Lanthanum group: Detection and correction of errors in orbital binding energy measurements of internal shells

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Abstract. Experimental data on electronic binding energies in a ground state of lanthanides are analyzed. Internal individual shells $K$, $L$, $M$, $N$ are studied in detail. The data scatter is discussed. Atomic number similarity law of orbital binding energies is shown and deviations from it in some experimental results are treated as measurement errors. Polynomial interpolation of patterns makes it possible to restore missing and correct erroneous data. Comparison is made with experimental data from other sources and theoretical results.

1. Introduction
The lanthanum group is the elements of atomic numbers $Z = 58–70$ in which the internal $4f$ shell is filled. At one time, the empirical Mosley law [1] of x-ray spectral lines dependence on atomic number solved the problem of this group location in the periodic table. Another empirical atomic number similarity law has been discovered in the paper [2], in which the semiclassical method [3] has been applied to the study of experimental orbital binding energies in individual $K$ and $L$ shells of many-electron atoms.

In present work, to answer this question if the similarity law also occurs for other electron shells, we extend our previous study to analyze the available experimental data [4–6] in $M$ and $N$ shells of the lanthanides. The binding energies [7] as computed in relativistic local density functional approximation (RLDA) [8] are also analyzed.

A comparison of different data sources reveals lack of some experimental data, a difference between experiment and theory, a scatter of experimental values in some cases. Another aim of our study is to organize existing data on internal orbital binding energies in the elements $Z = 57–70$ (lanthanum itself is also included in the study group) using the atomic number similarity law.

To analyze electron energy levels $\{E_{nlj}\}$ in atoms (where the orbital binding energy is equal to $|E_{nlj}|$), we use two functions $e_n(\sigma)$ and $d_{nlj}(\sigma)$ defined as follows:

$$\begin{align*}
\sigma_n &= \pi n Z^{-1/3}, \\
e_n &= E_{n0} Z^{-4/3}, \\
d_{nlj} &= (E_{nlj} - E_{n0}) Z^{-2/3} \lambda^{-2}.
\end{align*}$$

(1)

Here the values $\sigma$ and $e$ are the electron action and orbital energy for $Z = 1$, $n$ and $l$ are main and angular quantum numbers, $\lambda = l + 1/2$; for $l > 0$ $j = l \pm 1/2$ is a total electron momentum with account for relativistic spin-orbit interaction.

Hereinafter atomic units ($\hbar = m_e = \epsilon = 1$) are used if another is not indicated.
2. Orbital binding energies in internal shells \(K\), \(L\), \(M\), \(N\)

In figure 1 the experimental binding energies in \(K\) and \(L\) shells from database [4] are represented through the functions \(e\) and \(d\), see equation (1). Hereinafter in the figures smaller values \(\sigma\) correspond to larger atomic numbers \(Z\), number below or above the symbol is equal to \(Z\). The relativistic spin-orbit interaction effect for the electron states \(2p_{1/2}\) and \(2p_{3/2}\) is well seen in figure 1(b). The effect continuously increases from right to left as atomic number rises.

All experimental points in the figures form very smooth dependencies that are interpolated by quadratic polynomials

\[
\lg |e_n(\sigma)| = 2 \sum_{k=0}^{2} a_{k}^{(n)} \sigma^k, \quad \lg d_{nlj}(\sigma) = 2 \sum_{k=0}^{2} b_{k}^{(nlj)} \sigma^k, \tag{2}
\]

with their coefficients \(a_k^{(n)}\), \(b_k^{(nlj)}\) being in table A1 in appendix.

Using the relations

\[
E_{nlj} = Z^{4/3} e(\sigma_n) + Z^{2/3} d_{nlj}(\sigma_n) \lambda^2, \quad \sigma_n = \pi n Z^{-1/3}, \tag{3}
\]

and the function interpolations of form (2), one can estimate the orbital binding energies. The approximation error for shells \(K\), \(L\) does not exceed percent fractions.

Figure 2 shows the \(M\)-functions \(\lg |e_3(\sigma)|\), \(\lg d_{3lj}(\sigma)\) and \(N\)-functions \(\lg |e_4(\sigma)|\), \(\lg d_{4lj}(\sigma)\) for the lanthanides except promethium: there are no the values \(E_{3s}\), \(E_{4s}\) for it, although its other energies of these shells are available in [4].

