Relativistic configuration-interaction results for Xe^{32+}, Ba^{34+}, Nd^{38+}, and Gd^{42+} ''^5D'' $J=2$ to $J=3$ energy differences

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Errors in relativistic correlated *ab initio* results for the ''^5D'' $J=2$ to $J=3$ $M1$ transition, which is nearly constant with Z, have been reduced from 5% to 1.5% (400 cm^{-1}), on average. Beyond the Dirac-Coulomb level, the principal contributions are from the magnetic operator and certain $n=3$ single and double excitations (correlation effects). [S1050-2947(97)04209-1]

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I. INTRODUCTION

In 1991, a survey of $M1$ lines between ground configurations of highly ionized species was performed by Feldman *et al.* [1] at the Dirac-Fock level. Among other characteristics, they were seeking lines with wavelengths >2500 Å so transmission optics can be employed, and ''reasonably'' intense transitions, which could be used as a diagnostic tool for tokamaks. The ''^5D'' $J=2$ to $J=3$ transition associated with the $3d^4$ configuration (Ti I isoelectronic sequence) was predicted to be a good candidate, and had the unusual characteristic that the energy difference was nearly constant with Z.

In 1995, Morgan *et al.* [2] experimentally observed this line in Ba^{34+} and Xe^{32+}, and in 1996, Serpa *et al.* [3] measured it in Nd^{38+} and Gd^{42+}. *Ab initio* calculations on these lines by Feldman *et al.* [1] and more recently by Indelicato [4] yield energy differences that are characteristically 5% higher than experiment (~ 1400 cm^{-1}), an error that is large for so ''simple'' a system.

II. THEORY

Our wave functions are generated from the Dirac-Coulomb Hamiltonian. Correlation is included by the relativistic configuration interaction (RCI), which has been discussed in detail in earlier work [5,6]. Features important to this work are the following: (1) the reference or zeroth-order function is obtained from the newest version [7] of Desclaux's computer program; (2) correlation effects are well accounted for by single and double subshell excitations from the $n=3$ reference function subshells into unoccupied (virtual) subshells; (3) the virtuals are well represented by one or two (per lj) relativistic hydrogenic radial functions ($n=l+1$; l is that of the major component) providing they are carefully optimized during the RCI process.

Level-dependent magnetic effects are crucial to properly accounting for the transition energy; they are computed as an expectation value of a truncated correlated wave function. Their primary contribution is from the $3d^4$ configuration, and these results have been directly obtained from the Desclaux output [7]. Retardation and radiative effects both make marginal contributions to the transition energies. Both are obtained from the level dependent output of the Desclaux program [7]. In that program, radiative effects are obtained from the Welton picture.

III. RESULTS

The $1s^2 \cdots 3s^2\ 3p^6\ 3d^4$ configuration is a fairly complicated one (4 open subshell $3d$ electrons), with a good deal of energy associated with the $n=3$ electrons. Thus, correlation studies need to be done carefully, and making use of relevant earlier work can be quite useful. In this regard, our 1995

TABLE I. Contributions (in cm^{-1}) to $3d^4$ ''$^5D_3$''-''$^5D_2$'' energy differences.

Origin	Gd^{42+}	Nd^{38+}	Ba^{34+}	Xe^{32+}
Dirac-Coulomb	28 875	28 838	27 694	26 325
$3s \rightarrow 3d$	−386	−394	−357	−316
$3p^2 \rightarrow 3d^2$	258	−16	−164	−161
$3p \rightarrow vp$	152	158	138	117
$3d \rightarrow vs$	15	6	0	−1
$3d \rightarrow vd$	−44	−40	−38	−29
$3s^2 \rightarrow 3d^2$	−35	−40	−31	−24
$3d \rightarrow vg$	−143	−159	−146	−128
$3p \rightarrow vf$	−573	−406	−261	−197
$3d \rightarrow vi$	−19	−17	−14	−12
$3p \rightarrow vh$	−9	−2	−2	2
$3s \rightarrow vd$			−23	−18
Magnetic [a]	−684	−731	−930	−1054
Retardation [b]	4	4	3	3
Misc. [c]	−147			
Radiative [d]	−27	−22	−5	7
Total, this work	27 208	27 179	25 864	24 514
Experiment [e]	26 932	26 645	25 432	24 160
Error	276 (1.0%)	534 (2.0%)	432 (1.7%)	354 (1.4%)
Other theory [f]		Within 5%		

[a]DF + first 3 excitations, including nonaverage effects. DF calculations from 1994 Desclaux program [7].
[b]DF nonaverage.
[c]See Table II. Includes some magnetic contributions.
[d]1994 Desclaux program [7].
[e]Serpa *et al.* [3].
[f]Indelicato [4].

