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Designations of ds^2p energy levels in neutral zirconium, hafnium, and rutherfordium $(Z=104)$

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We have examined available data for the odd-parity energy-level structures in Zr and Hf, stimulated by the designations of four predicted $6d7s^27p$ levels in the homologous atom rutherfordium (Rf, $Z=104$) by Eliav *et al.* [Phys. Rev. Lett. **74**, 1079 (1995)]. We point out some errors and deficiencies in the Zr data and give the results of Hartree-Fock calculations for Hf $5d6s^26p$ and Rf $6d7s^27p$ levels. Configuration interactions within the $(d+s)^3p$ complexes were included. The resulting eigenvectors allow meaningful LS-coupling designations for most of the levels belonging mainly to Hf $5d6s^26p$ and for most of the predicted Rf levels belonging mainly to $6d7s^27p$. Some changes in the designations assigned to these levels in the literature are suggested: in particular, the lowest level of both Hf $5d6s^26p$ and Rf $6d7s^27p$ is most appropriately designated $^3\mathrm{F}^o_2$. We point out the need for systematic whole-row studies of the low odd-parity configurations in $4d$- and $5d$-shell spectra.

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I. INTRODUCTION

The actinide row of the Periodic Table ends with lawrencium (Lr, $Z=103$), which is followed by rutherfordium (Rf, $Z=104$). The ground-level electron configuration has not been experimentally determined for either of these atoms and is in both cases difficult to predict theoretically. Desclaux and Fricke [1] used multiconfiguration Dirac-Fock (MCDF) calculations and a correction based on data for lighter atoms to predict a [Rn] $5f^{14}\ 7s^27p_{1/2}$ ground level for Lr. This same prediction has recently been made by Eliav *et al.* as a pure *ab initio* result of relativistic coupled-cluster (RCC) calculations [2].

The large relativistic contributions associated with the $7p_{1/2}$ electron in Lr [1] would indicate a low energy for the $7s^27p^2_{1/2}$ $(J=0)$ level in Rf [3]. The most recent published calculations for Rf, however, predict that the ground level belongs mainly to the $6d7s^27p$ configuration [4,5] or to $6d^27s^2$ [6].

The MCDF calculations of Glebov *et al.* [4] and Johnson *et al.* [5] gave the lowest Rf $6d7s^27p$ level as having a J value of 2 and configurational purity of 80%, but no name was assigned in any coupling scheme (*LS*, *jj*, etc.). The recent paper on the low levels of Rf by Eliav *et al.* [6] includes RCC calculated energies and *LS* term designations for the four lowest $6d7s^27p$ levels. These designations were apparently made by analogy [7] with the Zr $4d5s^25p$ levels as tabulated by Moore [8].

Since the designations in [6] of the lowest Rf $6d7s^27p$ level as $^3\mathrm{D}_2$ and another Rf $6d7s^27p$ level as $^3\mathrm{D}_3$ appeared highly unlikely, we have examined the data for ds^2p and dp configurations in spectra of a number of elements, including Zr. In this paper we note some errors and deficiencies in the tabulated data, point out examples showing the expected order of levels in both *LS* and *jj* coupling, and give the results of Hartree-Fock calculations for Hf $5d6s^26p$ and Rf $6d7s^27p$ levels. These calculations include the configuration interactions appropriate to the $(d+s)^3p$ complex. The resulting eigenvectors allow meaningful *LS* coupling designations for most of the levels belonging mainly to Hf $5d6s^26p$ and Rf $6d7s^27p$.

We note here that our calculations are not expected to be as accurate as the more elaborate, fully relativistic calculations cited above [2,4–6], and we have not calculated energies for any Rf configurations other than $(6d+7s)^37p$; our results for Rf do *not* pertain to the question of the ground-level configuration.

II. ZIRCONIUM

The ground-level configurations of the lighter homologues of Rf are Ti $3d^24s^2$, Zr $4d^25s^2$, and Hf $5d^26s^2$. The lowest odd-parity levels in Zr belong to $4d^25s5p$, and the $4d5s^25p$ configuration overlaps both $4d^25s5p$ and $4d^35p$ [8]. Although no calculations of these three odd-parity configurations in Zr have been published, it is clear by analogy with Ti and Hf that strong configuration interactions occur within this $(4d+5s)^35p$ complex. In Ti [9], for example, the distribution of the $3d4s^24p$ eigenvector components among the $(3d+4s)^34p$ levels is such that only three levels can be meaningfully named according to $3d4s^24p$ basis states (the $3d4s^24p$ $^3\mathrm{F}^\circ_{2,3,4}$ levels, having $\sim$67% eigenvector purities). Similar strong configuration-interaction effects can be expected in Zr $(4d+5s)^35p$ and, in any case, the assignments of levels to Zr $4d5s^25p$ terms in [8] should be regarded as highly tentative pending a careful theoretical analysis. Even if such an analysis yields meaningful $4d5s^25p$ names, the order of the resulting terms will almost certainly be quite different from that in [8]. It should also be noted that, obviously by oversight, two separate three-level terms (near 39 000 cm^{-1} and 43 000 cm^{-1}) are designated as $4d5s^25p$ $^3\mathrm{F}^\circ$ in [8]. The Zr II "d^2D" parent term for the higher of these "$^3\mathrm{F}^\circ$" terms was later shown to be spurious [10].