One can see a smooth \(M\)-functions behavior in figure 2(a). The polynomial interpolation of the data gives a good fit (see the coefficients in table A1 in appendix) with an inaccuracy less 0.5%. In table 1 some estimated energies are shown in comparison with the experimental [4–6] and theoretical RLDA results [7]. Specifically the interpolation allows estimating the missing \(3s\)- and other energies for the promethium. The proximity of all the estimated its \(M\)-energies to the experimental data from [4–6] perfectly confirms the atomic number similarity law for the \(M\) shell.
Figure 2. The functions $\log|e_3(\sigma)|$, $\log d_{lj}(\sigma)$ (a) and $\log|e_4(\sigma)|$, $\log d_{lj}(\sigma)$ (b) from the data [4] for the lanthanides: symbol $\triangle$ is used for d-states ($l = 2$), symbol $\square$—for f-states ($l = 3$); full symbols are used for $j = l - 1/2$, open ones—for $j = l + 1/2$; other notations are the same as in figure 1.

Figure 3. The functions $\log|e_4(\sigma)|$ and $\log d_{lj}(\sigma)$ from the experimental data [6] (a) and from results of RLDA calculations [7] (b): notations are the same as in figures 1 and 2.

Figure 2(b) shows similar smooth dependencies for $N$ shell ($n = 4$) from experimental data [4] except for randomly scattered points $\log d_{4p1/2}(\sigma)$. However, discarding apparent outliers, in this case we used linear interpolation for the remaining values. Coefficients of polynomial interpolations (2) for $N$ shell are available in table A1 in appendix.

The validity of this approach is confirmed by figure 3. Atomic number similarity for the binding energies in the $N$ shell is clearly seen in experimental data [6] [see figure 3(a)] and
Table 1. Binding energies $|E_{nlj}|$ (eV) estimated by equation (3) in comparison with data from experiments [4–6] and RLDA calculations [7].

| Z  | n  | lj   | (3)  | [4]        | [5]        | [6]        | [7]        |
|----|----|------|------|------------|------------|------------|------------|
| 61 | 3  | s    | 1.650×10³ | —         | —          | 1.651×10³ | 1.586×10³ |
|    |    | p$_{1/2}$ | 1.472×10³ | 1.471×10³ | —          | 1.397×10³ | a 1.423×10³ |
|    |    | p$_{3/2}$ | 1.359×10³ | 1.357×10³ | 1.363×10³ | —          | 1.312×10³ |
|    |    | d$_{3/2}$ | 1.055×10³ | 1.052×10³ | —          | 1.040×10³ | a 1.025×10³ |
|    |    | d$_{5/2}$ | 1.029×10³ | 1.027×10³ | 1.034×10³ | —          | 1.001×10³ |
| 63 | 4  | s    | 3.320×10² | —         | 3.370×10² | 3.345×10² | 3.149×10² |
|    |    | p$_{1/2}$ | 2.581×10² | 2.420×10² | —          | 2.452×10² | a 2.525×10² |
|    |    | p$_{3/2}$ | 2.360×10² | 2.420×10² | 2.421×10² | —          | 2.280×10² |
| 64 | 4  | s    | 3.629×10² | 3.600×10² | (3.66–3.70)×10² | 3.618×10² | 3.442×10² |
|    |    | p$_{1/2}$ | 2.858×10² | 2.840×10² | 3.638×10² | b          | 2.669×10² | a 2.772×10² |
|    |    | p$_{3/2}$ | 2.578×10² | 2.570×10² | (2.53–2.61)×10² | —          | 2.482×10² |
| 70 | 4  | s    | 3.792×10² | 3.786×10² | 3.994×10² | —          | 3.774×10² | 3.664×10² |
|    |    | p$_{1/2}$ | 3.005×10² | 2.860×10² | —          | 2.785×10² | a 2.971×10² |
|    |    | p$_{3/2}$ | 2.694×10² | 2.710×10² | (2.71–2.73)×10² | —          | 2.655×10² |
|    |    | p$_{5/2}$ | 4.901×10² | 4.805×10² | (4.81–4.89)×10² | —          | 4.866×10² | 4.560×10² |
|    |    | p$_{3/2}$ | 4.018×10² | 3.887×10² | —          | 3.613×10² | a 3.718×10² |
|    |    | p$_{5/2}$ | 3.497×10² | 3.397×10² | (3.40–3.46)×10² | —          | 3.218×10² |

a Excluding spin-orbit splitting.
b Possible misprint in [5], it would be correct 2.638×10².

