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## Critical analysis of the methods of interpretation in the hyperfine structure of free atoms and ions. Case of the model space $(5d + 6s)^3$ of the lanthanum atom

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**Abstract.** In this work the method of quantitative determination of two-body contributions to the fine and the hyperfine structure, resulting from the excitations from electronic closed shells to open shells and from open shells to empty shells, is described. On the basis of experimental data, both own and available in the literature, the configuration  $(5d+6s)^3$  in the lanthanum atom was analyzed. Our investigations indicate that the operator

$$H_{\text{hfs}} = \sum_{K=1}^3 T_e^{(\kappa k)K} \cdot T_n^{(K)}$$

describes the partition of the observed hyperfine splittings into the contributions of ranks  $K=1,2$  and  $3$  within the experimental accuracy, while the operator

$$T_e^{(\kappa k)1} \cdot T_n^{(1)} = \frac{\mu_0 \mu_B}{2\pi} \sum_{i=1}^N \left[ \hat{l}_i \langle r^{-3} \rangle^{01} - \sqrt{10} \left( \hat{s}_i \hat{C}_i^2 \right)^{(1)} \langle r^{-3} \rangle^{12} + \hat{s}_i \langle r^{-3} \rangle^{10} \right] \cdot T_n^{(1)}$$

does not fully account for the partition of the interactions of rank  $K=1$  into contributions  $\kappa k = 01, 12$  and  $10$ .

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## 1. Introduction

On the basis of our earlier works, both experimental and theoretical [1–6], as well as work of another author [7], we feel qualified to submit a proposition, that the existing theories (e.g. [8–12]), which provide a semi-empirical description of the hyperfine interactions in the structure of a complex atom, are not sufficiently precise to yield a correct description and interpretation of the measured hyperfine splittings within the up-to-date experimental accuracy. Also the results of *ab initio* calculations for the hyperfine structure (*hfs*) parameters, such as magnetic dipole interaction constant  $A$  and electric quadrupole interaction constant  $B$ , usually differ, in some cases substantially, from their experimental counterparts [13, 14].

The main aim of this work is, among other things, an attempt to answer the following questions:

1. Is it possible to theoretically describe the hyperfine interactions within an atom with an accuracy comparable to the accuracy achieved in experiment?
2. What is the main reason of the observed discrepancies between the experiment and the theory: the applied approximations in the analysis of the atomic structure or incorrect experimental data?
3. Are the commonly applied assumptions concerning the mechanism of interaction between the nucleus and the electron shells (e.g. regarding the nucleus as a point magnetic dipole and the assumption that the quantum number  $I$ , which describes the angular momentum of the nucleus, is a "good" quantum number) correct?

It was proved [15–19] that the main source of discrepancies mentioned are difficulties with a precise description of the interactions of configurations system investigated with distant electron configurations originating from excitations of one or more electrons from open to empty shells or from closed to open shells. Moreover, Fenuille and Armstrong [20] showed, that correlation and relativistic effects in atomic hyperfine structure are of additive nature, and that effects of configurations interaction (contributions of the second order perturbation theory) can be treated within effective operator approximation, and thus they proved their  $SL$ -dependence. Thus one may expect, that a precise definition and development of a mathematical formalism, which yielded a complete description of these effects, should explain the observed discrepancies.

Another problem may be insufficient precision of determination of eigenvectors amplitudes describing particular electron states. The wavefunctions are determined on the basis of the atomic fine structure ( $f$ ) investigations. In this case availability of verified experimental data concerning energies of electronic levels combined with a correct assignment of  $J$  quantum number is a crucial point. Scarcity of experimental data has to be considered a severe shortcoming, if the structure of an atom is regarded in multiconfiguration approximation and all important theoretically predicted interactions are to be included. A serious problem constitute the erroneous data concerning energy values of electronic levels – sometimes energies of non-existing levels are given in literature (e.g. [21]), or incorrect  $J$  values are assigned to correct energy values (a critical analysis of some data of this kind was performed by Windholz [22]).

Another factor to be blamed for existing discrepancies is in some cases the method of determination of the hyperfine structure constants  $A$ ,  $B$ ,  $C$  and  $D$  from the measured hyperfine intervals – a simplified description of "repulsion" effect for the hyperfine structure sublevels with the same values of quantum number  $F$  yields a substantial distortion of the information concerning quadrupole and higher order interactions. This was first noticed by Casimir [23], who referred to them as "pseudoquadrupole" or "pseudooctupole" interactions. Therefore, in order to guarantee the correctness of determination of the hyperfine structure constants  $A$ ,  $B$ ,  $C$  and  $D$  in our approach, described below, a segment called "diagonalization of the hyperfine structure energy matrix" within the basis of states  $\Psi(\text{configuration}, vSLJF)$  was introduced. In this way we eliminate one of the possible sources of discrepancies.

In our group a procedure (schematically outlined below, Figure 1) of analysis of experimental

data concerning the structure of complex atoms was developed. In the updated procedure the segment "parametrization of one- and two-body hyperfine interactions" was improved with respect to the earlier applied method [2, 24, 25]. Now we include all one- and two-body contributions to *hfs* constants *A* and *B* which exhibit a dependence on the quantum numbers *SL* as well as on *N* (the number of equivalent electrons in an open shell) and which originate from the excitations "open shell - empty shell" or "closed shell - open shell". Our earlier method [24] was developed for the system  $(3d+4s)^N$ , and thus excitations of the kind "closed  $n_0d$  shell - open  $nd$  shell" are not occur.

In the lanthanum atom the configurations system  $(5d+6s)^N$  is well separated from the excited configurations. The closest excited configuration  $4f6s6p$  begins at ca.  $29000\text{ cm}^{-1}$ . Configurations originating as a result of "closed shell - open shell" excitations (core-excitations) certainly lie much above  $100000\text{ cm}^{-1}$  and have not been observed in lanthanum yet. Thus in the case of the lanthanum atom it can be assumed that the configurations system considered  $(3d+4s)^N$  is well isolated from any disturbing configurations and the conditions for application of the perturbation theory are fulfilled. It yields an excellent possibility of an alternative analysis of the contributions mentioned within the second order perturbation theory according to the excitation model either "open shell - empty shell" or "closed shell - open shell". A simultaneous application of both models is not possible because of the fact that in both models implicit linear dependence between angular coefficients corresponding to the certain radial parameters have to occur, which make the solution of a redundant set of linear equations impossible and thus hinder the determination of the respective radial parameters. It provides an excellent test confirming the correctness of the complex formulae derived, which in the case of consideration of e.g. configurations with three open shells require re-coupling of five or more angular momenta and strict observance of the electron permutation rules, in particular for interconfiguration matrix elements. When both the fine and the hyperfine structure are considered independently within the frame of both excitation models, two independent sets of radial parameters describing the atomic structure are obtained. On the basis of the theoretically predicted relations between the radial parameters originating from both models one can prove the correctness of the obtained description of the atomic structure, as well as precisely define the information provided by the radial parameters determined from the experimental data. In Section 5 the relations are given, which allow to recalculate the parameters obtained for the model space  $(5d+6s)^3$  within both excitation models: "closed shell - open shell" (c-o) and "open shell - empty shell" (o-e) into the radial parameters characteristic of the individual configurations  $5d^3$ ,  $5d^26s$  and  $5d6s^2$ .

In this analysis we apply experimental data available in the literature, in particular those obtained with Rabi method [26] and the method of double laser-rf resonance [13], as well as the results obtained within this work. In our experimental investigations it was not possible either to confirm the existence of the electronic level with the energy  $25414.63\text{ cm}^{-1}$  and the value of quantum number  $J = 5/2$  or to measure its hyperfine splitting; we also did not manage to find the level with the energy ca.  $25752\text{ cm}^{-1}$  and the value of quantum number  $J = 3/2$ . For the model space  $(5d+6s)^3$  the information concerning the hyperfine structure of the levels  $5d^3\ ^2D$  with  $J = 3/2$  and  $J = 5/2$  is still missing; however, in spite of the lack of these data we managed to describe quantitatively the one- and the two-body interactions in the fine and the hyperfine structure of the electronic levels which form this system.

## 2. Experimental details

Measurement of the hyperfine structure constants for electron levels belonging to the configuration  $5d^3$  of the lanthanum atom is a difficult task, first of all because of the lack of strong spectral lines involving those levels. In the commonly available tables of spectral lines [27] in the visible and near infrared regions no such lines can be found. Transitions to the levels belonging to configuration  $5d^3$ , which could be

conveniently excited with commonly available tunable lasers, involve odd-parity levels with energy values within the range  $32000\text{--}40000\text{ cm}^{-1}$ . However, most such levels belong to configurations differing from the configuration  $5d^3$  with states of two electrons. Because of selection rules electric dipole transitions in such a system of configurations can only occur as a result of "mixing" of the configurations in question with other configurations, for which electric dipole transitions to configuration  $5d^3$  are allowed. Since the admixtures of such configurations are usually minor, the resulting spectral lines are, as a consequence, very weak. In this situation the only chance of successful application of the experimental method based on laser induced fluorescence or optogalvanic spectroscopy consists in recording of the hyperfine structure for possibly great number of the strongest among the weak spectral lines and the reduction of experimental errors through statistical evaluation of the results.

In our two experimental works, which have recently appeared in *J.Phys.B* [28,29], we presented results of the measurements of the hyperfine structure constants for several hundreds electronic levels of both parities in the lanthanum atom. In those works also results of the measurements of constants  $A$  for 13 levels belonging to the configurations analyzed in the present work were included; these results were obtained for the first time. Since in the work [28] the values of constants  $A$  for several hundreds odd parity levels with energies above  $33000\text{ cm}^{-1}$  were also presented, it was possible to extend the investigations for the 13 levels mentioned, belonging to the model space, through the measurements of a greater number of spectral lines including them. Such an extension was performed within experimental investigations in the present work.

With the use of laser induced fluorescence or optogalvanic method the hyperfine structure of 71 spectral lines involving the levels investigated was recorded. In the case of 27 of the recorded lines both the signal to noise ratio and the observed hyperfine splitting enabled determination of the constants  $A$  with experimental uncertainty below 7 MHz. A compilation of those lines is presented in Table 1. In the case of the odd parity level with the energy  $E=33799.23\text{ cm}^{-1}$ , which is the upper level of the investigated spectral line with the wavelength  $\lambda = 594.797\text{ nm}$ , it proved necessary to change the assigned quantum number  $J$  from the value of  $5/2$  to  $3/2$ , since both the calculations of the hyperfine structure (including also the observed number of components) and the presence of such a line (the lower level has  $J=1/2$ ) indicate, that the value  $J=5/2$  encountered in the tables [30] cannot be correct. This question was already discussed in the work [28].

An additional verification of the results obtained was recording of the remaining 44 spectral lines, which were too weak for precise determination of the constants  $A$ , but their profiles allowed us to confirm the earlier determined values and in particular to eliminate the doubts concerned with the fact that for equal  $J$  values for both the lower and the upper level the change of the signs of both constants  $A$  along with the interchange of their values yields the identical pattern of the hyperfine structure of the line.

In the measurements an experimental setup described in the previous works [31–34] was used. This setup was earlier successfully applied in our lab in investigations of praseodymium [35–37] and lanthanum [38]. The source of the exciting radiation was a ring dye laser - a modified version of Coherent model CR 699-21. Because of the spectral regions applied the laser was operated in turn with several sets of optical elements with the use of the following dyes: Rhodamine 6G (565-615 nm) and DCM (615-650 nm). According to the width of the spectral line investigated, the dye laser frequency was precisely tuned over the range covered with the line's hyperfine structure, 5-40 GHz. Several elements were used for dye laser frequency control: a wavemeter (Burleigh, model WA-1500), an iodine cell and a mode analyzer. Along with LIF signal a transmission of a frequency marker (a Fabry-Perot interferometer with FSR=1497 MHz) was recorded.

The source of lanthanum ions was a discharge in a hollow cathode lamp. Fluorescence light from the discharge was collected and focused with the mirrors and lenses systems onto the entrance slit of a monochromator (SPM-2). Behind the exit slit a photomultiplier with a preamplifier was placed. Electric

signal from the photomultiplier was fed to a lock-in amplifier. As a reference signal for phase-sensitive detection a signal from a mechanical chopper, placed in the laser beam, was used. Exit signal from the lock-in amplifier was A/D converted and recorded by the computer. Determination of the frequency scale on the basis of frequency marker signal and calculation of the values of  $A$  and  $B$  constants for the levels involved in the transition investigated were performed with the use of a program Fitter, which was earlier used for such purposes both in our laboratory and elsewhere.

As a result of the investigations the values of the constants  $A$  presented in the works [28, 29] were confirmed for all 13 levels belonging to the model space. In the case of two levels  $5d^3\ ^4P_{1/2}$  with the energy  $16617.30\text{ cm}^{-1}$  and  $5d^3\ ^2D_{3/2}$  with the energy  $18037.64\text{ cm}^{-1}$  the experimental uncertainties were reduced.

