Theoretical multiconfiguration Dirac-Fock method study on the structure of L-X-ray satellite and hypersatellite lines of zirconium

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Abstract. Detailed multiconfiguration Dirac-Fock calculations with the inclusion of the transverse (Breit) interaction and QED corrections have been carried out on zirconium to elucidate the structure of various M-, N-shell satellite and L-shell hypersatellite \( L\alpha_{1,2} (L_3M_{4,5}) \) and \( L\beta_1 (L_2M_4) \) lines in its X-ray spectra. For each type of lines two theoretical spectra have been synthesized: one being a sum of the Lorentzian natural line shapes and the other one being a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response. The results are very helpful in reliable interpretation of various high-resolution \( L \)-X-ray spectra of zirconium target bombarded by different light and heavy projectiles.

1. Introduction
Numerous studies based on the interpretation of the K-, L- and M-X-ray spectra [1–10] have been performed in order to investigate the ionization in collision processes. The multiple ionization of various shells of target atoms makes the origin of the measured X-ray spectra very complex. In order to obtain from these X-ray spectra the information about the L- or M-shell ionization probability it is vital to make use of the results of theoretical calculations [11–15] of the positions and intensities of various X-ray lines. Recently, for the first time the M-shell satellite and L-shell hypersatellite of \( L\alpha_{1,2} (L_3M_{4,5}) \) and \( L\beta_1 (L_2M_4) \) X-ray lines of zirconium, molybdenum and palladium (induced by oxygen and neon ions) have been observed in the measured X-ray spectra by means of a high-resolution (of about 1 eV) von Hamos crystal spectrometer [8]. Very recently the M-shell satellite structure of \( L\alpha_{1,2} \) X-ray lines of palladium has been interpreted in terms of the multiconfiguration Dirac-Fock (MCDF) calculations [9].

2. MCDF calculations
In the present work detailed MCDF calculations with the inclusion of the transverse (Breit) interaction and QED corrections have been carried out on zirconium to elucidate the structure of various M-, N-shell satellite and L-shell hypersatellite of \( L\alpha_{1,2} \) and \( L\beta_1 \) lines in its X-ray spectra. The MCDF method has been described in detail in many papers (see, e.g., [15–17]). Within this method the effective Hamiltonian for an N-electron system is expressed by

\[
H = \sum_{i=1}^{N} h_D(i) + \sum_{j>i=1}^{N} C_{ij},
\]
where \( h_D(i) \) is the Dirac operator for \( i \)-th electron and the terms \( C_{ij} \) account for electron-electron interactions and come from one-photon exchange process. The latter are a sum of the Coulomb interaction operator (due to longitudinally polarized photons) and the transverse Breit operator (due to transversely polarized photons). In the MCDF method an atomic state function (ASF) with the total angular momentum \( J \) and parity \( p \) is assumed in the multiconfigurational form

\[
\Psi_s(Jp) = \sum_m c_m(s) \Phi(\gamma_m Jp),
\]

where \( \Phi(\gamma_m Jp) \) are configuration state functions (CSF), \( c_m(s) \) are the configuration mixing coefficients for state \( s \), \( \gamma_m \) represents all information required to uniquely define a certain CSF.

3. Results and discussion

The test calculations which examine the role of the particular contributions to the predicted line positions have been performed for zirconium. It has been found that the contribution of the transverse (Breit) interaction to the calculated \( L_{\alpha 1,2} \) and \( L_{\beta 1} \) line positions is very important (in the range of 3.8–5.2 eV), while the contribution of the QED corrections is small (~ 0.1 eV).

