X-ray $K$ and $L$ terms estimation in free many-electron atoms and ions

G V Shpatakovskaya
Keldysh Institute of Applied Mathematics of the Russian Academy of Sciences, Miusskaya Square 4, Moscow 125047, Russia
E-mail: shpagalya@yandex.ru

Abstract. Information about x-ray terms is necessary to calculate an ionization cross section of atoms or ions by intense energy beam of other particles, also for spectroscopic research method, astrophysical applications. In the paper the simple method is offered to estimate x-ray terms of many-electron atoms and ions. It is based on the atomic number and ionization degree scaling of electron orbital energies. The Dirac–Fock data of some ions of three elements (V, Pd, U) are used to construct the required dependence. One can calculate $K$ and $L$ x-ray terms of ions of the same and other elements using the appropriate polynomial approximations. The inaccuracy does not exceed 8%.

1. Introduction
The calculation and experimental measurement of the electron binding energies in free atoms and ions are still an actual problem [1, 2]. These values are necessary for spectroscopic research method, astrophysical applications, calculation an ionization cross section of atoms and ions by other particles and so on.

Experimental data on binding energies in the neutral atoms are summarized in the paper [1] and booklet [2]. Relativistic and other forms of the density functional theory (DFT) are applied to compute the binding energies in the neutral atoms and first ions for periodic table elements [3]. The Dirac–Fock model [4] and its many configuration modification (MCDF) [5] are used to calculate the electron binding energies in ions. In the MCDF-database [6] one can find the orbital energies in all the ions for elements with atomic numbers $Z = 1–58$ calculated by MCDF model. Orbital energies for ground-state configurations of all the uranium ions are published in [4]. However in spite of great success in the theory and computational capabilities, there is a lack of the data, especially for heavy ions. Therefore the method for an estimation of the missing data is highly claimed.

It has been shown in [7–10] that calculated orbital energies by the DFT [3], experimental data [2] in atoms and the MCDF electron binding energies in ions hold similarity on the atomic number $Z$ and ionization degree $\alpha$. Here, $\alpha = z/Z$, $z$ is the ion charge.

This similarity was suggested in the semiclassical approach. If one uses the semi-classical Thomas–Fermi model [11], Bohr–Zommerfeld quantization condition and assumption of the orbital energy $E_{nl}$ square-law dependence [12,13] on the orbital quantum number $l, n$ being a principal one, the $Z$-scaling of the semi-classical orbital energies is revealed (atomic units are
Figure 1. The functions (a) $\lg |e_1(\sigma, \alpha)|$ and (b) $\lg |e_2(\sigma, \alpha)|$ for V, Pd [6] and U [4] ions at the different ionization degrees ($\alpha = z/Z$) by symbols $\nabla$ and fitting curves down up: $\alpha = 0$—solid; 0.5218—dashed; 0.6956—dash-dot; 0.8696—long-dash.

(\ref{fig:1})

2. Analysis of $K$ and $L_I$ terms in some V, Pd, U ions

In order to build the dependence of the binding energy on the degree of ionization in a wide range of atomic numbers, one needs to have data for the light, medium and heavy atoms. However, although for the light and medium atoms ($Z = 1–58$) there are tables [6] of all the ions, we know the data for uranium [4] only of heavy elements. Therefore, we are forced to use the information only about three elements, the atomic numbers of which are related by proportion: 23 : 46 : 92. This makes it possible to choose ions with integer charges at the same degree of ionization, but of course limits the accuracy of our approximation. If the data for the element $Z = 69$ (Tm) were known, one could construct a more accurate cubic interpolation than the quadratic used below.