### 3. Diagonalization in $SLJF$ basis and determination of the constants $A$ , $B$ and $C$

The analysis of the  $hfs$  of the even configurations of La atom was performed in the basis of 3 configurations, taking into account all possible interactions predicted by many-body fine structure theory. In order to include the  $J$ -off-diagonal effects in the hyperfine structure, direct diagonalization of the matrix containing  $J$ -diagonal as well as  $J$ -off-diagonal elements has to be performed (in the basis of states  $\Psi(\text{configuration}, vSLJF)$ ). The effect of "repulsion" of the hyperfine structure sublevels with the same values of quantum number  $F$ , first noticed by Casimir, yields a distortion of the obtained values of the hyperfine structure constants of quadrupole and higher order interactions. Diagonalization of the hyperfine structure energy matrix within the basis of states  $\Psi(\text{configuration}, vSLJF)$  takes the effect referred by Casimir to as "pseudoquadrupole" interaction into account. It requires precision up to 16 significant digits. The diagonal part of this matrix consists of coefficients corresponding to the particular components of the energy of a hyperfine structure sublevel  $E_F$ : the center of gravity of the  $hfs$  energy  $W_J$  and the experimental  $hfs$  constants  $A$ ,  $B$ ,  $C$  and  $D$ . These parameters can be treated as free in the iterative fitting procedure of the experimental and the calculated  $hfs$  energies. The differences between  $E_F$  and  $E_{F\pm 1}$  values are equal to the experimentally determined hyperfine structure intervals. Values of  $J$ -off-diagonal  $hfs$  matrix elements are fixed.

As a result, we obtain improved values of the hyperfine structure constants, which in turn can be used to determine the radial  $hfs$  parameters. The final values are usually obtained after several iterations.

The accuracy of the experimental hyperfine structure intervals [13, 26] allows to determine only  $A$ ,  $B$  and  $C$  constants. If we treat these constants as free parameters, we obtain the agreement between the observed and the calculated interval values within the experimental error (see Table 2). The above result confirms, that the operator

$$H_{hfs} = \sum_{K=1}^3 T_e^{(\kappa k)K} \cdot T_n^{(K)}, \quad (1)$$

where  $T_e^{(\kappa k)K}$  and  $T_n^{(K)}$  denotes the electron and the nuclear operator, respectively, yields a complete description of the observed hyperfine structure splittings, and the constants  $A$ ,  $B$  and  $C$  obtained in this procedure are the "true" values, describing the interactions with ranks  $K = 1, 2$  and  $3$ .

In Table 3 a considerable "repulsion" effect can be observed for the levels  $^2G_{7/2}$  and  $^2G_{9/2}$ , for which the constants  $B$  were changed as a result of diagonalization by 44.05 MHz and 74.40 MHz, respectively.

### 4. Parametrization of the configurations interaction effects

The fine structure energy matrix was constructed in the way analogous to the one described e.g. by Cowan [39]. Moreover, our energy matrix is extended by the elements taking into account electrostatic coupling

and electrostatically correlated spin-orbit coupling between the configurations of the system considered and the distant configurations. Generally, for the configurations containing up to three open electronic shells, these matrix elements origin from the second order perturbation theory and can be schematically expressed as follows:

$$- \sum_{\psi_1 \neq \psi, \psi'} [\langle \psi | \mathbf{G} | \psi_1 \rangle \times \langle \psi_1 | \mathbf{G} | \psi' \rangle] / \Delta E = - (\text{angular part}) \times (\text{radial part}), \quad (2)$$

where:

$$\begin{aligned} \psi &= (n_0 l_0)^{4l_0+2} {}^1S, (n_1 l_1)^{N_1} S_1 L_1, ((n_2 l_2)^{N_2} S_2 L_2, (n_3 l_3)^{N_3} S_3 L_3) S_4 L_4; SL \\ \psi_1 &= (n_0 l_0)^{4l_0+1} {}^2L_0, (n_1 l_1)^{N_1+1} S_1'' L_1'', ((n_2 l_2)^{N_2} S_2'' L_2'', (n_3 l_3)^{N_3} S_3'' L_3'') S_4'' L_4''; SL \\ \psi' &= (n_0 l_0)^{4l_0+2} {}^1S, (n_1 l_1)^{N_1} S_1' L_1', ((n_2 l_2)^{N_2} S_2' L_2', (n_3 l_3)^{N_3} S_3' L_3') S_4' L_4'; SL \end{aligned} \quad (3)$$

for „closed shell – open shell” excitations, and

$$\begin{aligned} \psi &= (n_1 l_1)^{N_1} S_1 L_1, ((n_2 l_2)^{N_2} S_2 L_2, (n_3 l_3)^{N_3} S_3 L_3) S_4 L_4; SL \\ \psi_1 &= ((n_1 l_1)^{N_1-1} S_0'' L_0'', n' l'), S_1'' L_1'' ((n_2 l_2)^{N_2} S_2'' L_2'', (n_3 l_3)^{N_3} S_3'' L_3'') S_4'' L_4''; SL \\ \psi' &= (n_1 l_1)^{N_1} S_1' L_1', ((n_2 l_2)^{N_2} S_2' L_2', (n_3 l_3)^{N_3} S_3' L_3') S_4' L_4'; SL \end{aligned} \quad (4)$$

for "open shell – empty shell" excitations.

The angular coefficients result from the coupling of angular momenta of the operator  $\mathbf{G}$ . Radial parameters have denotations which code the interacting configurations and specify the interactions. Denotations of particular radial parameters take the form:  $P^t (n_i l_i n_j l_j, n_0 l_0 n_i l_i) P^{t'} (n_i l_i n_j l_j, n_0 l_0 n_i l_i)$ . In order to specify particular interactions more precisely the symbol  $P^t$  (where  $t$  stands for the order) is replaced respectively by  $D^t$  in the case of direct interactions,  $E^t$  for exchange interactions, or  $R^t$  for interactions involving two equivalent electrons. In our procedure excitations of one or two electrons from a closed shell to all open shells are considered, under the following conditions:

$$|l_i - l_0| = 0, 2 \quad \text{and} \quad N_1 + N_2 + N_3 = N_1' + N_2' + N_3' \quad (5)$$

Contributions from the second order perturbation theory for electrostatically correlated spin-orbit interactions (CSO) as well as for electrostatically correlated hyperfine interactions (CHFS), are defined as follows:

$$\begin{aligned} & - \sum_{\psi_1 \neq \psi, \psi'} \left[ \langle \psi | \mathbf{G} | \psi_1 \rangle \times \langle \psi_1 | \mathbf{T}^{(\kappa k)K} | \psi' \rangle + \langle \psi | \mathbf{T}^{(\kappa k)K} | \psi_1 \rangle \times \langle \psi_1 | \mathbf{G} | \psi' \rangle \right] / \Delta E = \\ & = - (\text{angular part}) \times (\text{radial part}), \end{aligned} \quad (6)$$

where:

$$\begin{aligned} \psi &= (n_0 l_0)^{4l_0+2} {}^1S, (n_1 l_1)^{N_1} S_1 L_1, ((n_2 l_2)^{N_2} S_2 L_2, (n_3 l_3)^{N_3} S_3 L_3) S_4 L_4; SLJ \\ \psi_1 &= (n_0 l_0)^{4l_0+1} {}^2L_0, (n_1 l_1)^{N_1+1} S_1'' L_1'', ((n_2 l_2)^{N_2} S_2'' L_2'', (n_3 l_3)^{N_3} S_3'' L_3'') S_4'' L_4''; S'' L'' J \\ \psi' &= (n_0 l_0)^{4l_0+2} {}^1S, (n_1 l_1)^{N_1} S_1' L_1', ((n_2 l_2)^{N_2} S_2' L_2', (n_3 l_3)^{N_3} S_3' L_3') S_4' L_4'; S' L' J \end{aligned} \quad (7)$$

for "closed shell – open shell" excitations, and

$$\begin{aligned}
\psi &= (n_1 l_1)^{N_1} S_1 L_1, ((n_2 l_2)^{N_2} S_2 L_2, (n_3 l_3)^{N_3} S_3 L_3) S_4 L_4; S L J \\
\psi_1 &= ((n_1 l_1)^{N_1-1} S_0'' L_0'', n_1' l_1'), S_1'' L_1'' ((n_2 l_2)^{N_2} S_2'' L_2'', (n_3 l_3)^{N_3} S_3'' L_3'') S_4'' L_4''; S'' L'' J \\
\psi' &= (n_1 l_1)^{N_1} S_1' L_1', ((n_2 l_2)^{N_2} S_2' L_2', (n_3 l_3)^{N_3} S_3' L_3') S_4' L_4'; S' L' J
\end{aligned} \tag{8}$$

for "open shell – empty shell" excitations.

In these cases also the angular coefficients result from the angular parts of the operators: a two-body electrostatic interaction operator  $\mathbf{G}$  and a one-body operator  $\mathbf{T}^{(\kappa k)K}$ ; the latter may represent either spin-orbit ( $H_{so}$ ) interaction or a hyperfine ( $H_{hfs}$ ) interaction.

The radial parameters  $P^t(n_i l_i n_0 l_0, n_i l_i n_i' l_i')$   $P^{\kappa k}(n_0 l_0, n_i l_i)$  specify the coupling between configurations. The radial integral  $P^t(n_i l_i n_0 l_0, n_i l_i n_i' l_i')$  describes electrostatic coupling of the configurations, i.e. it specifies the electrons involved and the type of their interaction. In the actual description the symbol  $P^t$  is replaced, as above, with  $D^t$  or  $E^t$ , respectively.  $P^{\kappa k}$  is the radial part of a one-body operator  $\mathbf{T}^{\kappa k}$ , which couples the electrons  $n_0 l_0$  and  $n_i l_i$ . In our procedure excitations of one electron from the closed shell  $(n_0 l_0)^{4l_0+2}$  to each of three open shells  $(n_1 l_1)^{N_1}$ ,  $(n_2 l_2)^{N_2}$  and  $(n_3 l_3)^{N_3}$  are considered. In the case of the spin-orbit interaction the symbol  $P^{\kappa k}$  is replaced by  $\zeta$ .

The above description of the parameters follows is a simplified notation. The parameters are actually defined as sums over all closed (or open) shells. For example, in the case of the lanthanum atom:

$$E^2(n_0 s 5d, 5d 6s) P^{10}(n_0 s, 6s) = 4\pi \sum_{n_0=1}^5 \Psi_{6s}(0) \Psi_{n_0 s}(0) E^2(n_0 s 5d, 5d 6s) / \Delta E, \tag{9}$$

where  $\Delta E$  is the energy difference between the relevant closed- and open-shell orbitals.

In the case of CSO the following condition has to be fulfilled:

$$|l_0 - l_1| = 0 \quad \text{and} \quad \kappa k = 11, K = 0. \tag{10}$$

The matrix elements determined from relations (2) and (6) under conditions (5) and (10) were included in the fine structure energy matrix (Figure 1).

In the case of CHFS the following relations hold: for magnetic dipole interactions  $K = 1$ :

$$|l_0 - l_1| = 0 \quad \text{if} \quad \kappa k = 01, 10 \quad \text{and} \quad |l_0 - l_1| = 0, 2 \quad \text{if} \quad \kappa k = 12 \tag{11}$$

and for electric quadrupole interactions  $K = 2$ :

$$|l_0 - l_1| = 0, 2 \quad \text{if} \quad \kappa k = 02 \quad \text{and} \quad |l_0 - l_1| = 0 \quad \text{if} \quad \kappa k = 11, 13. \tag{12}$$

The matrix elements resulting from relation (6) and conditions (11) and (12) were calculated by our computer code and included in the hyperfine structure energy matrix.

## 5. Determination of one- and two-body fine and hyperfine structure radial parameters

### 5.1. Interpretation of calculated $A$ and $B$ constants

Following our procedure presented in Figure 1, each  $hfs$   $A$  and  $B$  constant can be expressed as a linear combination of one- and two-body contributions as:

$$A(\psi) = \sum_{\kappa k, nl} \alpha_{nl}^{\kappa k}(\psi) a_{nl}^{\kappa k} + \sum_{\kappa k, i} \alpha_i^{\kappa k}(\psi) a_i^{\kappa k}, \quad (13)$$

$$B(\psi) = \sum_{\kappa k, nl} \beta_{nl}^{\kappa k}(\psi) b_{nl}^{\kappa k} + \sum_{\kappa k, i} \beta_i^{\kappa k}(\psi) b_i^{\kappa k}, \quad (14)$$

where  $\alpha_{nl}^{\kappa k}$ ,  $\beta_{nl}^{\kappa k}$  and  $\alpha_i^{\kappa k}$ ,  $\beta_i^{\kappa k}$  represent the angular coefficients at one- and two-body *hfs* operators respectively, while  $a_{nl}^{\kappa k}$ ,  $b_{nl}^{\kappa k}$  are the radial one-body parameters and  $a_i^{\kappa k}$ ,  $b_i^{\kappa k}$  are the traditionally used radial two-body parameters taken into account in the considered excitations. In our procedure the above parameters receive a full description introduced in Section 4, e.g.:  $D^2(5d, 5d, 5d, n'd) P^{02}(5d, n'd)$  denotes the contribution from excitation from the open shell 5d to the empty shells  $n'd$ , or  $D^2(n_0d, 5d, 5d, 5d) P^{02}(n_0d, 5d)$  denotes the contribution from excitation from the closed shell  $n_0d$  to the open shell 5d.