In Figs. 1–3, both stick (calculated line positions with their relative intensities) and synthesized spectra for the diagram and all considered types of the satellite and hypersatellite \( L_{\alpha 1,2} \) and \( L_{\beta 1} \) transitions are presented together with the summary spectra (constructed under the assumption that the weights of individual configurations depend only on the number of ways in which a particular initial hole state can be formed). Two synthesized spectra for all cases have been constructed: one being the sum of the Lorentzian natural line shapes with the width of 1.63 eV [18] (dotted lines) and, to better simulate the experimental spectra, the other one (solid lines) being a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having the width of 1.0 eV. It is worth noting that effect of the multi-vacancy configurations should enlarge the assumed natural line widths [9]. The number of transitions for each considered transition type and the theoretical relative “average” positions of each group of satellite and hypersatellite \( L_{\alpha 1,2} \) and \( L_{\beta 1} \) lines (with respect to \( L_{\alpha 1,2} \) and \( L_{\beta 1} \) diagram lines, denoted thus \( 2p^{-1} \to 3d^{-1} \)) for zirconium have been given in Table 1.

| Transition type | The number of transitions | Energy shifts (eV) |
|-----------------|---------------------------|--------------------|
| \( 2p^{-1} \to 3d^{-1} \) | 3 | 0.0 0.0 |
| \( (2p3s)^{-1} \to (3s3d)^{-1} \) | 11 | 8.5 8.4 |
| \( (2p3p)^{-1} \to (3p3d)^{-1} \) | 76 | 9.1 8.2 |
| \( (2p3d)^{-1} \to 3d^{-2} \) | 60 | 9.2 8.4 |
| M-shell satellite | 147 | 9.1 8.3 |
| \( (2p4s)^{-1} \to (3d4s)^{-1} \) | 11 | 0.2 0.2 |
| \( (2p4p)^{-1} \to (3d4p)^{-1} \) | 76 | 0.2 0.2 |
| N-shell satellite | 87 | 0.2 0.2 |
| \( (2s2p)^{-1} \to (2s3d)^{-1} \) | 11 | 43.5 54.7 |
| \( 2p^{-2} \to (2p3d)^{-1} \) | 34 | 64.9 69.0 |
| L-shell hypersatellite | 45 | 59.0 64.8 |

Table 1. The number of transitions and the relative “average” positions of each groups of satellite and hypersatellite \( L_{\alpha 1,2} \) and \( L_{\beta 1} \) lines (with respect to diagram lines) for zirconium.
Generally from Figs. 1–3 it can be observed that the structures of sticks for the $\text{L}_\alpha$ and $\text{L}_\beta$ satellite and hypersatellite lines are different for each discussed case. In the case of the M-shell satellite lines (see Fig. 1) the sticks are noticeably scattered and the corresponding stick and both kinds of the synthesized spectra (both the sum of the Lorentzian natural line shapes and the convolution of a sum of the Lorentzian line shapes with the Gaussian instrumental response) for an additional $3s$, $3p$, and $3d$ hole differ considerably one from each other. For the N-shell satellite lines (see Fig. 2) the sticks are close to each other and the shapes of all the synthesized spectra are similar to the shapes of the corresponding diagram lines (though the satellite bands are of course wider than the diagram ones). As for the L-shell hypersatellite
Figure 3. As in Figure 2, but for the $L\alpha_{1,2}$ and $L\beta_1$ diagram and L-shell hypersatellite transitions [(b)–(d)] in zirconium. Spectrum (d) is the summary spectrum [(b)+(c)].

lines (see Fig. 3), they are widely distributed in the range of about 50 eV. Both the sum of the Lorentzian natural line shapes and the convolution of a sum of the Lorentzian line shapes with the Gaussian instrumental response are mostly rich in structure. Generally it can be noticed that only the N-shell satellites of $L\beta_1$ lines can be quite well represented as the Voigt function. From Table 1 one can see that the L-shell hypersatellite lines have a substantial average energy shift (in the range of 43.5–69 eV), which is the biggest when the hole is in the $2p$ subshell. For the M-shell satellite lines the effect is much smaller (in the range of 8.2–9.2 eV) and for the N-shell satellite lines it is very small (in the range of about 0.2 eV).

The obtained theoretical results are absolutely essential to carry out reliable and quantitative interpretation of various experimental L-X-ray spectra of zirconium target bombarded by different light and heavy projectiles (such as O and Ne ions).

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