^8FG$	1.553	6183	6766	6024	
$(^7F)^8P^6P$	2.133	6654	7922	6940	
$(^7F)^8GF$	1.477	7126	11770	7516	
$(^7F)^6P^8D$	1.981	8265	13672	8833	106493
$(^7F)^6H$	0.312	11550	15636	11594	
$(^7F)^6FD$	1.435	15503	20138	15492	111745
$(^7F)^6DF$	1.458	18071	23543	18038	
$(^7F)^6G$	0.936	20320	25565	20112	118109
$(^5D)^6G$	0.926	22656	25845	22451	
$(^5D)^6F$	1.354	26747			
$(^5D)_{\text{mix}}$	1.617	29516			
$(^5D)^6D^4P$	1.452	31017			
$(^5D)_{\text{mix}}$	0.933	32193			
$(^5D)_{\text{mix}}$	1.510	33743			
$(^5G)^6F^4D$	1.278	34892			
$(^5G)^6HG$	0.572	35022			
$(^5G)^6GH$	0.690	35919			
$(^5D)^6PS$	1.579	36850			
$(^5G)_{\text{mix}}$	1.489	37574			
$(^5D)_{\text{mix}}$	1.401	37947			
$(^5G)^6D$	1.438	38718			

Notes:

1. Labels are given as $4f^6(\text{XX}) 5d \text{YY}$ as determined from the reference part of the wavefunction. Landé g -value are from the entire wavefunctions. Uses 325 out of 329P. Shift+Breit included. The $4f^6(^1H) 5d_{3/2}$ parents are missing (4 of them)
2. Experimental energies [14] are absolute values.