### 5.2. One-body parameters

Sandars and Beck [10] have developed a theory which simplifies calculation and interpretation of relativistic *hfs* effects in many electron atoms. This theory yields three effective radial integrals for each open shell ( $l > 0$ ) and for each multipole interaction, which should be handled as free adjustable parameters in order to take into account relativistic and configuration interaction effects. Therefore the following definitions of one-body radial parameters (if  $a_{nl}^{\kappa k}$ ,  $b_{nl}^{\kappa k}$  are expressed in MHz) for the considered configurations have been assumed :

$$\begin{aligned} a_{nl}^{\kappa k} &= \frac{2\mu_B}{h} g_I [\langle r^{-3} \rangle_{nl}^{\kappa k} + I_{n_0 l_0, n' l'}^{\kappa k}] = \frac{2\mu_B}{h} g_I \langle r^{-3} \rangle_{nl}^{\kappa k} \text{ eff}, \quad \kappa k = 01, 12, 10, \\ b_{nl}^{\kappa k} &= \frac{e^2}{h} Q [\langle r^{-3} \rangle_{nl}^{\kappa k} + I_{n_0 l_0, n' l'}^{\kappa k}] = \frac{e^2}{h} Q \langle r^{-3} \rangle_{nl}^{\kappa k} \text{ eff}, \quad \kappa k = 02. \end{aligned} \quad (15)$$

In above definitions,  $\langle r^{-3} \rangle_{nl}^{\kappa k}$  are the relativistic HFS radial integrals, as was shown by Lindgren and Rosen [12], which can be calculated *ab-initio* theoretically, and  $I_{n_0 l_0, n' l'}^{\kappa k}$  are radial parameters represented configuration interaction effects which reduced to one-body [40], commonly named "core polarization effects" [41].

The excitations of one electron from a closed shell  $n_0 l_0^{4l_0+2}$  to an empty shell  $n' l'$  are two-body *hfs* interactions which can be reduced to one-body interactions.

The radial parameter  $I_{n_0 l_0, n' l'}^{\kappa k}$  has been defined [41] as follows:

$$\begin{aligned} I_{n_0 l_0, n' l'}^{\kappa k} &= - \sum_{n_0 l_0, n' l'} \langle r^{-3} \rangle_{n_0 l_0, n' l'}^{\kappa k} \frac{2 t_{coeff}^{\kappa k}(n_0 l_0, n' l')}{t_{coeff}^{\kappa k}(nl, nl)} \\ &\times \left[ \frac{2\delta(\kappa, 0)}{2k+1} (l_0 \| C^k \| l') (l \| C^k \| l) R^k(n_0 l_0 n l, n' l' n l) / \Delta E(n_0 l_0, n' l') \right. \\ &+ \sum_t (-1)^{1+k+t} \left\{ \begin{matrix} l & k & l \\ l_0 & t & l' \end{matrix} \right\} (l \| C^t \| l') (l_0 \| C^t \| l) \\ &\left. \times R^t(n_0 l_0 n l, n l n' l') / \Delta E(n_0 l_0, n' l') \right]. \end{aligned} \quad (16)$$

where  $t_{coeff}^{\kappa k}(nl, nl)$  is the angular part of the *hfs* operator  $\mathbf{t}^{\kappa k}$  :  $\langle nl || \mathbf{t}^{\kappa k} || nl \rangle = t_{coeff}^{\kappa k}(nl, nl) \langle r^{-3} \rangle_{nl}^{\kappa k}$ ,  $\Delta E$  is the (positive) energy difference between the relevant closed- and empty-shell orbitals, and  $n'$  covers all empty shells including continuum.

The radial parameter determined from experimental data  $\langle r^{-3} \rangle_{nl \text{ eff}}^{\kappa k}$  should be interpreted as the sum of  $\langle r^{-3} \rangle_{nl}^{\kappa k}$  and  $I_{n_0 l_0, n' l'}^{\kappa k}$ :

$$\langle r^{-3} \rangle_{nl \text{ eff}}^{\kappa k} = \langle r^{-3} \rangle_{nl}^{\kappa k} + I_{n_0 l_0, n' l'}^{\kappa k}. \quad (17)$$

The relations between the one-body *hfs* parameters and the radial effective integrals are as follows [12] :

$$\begin{aligned} a_{5d}^{\kappa k} &= 95.4128 g_I \langle r^{-3} \rangle_{5d \text{ eff}}^{\kappa k} \quad \kappa k = 01, 12, \\ a_{6s}^{10} &= 63.6086 g_I \langle r^{-3} \rangle_{6s \text{ eff}}^{10} = 63.6086 g_I \left[ \frac{dP_{6s}(r)}{dr} \right]_{r=0}^2, \\ b_{5d}^{\kappa k} &= 234.9624 Q \langle r^{-3} \rangle_{5d \text{ eff}}^{\kappa k} \quad \kappa k = 02, 11, 13, \end{aligned} \quad (18)$$

where  $g_I$  is the nuclear  $g_I$ -factor expressed in nuclear magnetons (for the  $^{139}\text{La}$  nucleus  $g_I = +0.7931$ ); the values of the parameter  $a^{\kappa k}$  and  $b^{\kappa k}$  are given in MHz, and those of  $\langle r^{-3} \rangle_{\text{eff}}^{\kappa k}$  and  $\left[ \frac{dP_{6s}(r)}{dr} \right]_{r=0}^2$  - in atomic units.  $\langle r^{-3} \rangle_{\text{eff}}^{\kappa k}$  and  $\left[ \frac{dP_{6s}(r)}{dr} \right]_{r=0}^2$  are the sums of relativistic and configuration interaction effects contributions.

### 5.3. Two-body parameters

The effects of excitations of one electron from an open shell to an empty shell or from a closed shell to an open shell, are referred to as two-body *hfs* interactions (see Section 4).

The values of one- and two-body fine structure and hyperfine structure parameters (predicted by theory for the configuration system  $(5d+6s)^3$ ) determined in our procedure, and also values of the radial integrals, are listed in Table 6. The ratio of the two-body parameters  $\kappa k = 12$  and  $\kappa k = 01$  was assumed to amount to 1. For the parameters containing electrostatic integrals of the order  $t = 4$  the ratio with respect to the corresponding  $t = 2$  parameters was assumed to be equal to 0.65071 (from Hartree-Fock calculations). In the case of parameters with relative errors exceeding 100%, their values were set to 0, which resulted in improvement of the fit for the *hfs* constants in the least squares method.

### 5.4. Recalculation to radial one-configuration parameters

Each set of parameters for the models, (c-o) or (o-e), given in the Table 6, were determined in a totally independent way. In the constructed fine structure and hyperfine structure energy matrices the angular coefficients in the matrix elements originating from the first order perturbation theory are identical. However, the angular coefficients in the matrix elements originating from the second order perturbation theory are different for both models considered, but they involve the angular coefficients of the first order elements and form implicit linear dependencies. Thus a simultaneous use of the sets of parameters obtained in models (c-o) and (o-e) has to be excluded. If a linear dependence between two-body parameters vanishes, it indicates erroneous values of angular coefficients in the matrix elements; this was applied as a correctness test in construction of the energy matrix. A confirmation of the correctness of the model of description of atomic structure can also be provided by the values of two-body *fs* and *hfs* parameters, which should differ only by

their signs. Thus the values of two-body parameters, given in Table 6 , should be understood as algebraic sums of contributions from excitations of the type "closed shell - open shell" or the type "open shell - empty shell".

The respective one-body *fs* and *hfs* radial parameters obtained within both models are different, since in each model they effectively "include" a different combination of the contributions from one and two-body interactions.

The relations allowing elimination of those contributions and determination of the radial one-body parameters characteristic of the individual configurations  $5d^{\sharp}$ ,  $5d^26s$  and  $5d6s^2$ , forming the model space  $(5d+6s)^3$ , are as follows:

for excitations "closed shell – open shell"(c-o):

electrostatically correlated spin-orbit interaction:

$$\begin{aligned}\zeta(nd^N n' s^{N'}) &= \zeta(c - o) + 2N \times D^0(n_0 d 5d, 5d 5d) \zeta_{n_0 d, 5d} \\ &+ \frac{2}{7} \times D^2(n_0 d 5d, 5d 5d) \zeta_{n_0 d, 5d} \\ &- \frac{8}{21} \times D^4(n_0 d 5d, 5d 5d) \zeta_{n_0 d, 5d} \\ &- \frac{2}{5} \times E^2(5d 6s, 6s n_0 d) \zeta_{n_0 d, 5d} \delta(N', 2),\end{aligned}\quad (19)$$

electrostatically correlated *hfs* interactions:

$$\begin{aligned}a_{5d}^{01}(nd^N n' s^{N'}) &= a_{5d}^{01}(c - o) + 2N \times D^0(n_0 d 5d, 5d 5d) P^{01}(n_0 d, 5d) \\ &+ \frac{2}{7} \times D^2(n_0 d 5d, 5d 5d) P^{01}(n_0 d, 5d) \\ &- \frac{8}{25} \times D^4(n_0 d 5d, 5d 5d) P^{01}(n_0 d, 5d) \\ &- \frac{2}{5} \times E^2(n_0 d 6s, 6s 5d) P^{01}(n_0 d, 5d) \delta(N', 2),\end{aligned}\quad (20)$$

$$\begin{aligned}a_{5d}^{12}(nd^N n' s^{N'}) &= a_{5d}^{12}(c - o) + 2N \times D^0(n_0 d 5d, 5d 5d) P^{12}(n_0 d, 5d) \\ &- \frac{6}{49} \times D^2(n_0 d 5d, 5d 5d) P^{12}(n_0 d, 5d) \\ &+ \frac{8}{49} \times D^4(n_0 d 5d, 5d 5d) P^{12}(n_0 d, 5d) \\ &- \frac{2}{5} \times E^2(n_0 d 6s, 6s 5d) P^{12}(n_0 d, 5d) \delta(N', 2),\end{aligned}\quad (21)$$

$$a_{6s}^{10}(nd^N n' s) = a_{6s}^{10}(c - o) - 2N \times D^0(n_0 s 5d, 5d 6s) P^{10}(n_0 s, 6s),\quad (22)$$

$$\begin{aligned}b_{5d}^{02}(nd^N n' s^{N'}) &= b_{5d}^{02}(c - o) + 2N \times D^0(n_0 d 5d, 5d 5d) P^{02}(n_0 d, 5d) \\ &- \frac{62}{49} \times D^2(n_0 d 5d, 5d 5d) P^{02}(n_0 d, 5d)\end{aligned}$$

$$\begin{aligned}
& + \frac{8}{49} \times D^4(n_0d5d, 5d5d)P^{02}(n_0d, 5d) \\
& - \frac{2}{5} \times E^2(n_0d6s, 6s5d)P^{02}(n_0d, 5d)\delta(N', 2),
\end{aligned} \tag{23}$$

for excitations "open shell – empty shell"(o-e):  
electrostatically correlated spin-orbit interaction:

$$\begin{aligned}
\zeta(nd^N n' s^{N'}) & = \zeta(o - e) - 2(N - 1) \times D^0(5d5d, 5dn'd)\zeta_{5d, n'd} \\
& + \frac{2}{5} \times E^2(5d6s, 6sn'd)\zeta_{5d, n'd}\delta(N', 2),
\end{aligned} \tag{24}$$

electrostatically correlated *hfs* interactions:

$$\begin{aligned}
a_{5d}^{01}(nd^N n' s^{N'}) & = a_{5d}^{01}(o - e) - 2(N - 1) \times D^0(5d5d, 5dn'd)P^{01}(5d, n'd) \\
& + \frac{2}{5} \times E^2(5d6s, 6sn'd)P^{01}(5d, n'd)\delta(N', 2),
\end{aligned} \tag{25}$$

$$\begin{aligned}
a_{5d}^{12}(nd^N n' s^{N'}) & = a_{5d}^{12}(o - e) - 2(N - 1) \times D^0(5d5d, 5dn'd)P^{12}(5d, n'd) \\
& + \frac{2}{5} \times E^2(5d6s, 6sn'd)P^{12}(5d, n'd)\delta(N', 2),
\end{aligned} \tag{26}$$

$$a_{6s}^{10}(nd^N n' s) = a_{6s}^{10}(o - e) + 2N \times D^0(5d6s, 5dn's)P^{10}(6s, n's), \tag{27}$$

$$\begin{aligned}
b_{5d}^{02}(nd^N n' s^{N'}) & = b_{5d}^{02}(o - e) - 2(N - 1) \times D^0(5d5d, 5dn'd)P^{02}(5d, n'd) \\
& + \frac{2}{5} \times E^2(5d6s, 6sn'd)P^{02}(5d, n'd)\delta(N', 2).
\end{aligned} \tag{28}$$

The values of one-configuration parameters, obtained for both excitation models with the use of the above relations, are compiled in Table 7. The hyperfine structure parameters  $a^{\kappa k}$  and  $b^{\kappa k}$  given in this table for individual configurations are the *hfs* parameters obtained with the use of Sandars and Beck theory [10]. It can be seen that the respective values of the parameters obtained within two excitation models are equal up to third decimal place. It can serve as another test of correctness of the model of description of atomic structure.