The energies from the MCDF-database [6] for some ions of the vanadium ($Z = 23$), palladium ($Z = 46$) and uranium ($Z = 92$) data [4] are used. We suppose equation (1) to be true for all

\begin{align}
E_{n0}^1 &= Z^{4/3}e(\sigma_n, \alpha), \quad \ell = 0; \quad \sigma_n = \pi n Z^{-1/3}, \\
E_{nl}^1(Z, \alpha) &= Z^{4/3}e(\sigma_n, \alpha) + Z^{2/3}d(\sigma_n, \alpha) \lambda^2, \quad \lambda = \ell + 1/2, \quad \ell > 0.
\end{align}
Table 1. Fitting polynomial data \( b_{ik}^{(n)} \) in equation (4) calculated from the Dirac–Fock electron binding energies for certain \( \alpha \) in V, Pd and U ions, where \( n \) is a principal quantum number.

| \( i \) | \( k = 0 \) | \( k = 1 \) | \( k = 0 \) | \( k = 1 \) |
|---|---|---|---|---|
| 0 | 2.77247366 | −0.07273500 | 2.61453012 | −0.43540174 |
| 1 | −3.31077277 | 0.014062081 | −2.16805639 | 0.43892969 |
| 2 | 1.11609235 | 0.01337615 | 0.35177353 | −0.02037694 |

Table 2. Comparison of \( K \) and \( L_I \) x-ray terms calculated by the Dirac–Fock method and by equations (1), (4) and table 1 for certain ions.

| ion | \( K (-E_{10}) \) (eV) | \( L_I (-E_{20}) \) (eV) |
|---|---|---|
| Dirac–Fock | equation (1) | Dirac–Fock | equation (1) |
| \( _{23}\text{V}^{+3} \) | 5516 | 5500 | 680 | 706 |
| \( _{30}\text{Zn}^{+24} \) | 11 184 | 10 882 | 2437 | 2334 |
| \( _{40}\text{Zr}^{+10} \) | 18 202 | 18 227 | 2737 | 2918 |
| \( _{50}\text{Sn}^{+40} \) | 31 847 | 32 089 | 6928 | 6971 |
| \( _{56}\text{Ba}^{+12} \) | 37 674 | 38 295 | 6226 | 6573 |
| \( _{92}\text{U}^0 \) | 116 440 | 115 370 | 21 936 | 21 456 |
| \( _{92}\text{U}^{+28} \) | 117 220 | 117 950 | 22 702 | 23 602 |
| \( _{92}\text{U}^{+73} \) | 122 230 | 122 640 | 27 974 | 27 502 |

the data \( \{E_{n0}(Z, z)\} \) and find the couples of values for \( n = 1, 2 \):

\[
e_n(\alpha) = \frac{E_{n0}(\alpha)}{Z^{4/3}} \quad \text{and} \quad \sigma_n = \frac{\pi n}{Z^{1/3}}. \tag{3}
\]

The results obtained in this way for some values \( \alpha \) are shown in figure 1 for \( n = 1 \) and 2. The fitting curve polynomial

\[
\lg |e_n(\sigma, \alpha)| = \sum_{i=0}^{2} a_i^{(n)}(\alpha)\sigma^i
\]

may be transformed into

\[
\lg |e_n(\sigma, \alpha)| = \sum_{i=0}^{2} \sum_{k=0}^{1} b_{ik}^{(n)} \alpha^k \sigma^i, \tag{4}
\]

coefficients \( b_{ik}^{(n)} \) being shown in table 1.

Now one can use equations (1), (4) and table 1 to estimate binding energies \( E_{10}, E_{20} \) in any many-electron ion of elements with atomic numbers \( 23 \leq Z \leq 92 \). Table 2 demonstrates a comparison of some estimations with the Dirac–Fock results. The inaccuracy does not exceed 7%.
Figure 2. The functions $\lg d_{nlj}(\sigma, \alpha)$, $n = 2$, $l = 1$, $j = 1/2$ (a) and $3/2$ (b) for V, Pd [6] and U [4] ions at the different ionization degrees by symbols $\triangledown$ and fitting curves up down: $\alpha = 0$ to $0.5218$—solid; $0.6522$—dashed; $0.6956$—dash-dot.