TABLE II. Miscellaneous contributions (in cm^{-1}) to Gd^{42+} ''$^5D_3$''-''$^5D_2$'' splitting. E denotes electrostatic; M denotes magnetic.

$3d\rightarrow$	$vd\ (+91M)$
$3d^2\rightarrow$	$vs^2\ (-1E) + vp^2\ (0E) + vd^2\ (-127E) + vf^2\ (94E) + vg^2\ (1E) + [vd^2 + vf^2]\ (80M) + vsvd(0E) + vpvf\ (-102E) + vdvg\ (-14E) + vfvh\ (-40E) + vdvi\ (-10E) + vsvg\ (-7E)$
$3p\rightarrow$	$vf\ (-14M)$
$3p^2\rightarrow$	$3dvs\ (1E) + 3dvd\ (-1E, -50M) + 3dvg\ (12E)$
$3p3d\rightarrow$	$(0E)$
$3s\rightarrow$	$vs(20E,0M) + vd(-25E) + vg(-2E)$
$3s^2\rightarrow$	$3d^2\ (-2M)$
$3s3p\rightarrow$	$3d[vp+vf]\ (10E,-7M)$
$2p^2 + 2p3p\rightarrow$	$3d^2\ (26E,-3M)$
$2s\rightarrow$	$3d\ (-24E)$
$2p\rightarrow$	$[vp+vf]\ (-42E,0M)$
$3p^3\rightarrow$	$3d^2\ vf(11E)$

work on this configuration for Nb II [8], and the work of Jankowski *et al.* [9] on Zn III are particularly useful in helping to identify which correlation contributions are likely to contribute to the energy differences of interest. Although the latter work [9] is nonrelativistic, our RCI wave functions may be decomposed into LS pieces for the purpose of making some use of the nonrelativistic work. In particular, one can make ''educated guesses'' as to what angular symmetries are important for individual pair energies. Convergence tests for large contributions (to the total energy) are made by adding an additional optimized virtual function to the RCI function. Optimization tests are made by using the virtual function producing the lower energy for one J as input for the other J, and reoptimizing to see if the energy can be lowered further (for the second J). RCI optimization of the virtual effective Z is by brute force percentage change in Z; normally this change is in the 5% range, but for a few virtuals (viz. vd), a 1% change was found necessary to produce a well optimized result.

A summary of our results is given in Table I. As expected, the nearly degenerate internal (or within the complex) excitations $3s\rightarrow 3d$; $3p^2\rightarrow 3d^2$ and to a lesser extent $3s^2\rightarrow 3d^2$ play a big role. As suggested by our Nb II study [8], single excitations play a large differential role, and the largest of these is of the type $l\rightarrow l+2$. These effects are entirely consistent with our 1978 systematic analysis [10] of nonrelativistic correlation effects.

Many other correlation contributions have been explored; these are reported in Table II and their sum under Misc. in Table I. Most of these are of no more than moderate size; the largest correspond to the excitations $3d^2\rightarrow vd^2 + vf^2 + vpvf + vfvh$. It of interest to note that $3p\ 3d$ pair excitations play no role, although it requires thorough calculations to demonstrate this, as individual energies are large (<1 eV). It is also of interest to note the $l=5$ symmetries play a moderate role (symmetries up to $l=6$ were explored). One triple excitation is shown: $3p^3\rightarrow 3d^2\ vf$; $3s3p^2\rightarrow 3d^3$ and the quadruple $3p^4\rightarrow 3d^4$ were explored for $J=3$ (Gd^{42+}), but they are modest ($<60\ cm^{-1}$) and were not computed for $J=2$. Triple and quadruple candidates are chosen by looking for those formed from the products of the largest single and double excitations that most impact the energy difference. Specifically, these singles were $3p\rightarrow vf$; $3s\rightarrow 3d$ and the double $3p^2\rightarrow 3d^2$.

By far the largest contributor in Table I is the nonaverage magnetic part of the Breit operator. Of the ''Magnetic'' entry in Table I, all but a few tens of cm^{-1} come from the $3d^4$ configuration, as evaluated by the Desclaux program [7]. Other contributions (Tables I and II) have been evaluated from portions of the correlated function, using our RCI program [11]. From Table II, the largest of these are $3d\rightarrow vd$; $3d^2\rightarrow vd^2 + vf^2$ and $3p^2\rightarrow 3dvd$.

The ''Misc.'' contributions of Table II have not been calculated for the Nd, Ba, and Xe members of the isoelectronic sequence, and consequently their percentage errors are higher than that for Gd. One might anticpate the correction to be $\sim 150\ cm^{-1}$, which would lower the errors for these to 1.4%, 1.1%, and 0.9%, respectively.

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