## 6. Discussion of configuration interaction effects on the hyperfine structure

The influence of an excitation of an electron from a closed shell to an empty shell (a second-order effect) on the hyperfine structure is referred to as "hfs core-polarization effect". This term referees to both  $n_s$  and  $n_{0p}$ ,  $n_{0d}$  or  $n_{0f}$  electrons [41] which fill the closed shells in the atom. According to Lindgren and Morrison [40], the operators representing this effect are "pseudo-two-body operators" which can be reduced to the structure of one-body operators, and thus the corresponding radial parameters cause the effects of "screening or antiscreening" of the parameters of the first order perturbation theory in Sandars and Beck approach [10]. The most often discussed and analyzed effect is the one first described by Bauche and Judd, concerning the excitation of electrons from the closed shells  $n_s$  to the empty shells  $n's$ . In Sandars and

Beck theory the operator  $s$  and the radial parameter  $a_{nl}^{10}$  (where  $l > 0$ ) represent relativistic effects in the hyperfine structure. Thus, according to e.g. Feneuille and Armstrong [20], Armstrong [41] and Lindgren and Morrisson [40], the above mentioned effects are inseparable and cannot be independently determined in the least-squares procedure. Therefore in our method  $a_{nl}^{10} = 0$  for  $l > 0$  is assumed, while the effects of  $ns$  core polarization, which are different in each of the configurations  $5d^3$ ,  $5d^26s$  and  $5d6s^2$ , are described as follows:

- in configuration  $n_0s^25d^3$  closed shells are  $n_0 = 1, 2, \dots, 5$  and empty shells are  $n' = 6, 7, \dots$ ,
- in configuration  $n_0s^25d^26s$  closed shells are the same as above, but empty shells begin with  $n' = 7$ , and the shell  $6s$  is an open shell,
- in configuration  $n_0s^25d6s^2$  closed shells are from 1 to 6, an empty shells begin with  $7s$ .

Thus in the considered space  $(5d+6s)^3$  the core polarization effect should be described as follows:

- in configuration  $5d^3$ : with the use of parameter  $E^2(n_0s5d,5d6s) P^{10}(n_0s,6s) + E^2(n_0s5d,5dn's) P^{10}(n_0s,n's)$ , ( $n_0 = 1, 2, \dots, 5$ ,  $n' = 7, 8, \dots$ ),
- in configuration  $5d^26s$ : with the use of parameter  $E^2(n_0s5d,5d6s) P^{10}(n_0s,6s)$  ( $n_0 = 1, 2, \dots, 5$ ) representing the excitation from the closed shells  $n_0s$  to the open shell  $6s$ , as well as parameter  $E^2(n_0s5d,5dn's) P^{10}(n_0s,n's)$  representing the excitations from the five closed shells  $n_0s$  to the empty shells  $n's$  ( $n' = 7, 8, \dots$ )
- in configuration  $5d6s^2$ : with the use of parameter  $E^2(n_0s5d,5dn's) P^{10}(n_0s,n's)$ , ( $n_0 = 1, 2, \dots, 6$ ,  $n' = 7, 8, \dots$ ).

The determined values of those parameters are given in Table 6. With the use of relation  $P^{10} = 63.6086 g_I E^2(n_0s5d,5dn's) P^{10}(n_0s,n's)$

we can determine the radial integrals representing the electronic part of these interactions, which amount to:

- for excitations "closed shell  $n_0s$  - empty shell  $n's$ "  
 $E^2(n_0s5d,5dn's) P^{10}(n_0s,n's) = 4(3)$  au, ( $n_0 = 1, 2, \dots, 6$ ,  $n' = 7, 8, \dots$ )  
 $E^2(n_0s5d,5dn's) P^{10}(n_0s,n's) = -23(3)$  au, ( $n_0 = 1, 2, \dots, 5$ ,  $n' = 7, 8, \dots$ )
- for excitations "closed shell  $n_0s$  - open shell  $6s$ "  $E^2(n_0s5d,5d6s) P^{10}(n_0s,6s) = -19(2)$  au, ( $n_0 = 1, 2, \dots, 5$ )

From the above we can conclude, that excitations from the closed shells  $n_0s$  to an open or an empty shell  $6s$  plays a dominant role. For instance it can be seen that in the case of configuration  $5d^3$  the contribution of the core polarization effect (resulting from the second order of perturbation theory) to the observed hyperfine splittings is comparable to the contribution of the electrons  $5d$ , and in some cases the former even exceeds the latter. Moreover, one can see that in configuration  $5d6s^2$ , where the shell  $6s$  is closed and thus the excitation considered is excluded, only a small core polarization effect is observed. A negative-valued contribution from the excitations  $1s, 2s, \dots, 5s$  to  $7s, 8s, \dots$  is compensated by a positive contribution from the excitations of  $6s$  electron to empty shells. This resembles the picture resulting from theoretical calculations performed by Ron and Kelly [43] for configurations  $3d^64s^2$  in a Fe atom, where also the contributions of the excitations of the electrons  $1s, 2s, 3s$  to  $5s$  shell and the succeeding ones are negative, while the contributions of the excitations of the electron  $4s$  are positive.

As already mentioned above, it is not possible to determine the value of the relativistic parameter  $a_{5d}^{10}$  in the least squares procedure. We examined the behaviour of the values of the remaining hyperfine structure parameters in dependence on the value of the relativistic effect  $a_{5d}^{10}$ . As expected, changes of the values concerned only the parameters

$E^2(n_0s5d,5dn's) P^{10} (n_0 = 1,2,\dots,6, n' = 7,8,\dots$  and  $E^2(n_0s5d,5dn's) P^{10} (n_0 = 1,2,\dots,5, n' = 7,8,\dots$ , according to the linear dependence:

$$\begin{aligned} E^2(n_0s5d, 5dn's)P^{10}(n_0s, n's) &= -2.5a_{5d}^{10} + 181.310 \quad n_0 = 1, \dots, 6; n' = 7, 8, \dots \\ E^2(n_0s5d, 5dn's)P^{10}(n_0s, n's) &= -2.5a_{5d}^{10} - 190.270 \quad n_0 = 1, \dots, 5; n' = 7, 8, \dots \end{aligned} \quad (29)$$

where, for the parameter  $a_{5d}^{10}$  we can assume the values from *ab initio* theoretical calculations, performed with the use of differential methods [12].

Moreover, assumption of different values of parameter  $a_{5d}^{10}$  had no influence on the value of residuum.

From the relations (22) and (27), as well as Table 7 the following information about configuration interaction can be obtained:

$$a_{6s}^{10}(c-o) - a_{6s}^{10}(o-e) = 4 D^0(n_0s5d,6s5d)P^{10}(n_0s,6s) + D^0(5d6s,5dn's)P^{10}(6s,n's) = 149 \text{ MHz}$$

Thus we can determine the value of the contribution described in the second order perturbation theory as:

$$D^0(n_0s5d,6s5d)P^{10}(n_0s,6s) + D^0(5d6s,5dn's)P^{10}(6s,n's) = 37 \text{ MHz}$$

It results from Table 7, that in all the cases considered  $a_{5d}^{12} < a_{5d}^{01}$ . This result differs from the one expected on the basis of the relativistic theory of the hyperfine structure [12,42], where the expected relation for the 5d elements should be amounts to  $a^{12}/a^{01} > 1.25$ .

We can explain the results obtained within this work only if we assume, that the core polarization effects concerned with the excitations  $n_0s \rightarrow n'd$ ,  $n_0p \rightarrow n'p, n'f$  and  $n_0d \rightarrow n's, n'd, n'g$  are different, dependent on  $\kappa k = 01, 12$  or  $02$ , which specify the parameters  $a^{\kappa k}$  of the hyperfine structure. In order to explain such an effect of core polarization the full definitions of one-body radial parameters given below are very helpful:

$$\begin{aligned} \langle r^{-3} \rangle_{5d \text{ eff}}^{01} &= \langle 5d | r^{-3} | 5d \rangle^{01} + \sum_{n_0=2}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'p | r^{-3} | n_0p \rangle^{01} \\ &\quad \times \left[ \frac{2}{5} R^1(n_0p5d, 5dn'p) - \frac{6}{35} R^3(n_0p5d, 5dn'p) \right] \\ &\quad + \sum_{n_0=3}^4 \sum_{n'} \frac{1}{\Delta E} \langle n'd | r^{-3} | 5d \rangle^{01} \left[ 2R^0(n_0d5d, 5dn'd) \right. \\ &\quad \left. + \frac{2}{7} R^2(n_0d5d, 5dn'd) - \frac{8}{21} R^4(n_0d5d, 5dn'd) \right] \end{aligned} \quad (30)$$

$$\begin{aligned} \langle r^{-3} \rangle_{5d \text{ eff}}^{12} &= \langle 5d | r^{-3} | 5d \rangle^{12} + \sum_{n_0=1}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'd | r^{-3} | n_0s \rangle^{12} \frac{2}{5} R^2(n_0s5d, 5dn'd) \\ &\quad + \sum_{n_0=2}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'p | r^{-3} | n_0p \rangle^{12} \left[ \frac{14}{25} R^1(n_0p5d, 5dn'p) + \frac{18}{175} R^3(n_0p5d, 5dn'p) \right] \\ &\quad + \sum_{n_0=2}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'f | r^{-3} | n_0p \rangle^{12} \left[ \frac{6}{25} R^1(n_0p5d, 5dn'f) + \frac{72}{175} R^3(n_0p5d, 5dn'f) \right] \\ &\quad + \sum_{n_0=3}^4 \sum_{n'} \frac{1}{\Delta E} \langle n'd | r^{-3} | 5d \rangle^{12} \left[ 2R^0(n_0d5d, 5dn'd) - \frac{6}{49} R^2(n_0d5d, 5dn'd) \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{8}{49} R^4(n_0 d 5d, 5dn'd) \Big] \\
& + \sum_{n_0=3}^4 \sum_{n'} \frac{1}{\Delta E} \langle n'g | r^{-3} | 5d \rangle^{12} \left[ \frac{72}{245} R^2(n_0 d 5d, 5dn'g) + \frac{20}{49} R^4(n_0 d 5d, 5dn'g) \right]
\end{aligned} \tag{31}$$

$$\begin{aligned}
\langle r^{-3} \rangle_{5d \text{ eff}}^{02} & = \langle 5d | r^{-3} | 5d \rangle^{02} \\
& + \sum_{n_0=1}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'd | r^{-3} | n_0s \rangle^{02} \left[ -\frac{4}{5} R^2(n_0s5d, n'd5d) + \frac{2}{5} R^2(n_0s5d, 5dn'd) \right] \\
& + \sum_{n_0=2}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'p | r^{-3} | n_0p \rangle^{02} \left[ -\frac{24}{25} R^2(n_0p5d, n'p5d) + \frac{14}{25} R^1(n_0p5d, 5dn'p) \right. \\
& \quad \left. + \frac{18}{175} R^3(n_0p5d, 5dn'p) \right] \\
& + \sum_{n_0=2}^5 \sum_{n'} \frac{1}{\Delta E} \langle n'f | r^{-3} | n_0p \rangle^{02} \left[ -\frac{36}{25} R^2(n_0p5d, n'f5d) + \frac{6}{25} R^1(n_0p5d, 5dn'f) \right. \\
& \quad \left. + \frac{72}{175} R^3(n_0p5d, 5dn'f) \right] \\
& + \sum_{n_0=3}^4 \sum_{n'} \frac{1}{\Delta E} \langle n'''d | r^{-3} | 5d \rangle^{02} \left[ -\frac{8}{7} R^2(n_0d5d, n'd5d) + 2R^0(n_0d5d, 5dn'd) \right. \\
& \quad \left. - \frac{6}{49} R^2(n_0d5d, 5dn'd) + \frac{8}{49} R^4(n_0d5d, 5dn'd) \right] \\
& + \sum_{n_0=3}^4 \sum_{n'} \frac{1}{\Delta E} \langle n'g | r^{-3} | 5d \rangle^{02} \left[ -\frac{72}{35} R^2(n_0d5d, n'g5d) + \frac{72}{245} R^2(n_0d5d, 5dn'g) \right. \\
& \quad \left. + \frac{20}{49} R^4(n_0d5d, 5dn'g) \right].
\end{aligned} \tag{32}$$

When analyzing the above relations, we may assume, that in the case  $\kappa k = 12$  a larger compensation of the relativistic effects by polarization effects is possible than in the case  $\kappa k = 01$ , which might explain the least squares fit results, where the following ratio was obtained:  $a^{12}/a^{01} \approx 0.8$ . The authors of the papers [12, 42] noticed, that the experimental values for these ratios are reversed with respect to the theoretical ones. This is due to the influence of configurations interaction effects

One of the aims of our work was a precise definition of the radial integrals determined on the basis of the experimental data, which makes the determination of their contributions to the constants  $A$  and  $B$  possible. Comparison of such contributions, estimated from the experiment, with their counterparts calculated *ab-initio* theoretically would be definitely more interesting than the comparison given in Table 3, which is currently possible.