The Ti III $3d4p$ and Zr III $4d5p$ configurations are spectroscopically equivalent to the Ti $3d4s^24p$ and Zr $4d5s^25p$ configurations but are not subject to the strong $(d+s)^3p$ configuration interactions. Thus the observed order of the low terms for Ti III $3d4p$ [9] and Zr III $4d5p$ [11] is consistent with theoretical expectations for reasonably good

TABLE I. Energy levels of Hf $5d6s^2 6p$. All except two of the second percentages in the last column are from the $5d^2 6s6p$ configuration, the $5d^2$ grandparent terms being given in parentheses.

	Experiment		Calculation			
Name	Level (cm^{-1})	g_J	Level (cm^{-1})	g_J	Leading eigenvector percentages [a]	
$^3F^\circ_2$	10 509	0.805	10 867	0.808	43 $^3F^\circ$	27 $^1D^\circ$
$^3D^\circ_1$	14 018	0.542	13 905	0.531	71 $^3D^\circ$	17 $(^3F)^3D^\circ$
“$^1D^\circ_2$”	14 435	0.903	14 348	0.902	35 $^1D^\circ$	23 $^3F^\circ$
$^3F^\circ_3$	14 542	1.085	14 632	1.079	63 $^3F^\circ$	13 $(^1D)^3F^\circ$
$^3D^\circ_2$	16 163	1.172	16 282	1.169	62 $^3D^\circ$	16 $(^3F)^3D^\circ$
$^3P^\circ_1$	18 143	1.428	17 188	1.452	67 $^3P^\circ$	16 $(^1D)^3P^\circ$
$^3F^\circ_4$	18 225	1.246	18 038	1.242	59 $^3F^\circ$	16 $(^1D)^3F^\circ$
$^3P^\circ_0$	18 270		17 110		72 $^3P^\circ$	16 $(^1D)^3P^\circ$
$^3D^\circ_3$	18 382	1.287	18 204	1.311	66 $^3D^\circ$	17 $(^3F)^3D^\circ$
$^3P^\circ_2$	19 791	1.414	19 355	1.408	53 $^3P^\circ$	19 $(^1D)^3P^\circ$
$^1F^\circ_3$	23 645	1.074	24 190	1.059	69 $^1F^\circ$	8 $(^3F)^5D^\circ$
$^1P^\circ_1$	26 464	0.996				

[a] The full ancestry of the $5d^2 6s6p$ $^3D^\circ$ second percentages is $5d^2(^3F)6s$ $(^2F)6p$. The parent terms for the other $5d^2 6s6p$ second percentages are unambiguous.

LS coupling [12]; the $^1D^\circ_2$ level is lowest in both cases, followed by the $^3D^\circ$ term (Ti III) or by overlapping $^3F^\circ$ and $^3D^\circ$ terms (Zr III).

III. HAFNIUM

Wyart's theoretical analysis of the even-parity energy level system of Hf [13] included revisions of Meggers and Moore's designations [14] for a number of levels and also the addition of some new levels. Wyart also calculated the levels of the Hf odd-parity group $(5d+6s)^3 6p$, with values of the energy integrals adjusted parametrically to obtain a least-squares fit of the experimental levels from [14]. No calculated level values nor eigenvector components for the odd-parity group were given in [13], however. We have carried out *ab initio* calculations of the Hf $(5d+6s)^3 6p$ levels, since this method must of necessity be used for Rf.

Since $5d6s^2 6p$ is the lowest odd-parity configuration in Hf [14], it is less affected by the $(d+s)^3 p$ interactions than are the homologous $ds^2 p$ configurations in Ti and Zr. The experimental Hf $5d6s^2 6p$ levels [14] are given in order of energy in Table I, along with the experimental g_J magnetic splitting factors and our calculated values for these quantities. The calculations, which include the $(5d+6s)^3 6p$ configuration interactions, were made with Cowan's Hartree-Fock (HFR) code [15], all electrostatic interactions having been reduced to 85% of their *ab initio* values. For the final calculation, the average energies of both $5d^2 6s6p$ and $5d^3 6p$ were shifted by the same amount to give the lower $5d^2 6s6p$ levels at approximately their experimental positions with respect to the $5d6s^2 6p$ levels, and the energies of all three configurations were then shifted by an overall constant to obtain a least-squares fit to the experimental $5d6s^2 6p$ levels except for the $^3P^\circ$, $^1F^\circ$, and $^1P^\circ$ levels. The agreement between the calculated and experimental positions for the remaining seven $5d6s^2 6p$ levels is fairly good, and the agreement between the calculated and experimental g_J factors is either excellent (within the experimental errors) or good for ten of the eleven levels for which g_J is defined.