Table 3. Polynomial fit data $f_{ik}, p_{ik}$ in equation (6) and (7) calculated from electron binding energies for certain values $\alpha = z/Z$ in V, Pd and U ions.

| $\alpha$   | $i$ | $k = 0$ | $k = 1$ | $k = 2$ | $p_{ik}$ |
|------------|-----|---------|---------|---------|----------|
| 0–0.5218   | 0   | 1.6225  | 0       | 0       | 8.0758   |
|            | 1   | -1.7559 | 0       | 0       | -7.8610  |
|            | 2   | 0.3269  | 0       | 0       | 1.7737   |
| 0.5218–0.7 | 0   | 1.6490  | 3.9538  | -7.6743 | 12.5949  |
|            | 1   | -2.0184 | -4.4552 | 9.5024  | -13.7334 |
|            | 2   | 0.4682  | 1.3020  | -3.0142 | 3.6601   |

3. Analysis of $L_{II}$ and $L_{III}$ terms in some V, Pd, U ions
Here, we use the orbital energies in the same ions from the MCDF-database [6] of the vanadium, palladium and uranium data [4] and equation

$$ d_{nlj}(\alpha) = \frac{E_{nlj}(\alpha) - E_{n0}(\alpha)}{Z^{2/3} \lambda^2}, \quad j = l \pm 1/2 $$

(5)
to construct the dependence $d_{nlj}(\sigma, \alpha)$ for $n = 2$, $l = 1$, $j = 1/2$ and $j = 3/2$. Their plots one can see in figure 2 at the different values of ionization degree $\alpha$. It is seen that for the ionization degrees in the range $\alpha = 0$–0.5218, the function $\lg d_{nlj}(\sigma, \alpha)$ does not depend on $\alpha$. 
Table 4. Comparison of $L_{II}$ and $L_{III}$ x-ray terms calculated by Dirac–Fock method and by equations (2), (6), (7) and table 3 for certain ions.

| ion    | $L_{II}$ ($-E_{21j}$, $j = 1/2$) (eV) | $L_{III}$ ($-E_{21j}$, $j = 3/2$) (eV) |
|--------|--------------------------------------|---------------------------------------|
|        | Dirac–Fock equation (2)              | Dirac–Fock equation (2)               |
| $^{23}$V$^{+3}$ | 572                                 | 598                                   |
| $^{30}$Zn$^{+24}$ | 2357                                | 2311                                  |
| $^{40}$Zr$^{+10}$ | 2508                                | 2692                                  |
| $^{50}$Sn$^{+40}$ | 6651                                | 6864                                  |
| $^{56}$Ba$^{+12}$ | 5857                                | 6199                                  |
| $^{92}$U$^0$    | 21 126                               | 20 646                                |
| $^{92}$U$^{+28}$ | 21 894                               | 22 793                                |
| $^{92}$U$^{+73}$ | 27 183                               | 27 018                                |

The fitting curve polynomials are

$$\lg d_{21j}(\sigma, \alpha) = \sum_{i=0}^{2} \sum_{k=0}^{2} f_{ik} \alpha^k \sigma^i, \quad j = 1/2,$$

(6)

$$\lg d_{21j}(\sigma, \alpha) = \sum_{i=0}^{2} \sum_{k=0}^{2} p_{ik} \alpha^k \sigma^i, \quad j = 3/2,$$

(7)

coefficients $f_{ik}$ and $p_{ik}$ being shown in table 3.

The equations (2), (6), (7) and table 3 can be used to estimate binding energies $E_{21j}$, $j = 1/2$, $j = 3/2$ in any many-electron ion of elements with atomic numbers $23 \leq Z \leq 92$. Table 4 demonstrates a comparison of some estimations with the Dirac–Fock results. The inaccuracy does not exceed 8%.

4. Conclusion

In the paper, the x-ray terms K, $L_I$, $L_{II}$, $L_{III}$ in atoms and ions were studied. Atomic number and ionization degree similarity (scaling) and the Dirac–Fock data for some ions of only three elements V, Pd and U were used. The scaling enables to estimate the x-ray terms in any many-electron ion by means of two constructed independent of the atomic number functions $e_n(\sigma, \alpha)$ and $d_{nij}(\sigma, \alpha)$. The estimation inaccuracy for the free ions is less than 8%. Such a large enough error is due to a lack of data (only on three elements) for more accurate interpolation.

The proposed approach can be used to calculate the ionization cross section of many-electron heavy atoms and ions by other particles, for the x-ray diagnostic, recovery of missing information about the atomic and ionic K and L x-ray terms and the new data verification.

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