If the formalism describing the interaction between the electronic shell and the atomic nucleus were strictly correct, the ratios of two-body *hfs* radial parameters should be identical. On the basis of the data from Table 6 we obtain:

$$\begin{aligned}
D^0(5d5d, 5dnd)P^{01}(5d, nd)/D^0(5d5d, 5dnd)P^{02}(5d, nd) &= 0.94, \\
D^2(5d5d, 5dnd)P^{01}(5d, nd)/D^2(5d5d, 5dnd)P^{02}(5d, nd) &= 0.24, \\
E^2(5d5d, 5dnd)P^{01}(5d, nd)/E^2(5d5d, 5dnd)P^{02}(5d, nd) &= 0.46, \\
D^2(5dnd, 5d6s)P^{01}(5d, nd)/D^2(5dnd, 5d6s)P^{02}(5d, nd) &= 0.77, \\
E^2(5dnd, 6s5d)P^{01}(5d, nd)/E^2(5dnd, 6s5d)P^{02}(5d, nd) &= 0.92.
\end{aligned} \tag{33}$$

This indicates that the description of the configurations interaction within the frame of magnetic dipole or electric quadrupole interactions in the hyperfine structure is not fully correct.

## 7. Conclusions

On the basis of the analytical content of the tables in this work we tried to address the problems stated in Introduction. As can be seen from Table 2, application of the method of energy matrix diagonalization in the basis *SLJF* allows to describe the observed hyperfine splitting intervals with the use of the constants *A*, *B* and *C* within the accuracy of the measurements performed with the double resonance method (ABMR-LIRF), which is of the order of a few kHz. Thus, on the basis of the precise experimental data it can be stated that the operator of the form given in Equation (1) correctly describes the partition of the observed hyperfine splitting into the interactions of the ranks  $K = 1, 2, 3$ .

In Table 3 all the data concerning the constants *A* and *B*, available in the literature, were compiled; this concerns both the experimentally determined and the *ab initio* theoretically calculated values. From the comparison of the columns 4 and 5, or 7 and 8, one can rather speak of severe discrepancies and a few accidental coincidences between the experimental and the *ab initio* theoretical values. For instance, for the level at  $13238 \text{ cm}^{-1}$  three different values of the constant *A* were predicted: 86, -18 and 102 MHz, while the experimental value amounts to -19 MHz, and for the level at  $9910 \text{ cm}^{-1}$  the theoretical values are as follows 431, 471 and 333 MHz, in severe discrepancy with the experimental result of 559 MHz. It indicates a limited usefulness of the theoretical *ab initio* calculations for the understanding of the mechanism of interaction between the electronic shells and the atomic nucleus.

According to Sandars and Beck theory the magnetic dipole interactions (rank  $K = 1$ ) may be divided into the suborders  $\kappa k = 01, 12, 01$ , describing the interaction of the electronic shell with the magnetic dipole moment of the nucleus. In a similar way the interactions of the rank  $K = 2$  can be divided into interactions of suborders  $\kappa k = 02, 13, 11$  with the electric quadrupole moment of the nucleus. As evident from Table 5, for the electrostatic quadrupole interaction the agreement between  $B_{corr}$  and  $B_{calc}$  is of the order of the accuracy of their determination (differences between  $B_{exp,corr}$  [13] and  $B_{corr}$  (this work) reach even 5.7 MHz). Thus we can assume that the operator

$$T_e^{(\kappa k)2} \cdot T_n^{(2)} = \frac{e}{4\pi\epsilon_0} \sum_{i=1}^N \left[ -\hat{C}_i^2 \langle r^{-3} \rangle^{02} + \sqrt{\frac{3}{10}} \left( \hat{U}_i^{(13)2} \langle r^{-3} \rangle^{13} + \hat{U}_i^{(11)2} \langle r^{-3} \rangle^{11} \right) \right] \cdot T_n^{(2)}, \tag{34}$$

rather correctly describes the interaction between the electronic shells and the electric quadrupole moment of the nucleus. It should be stressed, that in our analysis 19 constants *B* determined with high precision from ABMR-LIRF experiments were applied. In the fit procedure 9 free parameters were used and the rms error amounted to 0.47 MHz. A drastically different picture emerges when we try to divide the interactions of the rank  $K = 1$  into the contributions grouped according to the operators subranks  $\kappa k = 01, 12, 01$ .

It can be seen in Table 5, that the differences between  $A_{corr}$  and  $A_{calc}$  reach even 20 MHz in some cases; this results e.g. in the difference between the total observed hyperfine splitting of the level  $^4F_{9/2}$  and its calculated counterpart of  $\approx 700$  MHz. Such differences are very large and they can be detected even with the classical optical methods. In the case of the analysis of magnetic dipole interactions we had at our disposal altogether 35 constants, among them 21 very precise ones (obtained with the ABMR-LIRF method) and 14 of an accuracy 1-4 MHz, from the LIF method. The number of free parameters amounted to 13 and the rms error amounted to ca. 12.1 MHz. Use of all one- and two-body parameters predicted by the theory (also of those given in Table 6 with the values set to 0) did not remove the discrepancies between the constants  $A$ , and it solely increased the rms error. Therefore for the parameters determined with an error considerably exceeding 100% in the final procedure the values 0 were assumed. The reason of the observed discrepancies could be the inaccurate eigenvectors' amplitudes, determined on the basis of the fine structure analysis. The source of such errors, as already mentioned in Introduction, might be e.g. assignment of an incorrect  $J$  value to the correct energy value. Thus in this work any doubts of this kind were removed due to investigations of the hyperfine structure with LIF method. Lack of data concerning the levels  $5d^2 \ ^1D$   $J = 3/2$ , as well as of the confirmation of the energy of the level  $J = 5/2$ , had no considerable influence on the accuracy of the obtained values of the eigenvectors' amplitudes. Their quality is proved by the excellent agreement between the experimental and the calculated values of  $f_{gJ}$  factors, as clearly visible in Table 5. We also supposed, that the reason of the discrepancies may be perturbation of the hyperfine structure by spin orbit coupling with distant configurations. This assumption was also examined in detail in the way analogous to the case described in Section 4; the electrostatic interaction operator  $\mathbf{G}$  in equation (6) was replaced by the spin-orbit interaction operators  $\mathbf{I}$ . The parameters describing the above coupling proved to exhibit linear dependence with the relativistic parameters resulting from Sandars and Beck theory [10]. It applies to both magnetic dipole and electric quadrupole hyperfine interactions. Thus we proved, in a different way, the theoretical considerations of Feneuille and Armstrong [20] about the impossibility of differentiation between the relativistic contributions and the contributions of configurations interactions solely on the basis of experimental data. In the case of the interactions  $K = 1$   $\kappa k = 01, 12$  and  $K = 2$   $\kappa k = 02$  relativistic and configurations interaction contributions are added to the nonrelativistic contribution. In the cases  $K = 1$   $\kappa k = 10$  and  $K = 2$   $\kappa k = 13, 11$ , where the nonrelativistic contribution amounts to 0, both the effects: the relativistic effect and the configurations interaction effect contribute to the non-zero value of the effective parameter. In our procedure of the analysis of atomic structure we critically analyzed all the available experimental data. In the theoretical description of the atomic structure all possible contributions originating from the second order perturbation theory were taken into account. They were independently described in the excitation models: (c-o) and (o-e). The consistency of the results obtained, as seen in Table 6, proves the correctness of the procedure and the formulae applied in construction of the energy matrix. Thus, on the basis of the results of this work, we may state, that the operator in the form

$$T_e^{(\kappa k)1} \cdot T_n^{(1)} = \frac{\mu_0 \mu_B}{2\pi} \sum_{i=1}^N \left[ \hat{l}_i \langle r^{-3} \rangle^{01} - \sqrt{10} \left( \hat{s}_i \hat{C}_i^2 \right)^{(1)} \langle r^{-3} \rangle^{12} + \hat{s}_i \langle r^{-3} \rangle^{10} \right] \cdot T_n^{(1)}, \quad (35)$$

does not fully describe the observed magnetic dipole interaction  $K = 1$  in the atomic hyperfine structure, i.e. its partition into the contributions  $\kappa k = 01, 12$  and  $10$ . In the near future we plan to undertake investigations of the model of magnetic dipole and magnetic octupole interactions in an atom, where a more complex structure of the nucleus is assumed than in hitherto existing models. For the full verification of the new model more precise measurements of the hyperfine splittings would be required, where the constants of magnetic octupole interaction could be determined with the relative accuracy of the order of 10%. The

present accuracy of the determined  $C$  constants (see Table 4) does not allow to put any hypothesis concerning this interaction.

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**Table 1.** Compilation of spectral lines used for measurement of the hyperfine structure constants of levels belonging to even parity configurations in lanthanum atom, performed with the method of LIF in a hollow cathode discharge. Spectroscopic description of the levels belonging to odd-parity configurations on the basis of [33]. Value of J quantum number for the level with energy  $E=33799.23[\text{cm}^{-1}]$ , that was changed from 5/2 to 3/2 on the basis of the investigations performed, has been marked with asterisk

No	Line		Lower level			Upper Level		
	$\lambda_{air}[\text{nm}]$	$k_{vac}[\text{cm}^{-1}]$	Designation	Energy $[\text{cm}^{-1}]$	J	Designation	Energy $[\text{cm}^{-1}]$	J
1	602.724	16586.75	$5d^3\ ^4P$	16617.30	1/2	$4f\ 5d6s\ (^1D)\ ^2P$	33204.05	3/2
2	594.797	16807.81	$5d^2(^1S)6s\ ^2S$	16991.42	1/2	$4f\ 6s6d\ (^3D)\ ^2P$	33799.23	*3/2
3	587.231	17024.34	$5d^2(^1S)6s\ ^2S$	16991.42	1/2	$5d^2(^3F)7p\ ^4F$	34015.76	3/2
4	662.503	15090.10	$5d^3\ ^2P$	20392.60	1/2	$5d\ 6s7p\ (^3P)\ ^4P$	35482.70	1/2
5	607.036	16468.91	$5d^3\ ^4P$	16735.14	3/2	$4f\ 5d6s\ (^1D)\ ^2P$	33204.05	3/2
6	569.189	17563.97	$5d^3\ ^4P$	16735.14	3/2	$5d^2(^3F)7p\ ^2D$	34299.11	3/2
7	633.431	15782.67	$5d^3\ ^2D$	18037.64	3/2	$4f\ 6s6d\ (^3D)\ ^2P$	33820.31	1/2
8	573.069	17445.06	$5d^3\ ^2D$	18037.64	3/2	$5d\ 6s7p\ (^3P)\ ^4P$	35482.70	1/2
9	630.369	15859.33	$5d^3\ ^2P$	21037.30	3/2	$6s^2(^1S)7p\ ^2P$	36896.63	1/2
10	597.412	16734.23	$5d^3\ ^2P$	21037.30	3/2	$4f\ 5d^2\ (^3F)\ ^4D$	37771.53	5/2
11	587.234	17024.27	$5d^3\ ^2P$	21037.30	3/2	$4f\ 5d^2\ (^1D)\ ^2D$	38061.57	3/2
12	656.023	15239.14	$5d^3\ ^2D$	18776.62	5/2	$5d^2(^3F)7p\ ^4F$	34015.76	3/2
13	654.440	15276.02	$5d^3\ ^2F$	21969.32	5/2	$5d\ 6s7p\ (^3P)\ ^2F$	37245.34	5/2
14	634.251	15762.27	$5d^3\ ^2F$	21969.32	5/2	$4f\ 5d^2\ (^3F)\ ^4F$	37731.59	5/2
15	632.027	15817.72	$5d^3\ ^2F$	21969.32	5/2	$4f\ 5d^2\ (^3F)\ ^4P$	37787.04	3/2
16	629.808	15873.45	$5d^3\ ^2F$	21969.32	5/2	$4f\ 5d^2\ (^3F)\ ^4D$	37842.77	7/2
17	625.139	15992.02	$5d^3\ ^2F$	21969.32	5/2	$4f\ 5d^2\ (^3F)\ ^4F$	37961.34	5/2
18	624.306	16013.36	$5d^3\ ^2F$	21969.32	5/2	$4f\ 5d^2\ (^1D)\ ^2G$	37982.68	7/2
20	580.683	17216.31	$5d^3\ ^2G$	17023.36	7/2	$4f\ 6s6d\ (^3D)\ ^2H$	34239.61	9/2
21	653.348	15301.54	$5d^3\ ^2F$	21943.80	7/2	$5d\ 6s7p\ (^3P)\ ^2F$	37245.34	5/2
22	633.226	15787.79	$5d^3\ ^2F$	21943.80	7/2	$4f\ 5d^2\ (^3F)\ ^4F$	37731.59	5/2
23	623.312	16038.88	$5d^3\ ^2F$	21943.80	7/2	$4f\ 5d^2\ (^1D)\ ^2G$	37982.68	7/2
24	580.043	17235.31	$5d^3\ ^2F$	21943.80	7/2	$4f\ 5d^2\ (^1D)\ ^2G$	39179.11	5/2
25	584.677	17098.71	$5d^3\ ^2G$	17140.90	9/2	$4f\ 6s6d\ (^3D)\ ^2H$	34239.61	9/2
26	584.491	17104.15	$5d^3\ ^2G$	17140.90	9/2	$4f\ 6s6d\ (^3D)\ ^2H$	34245.05	11/2
27	627.820	15923.73	$5d^3\ ^2H$	18315.88	9/2	$4f\ 6s6d\ (^3D)\ ^2H$	34239.61	9/2
28	627.605	15929.17	$5d^3\ ^2H$	18315.88	9/2	$4f\ 6s6d\ (^3D)\ ^2H$	34245.05	11/2
29	590.252	15937.22	$5d^3\ ^2H$	18315.88	9/2	$5d^2(^3F)7p\ ^2F$	35253.10	7/2
30	583.453	17134.59	$5d^3\ ^2H$	18315.88	9/2	$5d^2(^3F)7p\ ^4F$	35450.47	9/2
31	627.410	15934.13	$5d^3\ ^2H$	18310.92	11/2	$4f\ 6s6d\ (^3D)\ ^2H$	34245.05	11/2
32	583.284	17139.55	$5d^3\ ^2H$	18310.92	11/2	$5d^2(^3F)7p\ ^4F$	35450.47	9/2