The two largest percentages from the calculated eigenvectors are included in Table I, except for the $^1P^\circ$ level. Second-percentage terms from the $5d^2 6s6p$ configuration are given with the $5d^2$ grandparent term in parentheses; all the nominal $5d6s^2 6p$ levels have $5d^2 6s6p$ second percentages except the two lowest levels having $J=2$. The relatively poor fit obtained for the $^3P^\circ_1$ and $^3P^\circ_0$ levels probably arises from effects of the $(5d6s^2+5d^2 6s)6p$ configuration interaction that are not accurately accounted for in our calculation.

The $5d6s^2 6p$ levels above the $^3D^\circ_2$ level (16 163 cm^{-1}) are interspersed among $5d^2 6s6p$ $^5G^\circ$, $^5F^\circ$, $^5D^\circ$ levels [14]. We have omitted any calculated results for the $^1P^\circ_1$ level in Table I because our calculations gave most of the $5d6s^2 6p$ $^1P^\circ_1$ composition distributed among the eigenvectors for three levels above 27 000 cm^{-1}, the largest of these percentages being only 36% and the predicted g_J value being 1.234. The experimental $^1P^\circ_1$ level in Table I is well established, with g_J = 0.996 [14]; an accurate eigenvector for this level probably can be obtained only from a calculation that more accurately predicts its position relative to the nearby $5d^2 6s6p$ levels.

The lowest level in Table I was designated $^1D^\circ_2$ in [14]. We find a total $^3F^\circ_2$ character of 58% for this level, including $^3F^\circ_2$ contributions totaling 15% from $5d^2 6s6p$ and $5d^3 6p$. No *LS* term designation is really appropriate for the level at 14 435 cm^{-1}, named $^3F^\circ_2$ in [14], the largest sum of percentages for a particular term type in its eigenvector being 43% $^1D_2$. The total percentages for particular *LS* term types in our calculated eigenvectors are expected to be rather accurate because of the good agreement between the calculated and observed g_J values.

IV. RUTHERFORDIUM ($Z=104$)

We calculated Rf $(6d+7s)^3 7p$ using a 15% reduction of all electrostatic-interaction integrals for the individual con-

TABLE II. Predicted energy levels of Rf $6d7s^27p$. The four highest levels are omitted.

	Level (eV)		Leading eigenvector	
Name	Ref. [6]	H-F	Percentages^a	
$^3F^\circ_2$	0.274	0.354	53 $^3F^\circ$	23 $^1D^\circ$
$^3D^\circ_1$	1.081	0.996	64 $^3D^\circ$	11$^1P^\circ$
‘‘$^1D^\circ_2$’’	1.366	1.432	34 $^1D^\circ$	21 $^3F^\circ$
$^3F^\circ_3$	1.489	1.428	69 $^3F^\circ$	11 $(^1D)^3F^\circ$
$^3D^\circ_2$		1.743	70 $^3D^\circ$	11 $(^3F)^3D^\circ$
$^3P^\circ_1$		1.802	58 $^3P^\circ$	12 $^3D^\circ$
$^3P^\circ_0$		1.820	78 $^3P^\circ$	12 $(^1D)^3P^\circ$
$^3D^\circ_3$		2.220	53 $^3D^\circ$	25 $^1F^\circ$

[a] Second percentages from the $6d^27s7p$ configuration are given with the $6d^2$ grandparent term in parentheses.

figurations obtained from Cowan's code, in accordance with our Hf calculation, but with the configuration-interaction integrals kept at their full Hartree-Fock values. This procedure gave a $6d7s^27p$ configurational purity near 80% for the lowest $J=2$ level, in agreement with the results of [4] and [5]. For the final diagonalization, we decreased the calculated average energies of both $6d^27s7p$ and $6d^37p$ by a small amount (600 cm^{-1}) relative to $6d7s^27p$ to further adjust this purity to 80.2%.

The results of our calculation for the eight lowest levels belonging mainly to $6d7s^27p$ are given in Table II, along with the energies of the lowest four of these levels calculated by Eliav *et al.* [6]. We have shifted all our calculated levels by a constant to obtain a least-squares fit to the four levels from [6], but deviations as large as 0.08 eV remain between the two sets of values. We believe, however, that, as for Hf, the main eigenvector components from our calculation are accurate enough to determine appropriate designations for these levels. The $^3F^\circ_2$ and $^3F^\circ_3$ levels in Table II were designated as $^3D^\circ_2$ and $^3D^\circ_3$ in [6].