Theoretical RLDA results [7] [see figure 3(b)]. Although the energies in the database [6] are given without taking into account the spin-orbit level splitting, we use these data to compare when no other data are available. In addition, the spin-orbit effects are most pronounced for p-states, for $l > 1$ the splitting is small, that is well shown by theoretical calculations in figure 3(b).

Estimates of $N$-energies for some elements ($Z = 61, 63, 64, 70$) are listed in table 1, including the missing promethium 4$s$-energy in [4]. The corrected 4$p_{1/2}$-energies for these elements are also presented. The estimated energies are compared with data from experimental [4–6] and theoretical [7] sources. A scatter of the experimental binding energies of some elements in the database [5] is explained by a chemical shift. This is a change in binding energy of a core electron due to a change in the chemical bonding of that element.

3. Conclusions

The analysis of available experimental data on the binding energies of internal electron shells $K$, $L$, $M$, $N$ [4–6] for lanthanum group elements confirmed the atomic-number similarity law. The regularities from [4] were interpolated and used for analytical estimates of the orbital binding energies. Their comparison for some atoms with data from the other experimental bases [5, 6] allowed to select more correct values and restore missing binding energies. The given polynomial coefficients make it possible to estimate all the binding energies in the inner shells $K$, $L$, $M$, $N$ of the lanthanum group elements $Z = 57–70$.

The considered theoretical model results [7] also indicated the atomic-number similarity law. They were shown to underestimate the binding energy, differing in the third significant position.
Table A1. Polynomial coefficients in equation (2).

| $a_k^{(n)}$, $b_k^{(nlj)}$ | $k = 0$ | $k = 1$ | $k = 2$ | $\sigma_n$ range |
|-----------------------------|---------|---------|---------|-----------------|
| $a_1^{(1)}$                | 3.019767842369 | -4.040765760217 | 1.640479796628 | 0.762–0.816 |
| $a_2^{(2)}$                | 2.425506128472 | -2.014128003514 | 0.331679254342 | 1.525–1.633 |
| $b_2^{(2p1/2)}$            | 1.210424383094 | -1.301602399007 | 0.199306657235 |
| $b_2^{(2p3/2)}$            | 3.486289797519 | -2.177363632681 | 0.00            |
| $a_3^{(3)}$                | 0.664870159640 | -0.279772305848 | -0.10340695025 | 2.287–2.449 |
| $b_3^{(3p1/2)}$            | -1.432374236770 | 1.113802162927 | -0.34205549260 |
| $b_3^{(3p3/2)}$            | 2.712821078023 | -1.387392278270 | 0.016721231520 |
| $b_3^{(3d3/2)}$            | 5.154711752601 | -4.001640497945 | 0.659373793545 |
| $b_3^{(3d5/2)}$            | 4.632511196491 | -3.469228213790 | 0.531285177124 |
| $a_4^{(4)}$                | 4.284502780604 | -2.922806338307 | 0.368165668184 | 3.049–3.265 |
| $b_4^{(4p1/2)}$            | -0.271770344888 | -0.262141781344 | 0.00            |
| $b_4^{(4p3/2)}$            | 1.798200519612 | -0.874952721175 | 0.00            |
| $b_4^{(4d3/2)}$            | 5.836677836757 | 3.874403634012 | 0.748901880941 |
| $b_4^{(4d5/2)}$            | -7.977131265802 | 5.295013056112 | -0.984137473323 |
| $b_4^{(4f5/2)}$            | 9.931525538903 | -6.211856990645 | 0.853985634903 |

Appendix

In table A1 there are polynomial coefficients $a_k^{(n)}$, $b_k^{(nlj)}$ for functions $\log |\varepsilon_n(\sigma)|$ and $\log d_{nlj}(\sigma)$ in equation (2). The coefficients were obtained from data [4] approximation. For each $n$-shell, the $\sigma_n = \pi n Z^{-1/3}$ change range is indicated.

References

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