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Table 2: Comparison of the experimental and calculated hyperfine structure intervals

Energy $[\text{cm}^{-1}]$	J	$F \leftrightarrow F'$	interval [MHz]		
			observed	calculated	obs.– calc.
0.00	3/2	$3 \leftrightarrow 2$	391.603(10) [44]	391.601	0.002

Table 2: (continued)

Energy [cm <sup>-1</sup> ]	J	F ↔ F'	interval [MHz]		
			observed	calculated	obs. - calc.
1053.16	5/2	4 ↔ 3	551.987(5) [44]	551.989	-0.002
		5 ↔ 4	737.967(15) [44]	737.966	0.001
		3 ↔ 2	529.090(10) [44]	529.088	0.002
		4 ↔ 3	716.288(3) [44]	716.292	-0.004
		5 ↔ 4	912.793(5) [44]	912.789	0.004
		6 ↔ 5	1120.902(5) [44]	1120.904	-0.002
2668.19	3/2	3 ↔ 2	-1451.728(20) [13]	-1451.727	-0.001
		4 ↔ 3	-1925.506(20) [13]	-1925.507	0.001
		5 ↔ 4	-2390.615(20) [13]	-2390.614	-0.001
3010.00	5/2	4 ↔ 3	1199.787(15) [26]	1199.792	-0.005
		5 ↔ 4	1503.210(18) [26]	1503.204	0.006
		6 ↔ 5	1808.936(12) [26]	1808.939	-0.003
3494.53	7/2	4 ↔ 3	1847.837(12) [26]	1847.836	0.001
		5 ↔ 4	2312.531(20) [26]	2312.531	0.000
		6 ↔ 5	2779.047(7) [26]	2779.047	0.000
		7 ↔ 6	3247.744(6) [26]	3247.744	0.000
4121.57	9/2	4 ↔ 3	1952.018(20) [26]	1952.017	0.001
		5 ↔ 4	2442.885(22) [26]	2442.885	0.000
		6 ↔ 5	2935.669(10) [26]	2935.669	0.000
		7 ↔ 6	3430.754(13) [26]	3430.755	-0.001
		8 ↔ 7	3928.536(27) [26]	3928.536	0.000
7011.91	5/2	4 ↔ 3	1211.072(15) [26]	1211.076	-0.004
		5 ↔ 4	1522.871(15) [26]	1522.866	0.005
		6 ↔ 5	1840.665(15) [26]	1840.667	-0.002
7231.41	1/2	4 ↔ 3	9840.644(40) [13]	9840.647	-0.003
7490.52	3/2	3 ↔ 2	2762.278(20) [13]	2762.279	-0.001
		4 ↔ 3	3707.825(20) [13]	3707.824	0.001
		5 ↔ 4	4674.682(20) [13]	4674.682	0.000
7679.94	5/2	2 ↔ 1	1614.096(20) [13]	1614.100	-0.004
		3 ↔ 2	2417.501(20) [13]	2417.500	0.001
		4 ↔ 3	3216.524(20) [26]	3216.519	0.005
		5 ↔ 4	4009.667(20) [13]	4009.673	-0.006
		6 ↔ 5	4795.439(20) [13]	4795.436	0.003
8052.16	7/2	3 ↔ 2	-600.341(20) [13]	-600.341	0.000
		4 ↔ 3	-796.573(20) [13]	-796.573	0.000
		5 ↔ 4	-989.476(20) [13]	-989.477	0.001
		6 ↔ 5	-1178.223(20) [13]	-1178.222	-0.001
		7 ↔ 6	-1361.981(20) [13]	-1361.982	0.001
		8 ↔ 7	-1545.734(20) [13]	-1545.734	0.000
8446.04	3/2	3 ↔ 2	-1262.378(20) [13]	-1262.382	0.004
		4 ↔ 3	-1687.663(20) [13]	-1687.659	-0.004
		5 ↔ 4	-2116.822(20) [13]	-2116.824	0.002
9044.21	1/2	4 ↔ 3	907.569(20) [13]	907.572	-0.003
9183.80	5/2	2 ↔ 1	1753.431(20) [13]	1753.413	0.018
		3 ↔ 2	2629.855(20) [13]	2629.863	-0.008
		4 ↔ 3	3505.908(20) [13]	3505.924	-0.016
		5 ↔ 4	4381.492(20) [13]	4381.471	0.021
		6 ↔ 5	5256.493(40) [13]	5256.503	-0.010

Table 2: (continued)

Energy [cm <sup>-1</sup> ]	J	F ↔ F'	interval [MHz]		
			observed	calculated	obs. - calc.
9719.44	3/2	3 ↔ 2	-1941.658(20) [13]	-1941.655	-0.003
		4 ↔ 3	-2611.058(20) [13]	-2611.062	0.004
		5 ↔ 4	-3299.435(20) [13]	-3299.433	-0.002
9919.82	9/2	4 ↔ 3	2200.726(20) [13]	2200.717	0.009
		5 ↔ 4	2768.920(20) [13]	2768.920	0.000
		6 ↔ 5	3349.169(20) [13]	3349.178	-0.009
		7 ↔ 6	3943.948(20) [13]	3943.940	0.008
		8 ↔ 7	4555.752(20) [13]	4555.755	-0.003
9960.90	7/2	1 ↔ 0	-299.185(20) [13]	-299.174	-0.011
		2 ↔ 1	-596.977(20) [13]	-596.982	0.005
		3 ↔ 2	-891.992(20) [13]	-891.998	0.006
		4 ↔ 3	-1182.851(20) [13]	-1182.845	-0.006
		5 ↔ 4	-1468.190(20) [13]	-1468.190	0.000
		6 ↔ 5	-1746.699(20) [13]	-1746.701	0.002
		7 ↔ 6	-2016.965(20) [13]	-2016.964	-0.001
12430.61	3/2	4 ↔ 3	1784.934(20) [13]	1784.929	0.005
		5 ↔ 4	2213.952(20) [13]	2213.955	-0.003
12787.40	5/2	3 ↔ 2	297.843(20) [13]	297.843	0.000
		4 ↔ 3	393.815(20) [13]	393.815	0.000
		5 ↔ 4	486.956(20) [13]	486.956	0.000
		6 ↔ 5	576.565(20) [13]	576.565	0.000
13238.32	7/2	5 ↔ 4	-93.382(20) [13]	-93.383	0.001
		6 ↔ 5	-116.751(20) [13]	-116.751	0.000
		7 ↔ 6	-142.677(20) [13]	-142.676	-0.001
13747.28	9/2	4 ↔ 3	-250.101(20) [13]	-250.101	0.000
		5 ↔ 4	-315.071(20) [13]	-315.071	0.000
		6 ↔ 5	-381.671(20) [13]	-381.671	0.000
		7 ↔ 6	-450.228(20) [13]	-450.228	0.000
		8 ↔ 7	-521.066(20) [13]	-521.066	0.000

Table 3: Experimental and corrected values of the  $hfs$  A and B constants [MHz] for the even parity energy levels of lanthanum atom. The values of  $A_{th}$  and  $B_{th}$  are taken from Childs and Nielsen (MCDF method) [13]<sup>(a)</sup>, from Beck (MCDF and RCI method) [45]<sup>(b)</sup> and from Karacoban (MCHF method) [46]<sup>(c)</sup>. The experimental values are taken from Ting [44]<sup>(d)</sup>, Childs and Goodman [26]<sup>(e)</sup>, Childs and Nielsen [13]<sup>(a)</sup>, Furmann et al [28,29]<sup>(f)</sup> and from our measurements. The values of  $A_{corr}$ ,  $B_{corr}$  and  $A_{calc}$ ,  $B_{calc}$  are obtained from our calculations

Energy [cm <sup>-1</sup> ]	Designation	$A_{th}$	$A_{exp}$	$A_{corr}$	$A_{calc}$	$B_{th}$	$B_{exp}$	$B_{exp,corr}$	$B_{corr}$	$B_{calc}$
0.00	$5d6s^2\ 2D_{3/2}$	111.23 <sup>a</sup> 129.7 <sup>b</sup> 143.27 <sup>c</sup>	141.1959 <sup>d</sup>	141.1961	144	29.59 <sup>a</sup> 29.9 <sup>b</sup> 27.57 <sup>c</sup>	44.781 <sup>d</sup>	44.781 <sup>d</sup>	44.776	44.853
1053.16	$5d6s^2\ 2D_{5/2}$	235.64 <sup>a</sup> 184.10 <sup>c</sup>	182.1706 <sup>d</sup>	182.1702	163	32.21 <sup>a</sup> 37.57 <sup>c</sup>	54.213 <sup>d</sup>	54.213 <sup>d</sup>	54.168	54.197
2668.19	$5d^2\ 6s\ 4F_{3/2}$	-398.55 <sup>a</sup> -414.7 <sup>b</sup> -322.87 <sup>c</sup>	-480.312 <sup>e</sup> -480.292 <sup>a</sup>	-480.208	-501	14.84 <sup>a</sup> 10.7 <sup>b</sup> 11.66 <sup>c</sup>	15.082 <sup>e</sup> 15.188 <sup>a</sup>	14.2 <sup>e</sup> 16.343 <sup>a</sup>	13.983	14.108
3010.00	$5d^2\ 6s\ 4F_{5/2}$	250.19 <sup>a</sup> 246.44 <sup>c</sup>	300.583 <sup>e</sup>	300.643	321	11.41 <sup>a</sup> 11.62 <sup>c</sup>	10.873 <sup>e</sup>	14.0 <sup>e</sup> 7.800 <sup>e</sup>	13.505	13.377
3494.53	$5d^2\ 6s\ 4F_{7/2}$	392.78 <sup>a</sup> 411.3 <sup>b</sup> 379.86 <sup>c</sup>	462.868 <sup>e</sup>	462.891	480	15.45 <sup>a</sup> 17.9 <sup>b</sup> 16.08 <sup>c</sup>	17.925 <sup>e</sup>	19.3 <sup>e</sup> 16.102 <sup>a</sup>	18.840	18.981
4121.57	$5d^2\ 6s\ 4F_{9/2}$	451.32 <sup>a</sup> 440 <sup>b</sup> 410.92 <sup>c</sup>	489.534 <sup>e</sup>	489.533	505	26.17 <sup>a</sup> 24.2 <sup>b</sup> 24.22 <sup>c</sup>	32.180 <sup>e</sup>	31.9 <sup>e</sup> 31.535 <sup>a</sup>	31.980	32.010
7011.91	$5d^2\ 6s\ 2F_{5/2}$	271.92 <sup>a</sup> 209.15 <sup>c</sup>	304.372 <sup>e</sup>	304.376	308	20.04 <sup>a</sup> 21.26 <sup>c</sup>	28.091 <sup>e</sup>	27.8 <sup>e</sup> 28.289 <sup>a</sup>	28.295	28.146
7231.41	$5d^2\ 6s\ 4P_{1/2}$	1913.46 <sup>a</sup> 2137.07 <sup>c</sup>	2460.119 <sup>e</sup> 2460.161 <sup>a</sup>	2460.229	2464					
7490.52	$5d^2\ 6s\ 4P_{3/2}$	844.26 <sup>a</sup> 842.6 <sup>b</sup> 822.32 <sup>c</sup>	930.0 <sup>e</sup> 929.618 <sup>a</sup>	929.666	918	28.58 <sup>a</sup> 25.0 <sup>b</sup> 23.27 <sup>c</sup>	42.1 <sup>e</sup> 37.221 <sup>a</sup>	37.2 <sup>e</sup> 34.723 <sup>a</sup>	37.066	36.184
7679.94	$5d^2\ 6s\ 4P_{5/2}$	731.87 <sup>a</sup> 604.60 <sup>c</sup>	802.8 <sup>e</sup> 802.172 <sup>a</sup>	802.166	795	-36.09 <sup>a</sup> -17.17 <sup>c</sup>	-23.9 <sup>e</sup> -34.186 <sup>a</sup>	-40 <sup>e</sup> -36.365 <sup>a</sup>	-34.793	-34.246
8052.16	$5d^2\ 6s\ 2F_{7/2}$	-12.80 <sup>a</sup> -170.7 <sup>b</sup> -11.01 <sup>c</sup>	-197.066 <sup>e</sup> -197.064 <sup>a</sup>	-197.065	-212	29.02 <sup>a</sup> 37.5 <sup>b</sup> 27.46 <sup>c</sup>	40.677 <sup>e</sup> 40.754 <sup>a</sup>	41.4 <sup>e</sup> 40.349 <sup>a</sup>	41.896	42.191
8446.04	$5d^2\ 6s\ 2D_{3/2}$	-321.39 <sup>a</sup>	-424.7 <sup>e</sup>	-422.419	-415	-0.85 <sup>a</sup>	-11.3 <sup>e</sup>	-13 <sup>e</sup>	-6.964	-7.295