V. TENDENCY TOWARDS *jj* COUPLING IN Hf $5d6s^26p$ AND Rf $6d7s^27p$

Large deviations from *LS* coupling for Hf $5d6s^26p$ and Rf $6d7s^27p$ are apparent from the order of the levels, as well as from the eigenvector percentages, in Tables I and II; the Rf $6d7s^27p$ $^3P^\circ_1$ and $^3P^\circ_0$ levels are the only nominal triplet levels in either table not separated by one or more intervening levels of another term. Although the calculated *jj*-coupling purity of these ds^2p levels in Hf and Rf is rather low, the order of the levels is in fact close to that expected for *jj* coupling with ζ_p (the spin-orbit interaction energy) substantially larger than ζ_d: the theoretical energies of the $(j_dj_p)^\circ$ terms in this case have the order $(\frac{3}{2}\frac{1}{2})^\circ_{2,1}$, $(\frac{5}{2}\frac{1}{2})^\circ_{3,2}$, $(\frac{3}{2}\frac{3}{2})^\circ_{3,2,1,0}$, and $(\frac{5}{2}\frac{3}{2})^\circ_{4,3,2,1}$. The order of the resulting four sets of total J values corresponds to the predicted Rf $5d6s^26p$ structure, the four highest levels not given in Table II having J values appropriate for the $(\frac{5}{2}\frac{3}{2})^\circ$ term. The Hf levels have this same order except that the $^3F^\circ_4$ level is lower.

The tendency of the Hf and Rf levels towards *jj* coupling can be verified by comparison with the $5d6p$ levels in higher spectra of the Yb isoelectronic sequence. In Re VI $5d6p$, for example, the four *jj*-coupling terms are well separated and the *jj*-coupling purity is high [16]. On the basis of calculated eigenvector percentages, these Re VI levels were also assigned alternate, less appropriate, *LS* names [16]. Using these *LS* names for the Re VI levels ordered according to energy, one finds an order very similar to the order of the Hf and Rf levels; aside from the relatively low position of the Hf $^3F^\circ_4$ level, the main difference is an interchange of the $^3D^\circ_2$ and “$^1D^\circ_2$” levels in Re VI as compared with Hf and Rf.

That the Hf and Rf ds^2p configurations are, nevertheless, quite far from *jj* coupling is due not only to the strength of the dp electrostatic interactions but also to electrostatic configuration interactions that do not exist, or are negligible, for Re VI $5d6p$.

VI. CONCLUDING REMARKS ABOUT ENERGY LEVEL DATA FOR *d*-SHELL ATOMS

In addition to extensive calculations for individual atoms and ions of the $3d$ shell, systematic “general least-squares” calculations have been carried out for the lower configurations of both parities in $3d$-shell spectra [17]. In these studies, the matrices for the configurations of a particular parity in species of the same ionization stage are diagonalized in a whole-row calculation in which the experimental levels for all species are used in a single least-squares-fit optimization of the interaction parameters taken as simple functions of Z. The greater accuracy of the interaction-parameter values thus obtained for poorly analyzed spectra yielded more reliable interpretations and predictions for missing levels.

Only a few calculations of this type have been published for $4d$- and $5d$-shell spectra, no doubt in part because the experimental data are less abundant. Shadmi's systematic treatment of the $(4d+5s)^N$ configurations in the neutral palladium-group atoms [18] was apparently never published, and to our knowledge no systematic calculation has been made for the $(4d+5s)^{N-1}5p$ odd-parity configurations in these atoms. Shadmi's calculations included Zr $(4d+5s)^4$, and the levels of this complex were also calculated by Büttgenbach *et al.* [19]; both investigations indicated the need for revisions of the Zr analysis in [8].

Wyart's systematic treatments of even-parity configurations for the neutral and singly ionized sequences of the platinum ($5d$-shell) group also demonstrate the need for more work of this type [13,20]. He revised and extended the energy-level analyses of several spectra of both sequences including, as noted above, Hf I. On the basis of a preliminary study, Wyart indicated the need for similar revisions for odd-parity configurations in several spectra of the $5d$-shell neutral sequence [13]. Aside from the parametric values obtained for the Hf $(5d+6s)^3\,6p$ energy integrals, however, few details were given.

It is clear that more complete and reliable energy-level analyses are needed for a number of $4d$- and $5d$-shell spectra. Systematic theoretical studies of the odd-parity configurations would be a useful guide in improving these analyses, not least in helping to identify those spectra for which new experimental observations are especially needed.

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