Table 3: (continued)

Energy [cm <sup>-1</sup> ]	Designation	A <sub>lth</sub>	A <sub>exp</sub>	A <sub>corr</sub>	A <sub>calc</sub>	B <sub>th</sub>	B <sub>exp</sub>	B <sub>exp,corr</sub>	B <sub>corr</sub>	B <sub>calc</sub>
9044.21	5d <sup>2</sup> 6s <sup>2</sup> P <sub>1/2</sub>	-422.9 <sup>b</sup>	-422.399 <sup>a</sup>	226.837	231	-4.45 <sup>b</sup>	-6.753 <sup>a</sup>	-6.006 <sup>a</sup>		
9183.80	5d <sup>2</sup> 6s <sup>2</sup> D <sub>5/2</sub>	111.84 <sup>a</sup> 575.10 <sup>a</sup>	226.892 <sup>e</sup> 881.0 <sup>e</sup>	876.295	879	2.51 <sup>a</sup>	22 <sup>e</sup>	22 <sup>e</sup>	-4.474	-4.287
9719.44	5d <sup>2</sup> 6s <sup>2</sup> P <sub>3/2</sub>	-188.96 <sup>a</sup> -530.7 <sup>b</sup>	876.319 <sup>a</sup> -655.138 <sup>a</sup>	-655.208	-649	-22.16 <sup>a</sup> -24.2 <sup>b</sup>	-2.772 <sup>a</sup> -33.249 <sup>a</sup>	-5.404 <sup>a</sup> -33.539 <sup>a</sup>	-31.841	-31.546
9919.82	5d <sup>2</sup> 6s <sup>2</sup> G <sub>9/2</sub>	431.58 <sup>a</sup> 471 <sup>b</sup>	559.812 <sup>a</sup>	559.237	567	85.78 <sup>a</sup> 108 <sup>b</sup>	202.638 <sup>a</sup>	127.251 <sup>a</sup>	129.240	128.240
9960.90	5d <sup>2</sup> 6s <sup>2</sup> G <sub>7/2</sub>	333.93 <sup>c</sup> -178.47 <sup>a</sup> -253.7 <sup>b</sup>	-292.267 <sup>a</sup>	-293.000	-295	70.67 <sup>c</sup> 76.66 <sup>a</sup> 113 <sup>b</sup>	67.537 <sup>a</sup>	111.512 <sup>a</sup>	110.089	111.587
12430.61	5d <sup>3</sup> <sup>4</sup> F <sub>3/2</sub>	-98.07 <sup>c</sup> 176.15 <sup>a</sup> 391.8 <sup>b</sup>	445.086 <sup>a</sup>	445.098	435	79.38 <sup>c</sup> -12.02 <sup>a</sup> -9.87 <sup>b</sup>	-16.068 <sup>a</sup>		-16.240	-16.138
12787.40	5d <sup>3</sup> <sup>4</sup> F <sub>5/2</sub>	109.78 <sup>c</sup> 105.89 <sup>a</sup>	97.510 <sup>a</sup>	97.526	93	-12.02 <sup>c</sup> -12.91 <sup>a</sup>	-16.521 <sup>a</sup>		-16.141	-16.309
13238.32	5d <sup>3</sup> <sup>4</sup> F <sub>7/2</sub>	182.90 <sup>c</sup> 86.06 <sup>a</sup> -18.2 <sup>b</sup>	-19.103 <sup>a</sup>	-19.095	-20	-14.69 <sup>c</sup> -17.80 <sup>a</sup> -19.3 <sup>b</sup>	-20.898 <sup>a</sup>		-20.545	-20.638
13747.28	5d <sup>3</sup> <sup>4</sup> F <sub>9/2</sub>	102.15 <sup>c</sup> 82.06 <sup>a</sup> -53 <sup>b</sup>	-63.829 <sup>a</sup>	-63.827	-64	-14.33 <sup>c</sup> -23.87 <sup>a</sup> -20.6 <sup>b</sup>	-27.385 <sup>a</sup>		-27.104	-27.081
16617.30	5d <sup>3</sup> <sup>4</sup> P <sub>1/2</sub>	155.31 <sup>c</sup> -110.46 <sup>c</sup>	-696.6	-696.6	-709	-3.29 <sup>c</sup>				
16991.42	5d <sup>2</sup> 6s <sup>2</sup> S <sub>1/2</sub>	2543.29 <sup>c</sup>	4135.4 <sup>f</sup>	4135.4	4129					
20392.60	5d <sup>3</sup> <sup>2</sup> P <sub>1/2</sub>	128.12 <sup>c</sup>	258.9 <sup>f</sup>	258.9	264					
16735.14	5d <sup>3</sup> <sup>4</sup> P <sub>3/2</sub>	-231.8 <sup>b</sup> 74.03 <sup>c</sup>	-259.4 <sup>f</sup>	-259.4	-242	-17.7 <sup>b</sup> -26.67 <sup>c</sup>				-31.516
18037.64	5d <sup>3</sup> <sup>2</sup> D <sub>3/2</sub>	190.2 <sup>b</sup> 156.69 <sup>c</sup>	227.1	227.1	222	-24.3 <sup>b</sup> -29.35 <sup>c</sup>				-37.964
21037.30	5d <sup>3</sup> <sup>2</sup> P <sub>3/2</sub>	-64.0 <sup>b</sup> 61.99 <sup>c</sup>	-88.8 <sup>f</sup>	-88.8	-84	-14.1 <sup>b</sup> -19.64 <sup>c</sup>				-25.487
17099.38	5d <sup>3</sup> <sup>2</sup> D <sub>3/2</sub>	212.6 <sup>b</sup> 197.08 <sup>c</sup>			236	36.4 <sup>b</sup> 46.24 <sup>c</sup>				55.123
	5d <sup>3</sup> <sup>4</sup> P <sub>5/2</sub>	42.97 <sup>c</sup>	-222	-222	-221	32.72 <sup>c</sup>				36.267

Table 3: (continued)

Energy [ $\text{cm}^{-1}$ ]	Designation	$A_{th}$	$A_{exp}$	$A_{corr}$	$A_{calc}$	$B_{th}$	$B_{exp}$	$B_{exp,corr}$	$B_{corr}$	$B_{calc}$
18776.62	$5d^3 \ ^2D_{5/2}$	135.79 <sup>c</sup>	9.6 <sup>f</sup>	9.6	3	-33.61 <sup>c</sup>				-40.024
21969.32	$5d^3 \ ^2F_{5/2}$	129.85 <sup>c</sup>	165.5 <sup>f</sup>	165.5	181	31.65 <sup>c</sup>				46.810
25414.63	$5d^3 \ ^2D_{5/2}$	107.85 <sup>c</sup>			3	55.60 <sup>c</sup>				60.983
17023.36	$5d^3 \ ^2G_{7/2}$	137.7 <sup>b</sup>	161.8 <sup>f</sup>	161.8	143	35.1 <sup>b</sup>				42.159
21943.80	$5d^3 \ ^2F_{7/2}$	133.92 <sup>c</sup>	59.6 <sup>f</sup>	59.6	49	36.80 <sup>c</sup>				34.014
		50.8 <sup>b</sup>				28.5 <sup>b</sup>				
		132.71 <sup>c</sup>				21.68 <sup>c</sup>				
17140.90	$5d^3 \ ^2G_{9/2}$	69 <sup>b</sup>	111.2 <sup>f</sup>	111.2	115	34.3 <sup>b</sup>				63.322
		154.02 <sup>c</sup>				43.79 <sup>c</sup>				
18315.88	$5d^3 \ ^2H_{9/2}$	104 <sup>b</sup>	111.6 <sup>f</sup>	111.6	117	47.2 <sup>b</sup>				55.579
		135.09 <sup>c</sup>				61.48 <sup>c</sup>				
18310.92	$5d^3 \ ^2H_{11/2}$	129.71 <sup>c</sup>	57.4 <sup>f</sup>	57.3	63	73.14 <sup>c</sup>				90.505

**Table 4.** Corrected values of the *hfs* C constant [kHz] for the even parity energy levels of lanthanum atom.

Energy [cm <sup>-1</sup> ]	Designation	C <sub>corr</sub> (Ref.)	C <sub>corr</sub> (this work)	Ref.
0.00	5d6s <sup>2</sup> <sup>2</sup> D <sub>3/2</sub>	0.15(44)	0.2(1.3)	[44]
1053.16	5d6s <sup>2</sup> <sup>2</sup> D <sub>5/2</sub>	-0.6(1.0)	-0.2(3.0)	[44]
3010.00	5d <sup>2</sup> 6s <sup>4</sup> F <sub>5/2</sub>	2(3)	-0.9(2.1)	[26]
3494.53	5d <sup>2</sup> 6s <sup>4</sup> F <sub>7/2</sub>	-2(2)	-2.8(2.4)	[26]
4121.57	5d <sup>2</sup> 6s <sup>4</sup> F <sub>9/2</sub>	3(4)	2.5(2.9)	[26]
7011.91	5d <sup>2</sup> 6s <sup>2</sup> F <sub>5/2</sub>	-2(3)	-2.8(2.1)	[26]
7679.94	5d <sup>2</sup> 6s <sup>4</sup> P <sub>5/2</sub>		-0.7(2.1)	
8052.16	5d <sup>2</sup> 6s <sup>2</sup> F <sub>7/2</sub>		-0.5(2.4)	
9919.82	5d <sup>2</sup> 6s <sup>2</sup> G <sub>9/2</sub>		6.8(2.9)	
9960.90	5d <sup>2</sup> 6s <sup>2</sup> G <sub>7/2</sub>		-0.2(2.4)	
12787.40	5d <sup>3</sup> <sup>4</sup> F <sub>5/2</sub>		0.3(1.1)	
13238.32	5d <sup>3</sup> <sup>4</sup> F <sub>7/2</sub>		-0.5(2.4)	
13747.28	5d <sup>3</sup> <sup>4</sup> F <sub>9/2</sub>		-0.1(2.9)	

Table 5: Comparison of the experimental and calculated energy values [ $\text{cm}^{-1}$ ] and hfs A and B constants [MHz]

$E_{exp}$	$E_{calc}$	%	Main comp.	%	Sec. comp.	$g_{J_{calc}}$	$g_{J_{exp}}$	$A_{exp}$	$A_{calc}$	$\Delta A$	$B_{exp}$	$B_{calc}$	$\Delta B$
J= 1/2													
7231.407	7232	98.41	$5d^2(^3P)6s^4P$	0.98	$5d^2(^1S)6s^2S$	2.652	2.653	2460.229	2456	4			
9044.214	9033	67.87	$5d^2(^3P)6s^2P$	31.02	$5d^3^2P$	0.686	0.690	226.837	227	0			
16617.300	16632	96.15	$5d^3^4P$	2.17	$5d^2(^1S)6s^2S$	2.623		-696.6	-709	12			
16991.420	16990	95.52	$5d^2(^1S)6s^2S$	2.48	$5d^3^4P$	2.010		4135.4	4131	5			
20392.600	20395	66.78	$5d^3^2P$	30.95	$5d^2(^3P)6s^2P$	0.705	0.709	258.9	264	-5			
J= 3/2													
0.000	9	86.90	$5d^2(^3P)6s^2D$	10.06	$5d^2(^1D)6s^2D$	0.798	0.798	141.1961	139	2	44.776	44.830	-0.054
2668.188	2655	98.63	$5d^2(^3F)6s^4F$	0.75	$5d^2(^3D)6s^2D$	0.404	0.404	-480.208	-504	23	13.983	14.009	-0.026
7490.521	7494	96.53	$5d^2(^3P)6s^4P$	2.77	$5d^2(^1D)6s^2D$	1.703	1.704	929.666	915	15	37.066	35.864	1.202
8446.044	8458	62.32	$5d^2(^1D)6s^2D$	14.87	$5d^2(^3P)6s^2P$	0.930	0.936	-422.419	-420	-2	-6.964	-7.693	0.729
9719.439	9730	52.69	$5d^2(^3P)6s^2P$	26.01	$5d^3^2P$	1.231	1.220	-655.208	-653	-2	-31.841	-31.468	-0.373
12430.609	12419	97.98	$5d^3^4F$	0.95	$5d^3^2D$	0.407	0.411	445.098	435	10	-16.240	-16.299	0.059
16735.140	16739	92.74	$5d^3^4P$	2.15	$5d^2(^3P)6s^2P$	1.688	1.698	-259.4	-242	-17	-31.917	-31.917	0.000
18037.640	18053	57.17	$5d^3^2D$	26.31	$5d^3^2D$	0.859		227.1	221	6	-38.011	-38.011	0.000
21037.300	21033	63.72	$5d^3^2P$	28.51	$5d^2(^3P)6s^2P$	1.313	1.316	-88.8	-81	-8	-26.431	-26.431	0.000
	25707	66.78	$5d^3^2D$	31.91	$5d^3^2D$	0.800			232		55	55	0.000
J= 5/2													
1053.164	1044	83.08	$5d^2(^3P)6s^2D$	13.47	$5d^2(^1D)6s^2D$	1.200	1.199	182.1702	179	4	54.168	54.302	-0.134
3010.002	3005	98.14	$5d^2(^3F)6s^4F$	0.86	$5d^2(^3D)6s^2D$	1.029	1.029	300.643	320	-19	13.505	13.388	0.117
7011.909	7007	85.43	$5d^2(^3F)6s^2F$	5.41	$5d^2(^1D)6s^2D$	0.905	0.898	304.376	313	-8	28.295	28.310	-0.015
7679.939	7677	80.60	$5d^2(^3P)6s^4P$	9.86	$5d^2(^1D)6s^2D$	1.500	1.506	802.166	797	6	-34.793	-34.051	-0.742
9183.797	9173	64.97	$5d^2(^1D)6s^2D$	16.47	$5d^2(^3P)6s^4P$	1.254	1.254	876.295	884	-7	-4.474	-4.044	-0.430
12787.404	12789	99.20	$5d^3^4F$	0.39	$5d^3^2D$	1.030	1.026	97.526	94	4	-16.141	-16.361	0.220
17099.380	17082	96.10	$5d^3^4P$	2.05	$5d^3^2D$	1.586		-222.	-220	-2	36.966	36.966	0.000
18776.620	18762	67.95	$5d^3^2D$	21.66	$5d^3^2D$	1.212		9.6	7	2	-40.495	-40.495	0.000
21969.320	21985	92.95	$5d^3^2F$	3.65	$5d^2(^3F)6s^2F$	0.869		165.5	180	-15	48.088	48.088	0.000
25414.630	25415	72.08	$5d^3^2D$	23.27	$5d^3^2D$	1.192			1		61	61	0.000
J= 7/2													

Table 5: (continued)

$E_{exp}$	$E_{calc}$	%	Main comp.	%	Sec. comp.	$g_{J_{calc}}$	$g_{J_{exp}}$	$A_{exp}$	$A_{calc}$	$\Delta A$	$B_{exp}$	$B_{calc}$	$\Delta B$
3494.526	3505	99.25	$5d^2(^3F)6s^4F$	0.66	$5d^2(^3F)6s^2F$	1.238	1.237	462.891	480	-17	18.840	19.045	-0.205
8052.162	8056	91.69	$5d^2(^3F)6s^2F$	3.97	$5d^3^2F$	1.134	1.135	-197.065	-211	13	41.896	42.034	-0.138
9960.904	9962	86.42	$5d^2(^1G)6s^2G$	9.69	$5d^3^2G$	0.899	0.892	-293.000	-296	3	110.089	111.621	-1.532
13238.323	13244	99.26	$5d^3^4F$	0.44	$5d^3^2G$	1.236	1.228	-19.095	-20	0	-20.545	-20.634	0.089
17023.360	17034	89.19	$5d^3^2G$	9.74	$5d^2(^1G)6s^2G$	0.892	0.880	161.8	143	19	41.863	41.863	0
21943.800	21928	95.32	$5d^3^2F$	4.18	$5d^2(^3F)6s^2F$	1.142	59.6	59.6	51	9	35.353	35.353	0
J= 9/2													
4121.572	4129	99.51	$5d^2(^3F)6s^4F$	0.48	$5d^2(^1G)6s^2G$	1.333	1.333	489.533	504	-15	31.980	32.072	-0.092
9919.821	9920	91.08	$5d^2(^1G)6s^2G$	8.31	$5d^3^2G$	1.113	1.107	559.237	569	-9	129.240	128.286	0.954
13747.276	13751	97.52	$5d^3^4F$	1.88	$5d^3^2G$	1.329		-63.827	-64	0	-27.104	-27.094	-0.010
17140.900	17130	58.12	$5d^3^2G$	34.54	$5d^3^2H$	1.046		111.2	111	0	63.357	63.357	0
18315.880	18312	65.40	$5d^3^2H$	31.68	$5d^3^2G$	0.980	0.970	111.6	117	-5	56.038	56.038	0
J=11/2													
18310.920	18316	100.00	$5d^3^2H$			1.091		57.4	62	-5	91.203	91.203	0

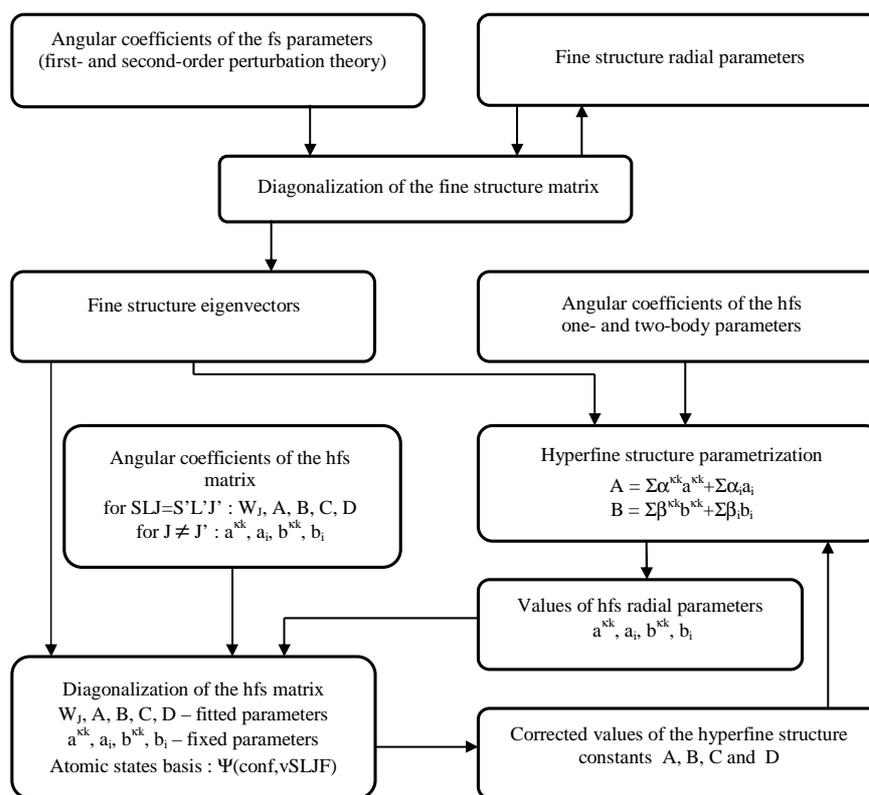


Figure 1. Scheme of the atomic structure calculations

**Table 6.** One- and two-body radial parameters [MHz] for the model space  $(5d + 6s)^3$  ( $n_0$  denote electrons of closed shells,  $n'$  denote electrons excited to empty shells)

closed shells $\rightarrow$ open shells		open shells $\rightarrow$ empty shells	
Spin-orbit and electrostatically correlated spin-orbit interactions			
$\zeta_{5d}$	596.425 (30.)	$\zeta_{5d}$	525.024 (20.)
$D^0(n_0d5d, 5d5d)\zeta_{n_0d,5d}$	-36.770 (5.4)	$D^0(5d5d, 5dn'd)\zeta_{5d,n'd}$	36.771 (5.4)
$D^2(n_0d5d, 5d5d)\zeta_{n_0d,5d}$	56.410 (28.)	$D^2(5d5d, 5dn'd)\zeta_{5d,n'd}$	-56.414 (28.)
$D^4(n_0d5d, 5d5d)\zeta_{n_0d,5d}$	36.707	$D^4(5d5d, 5dn'd)\zeta_{5d,n'd}$	-36.710
$E^2(5d6s, 6sn_0d)\zeta_{n_0d,5d}$	86.837 (28.)	$E^2(5d6s, 6sn'd)\zeta_{5d,n'd}$	-86.844 (28.)
$D^2(5d6s, 5dn_0d)\zeta_{n_0d,5d}$	-137.127 (63.)	$D^2(5d6s, 5dn'd)\zeta_{5d,n'd}$	137.141 (63.)
$E^2(5d6s, n_0d5d)\zeta_{n_0d,5d}$	-125.740 (61.)	$E^2(5d6s, n'd5d)\zeta_{5d,n'd}$	125.729 (61.)
$D^2(5d5d, n_0d6s)\zeta_{n_0d,5d}$	-79.676 (63.)	$D^2(5d5d, n'd6s)\zeta_{5d,n'd}$	79.691 (63.)
$D^2(n_0d5d, 6s6s)\zeta_{n_0d,5d}$	0	$D^2(5dn'd, 6s6s)\zeta_{5d,n'd}$	0
Magnetic-dipole <i>hfs</i> interactions			
$a_{5d}^{01}$	218.970 (20.)	$a_{5d}^{01}$	182.791 (12.)
$a_{5d}^{12}$	175.074 (22.)	$a_{5d}^{12}$	139.040 (17.)
$a_{6s}^{10}$	3897.652 (45.)	$a_{6s}^{10}$	3749.025 (74.)
$D^0(n_0d5d, 5d5d)P^{01}(n_0d, 5d)$	-18.039 (4.0)	$D^0(5d5d, 5dn'd)P^{01}(5d, n'd)$	18.039 (4.0)
$D^2(n_0d5d, 5d5d)P^{01}(n_0d, 5d)$	-2.717 (12.)	$D^2(5d5d, 5dn'd)P^{01}(5d, n'd)$	2.717 (12.)
$D^4(n_0d5d, 5d5d)P^{01}(n_0d, 5d)$	-1.807	$D^4(5d5d, 5dn'd)P^{01}(5d, n'd)$	1.807
$E^2(n_0s5d, 5d6s)P^{10}(n_0s, 6s)$	-918.597 (76.)	$E^2(n_0s5d, 5dn's)P^{10}(n_0s, n's)$	-1108.850 (16.)
$E^2(n_0s5d, 5dn's)P^{10}(n_0s, n's)$	-190.249 (70.)	$E^2(5d6s, 6sn'd)P^{01}(5d, n'd)$	-34.279 (17.)
$E^2(n_0d6s, 6s5d)P^{01}(n_0d, 5d)$	34.275 (17.)	$D^2(5d5d, 5dn's)P^{12}(5d, n's)$	0
$D^2(n_0s5d, 5d5d)P^{12}(n_0s, 5d)$	0	$a_{5d,6s}^{12}$	65.497 (36.)
$a_{5d,6s}^{12}$	123.967 (36.)	$D^2(5dn'd, 5d6s)P^{01}(5d, n'd)$	204.683 (66.)
$D^2(n_0d5d, 5d6s)P^{01}(n_0d, 5d)$	-204.689 (66.)	$E^2(5dn'd, 6s5d)P^{01}(5d, n'd)$	52.146 (84.)
$E^2(n_0d5d, 6s5d)P^{01}(n_0d, 5d)$	-52.146 (84.)	$D^2(5d5d, 5dn's)P^{10}(6s, n's)$	-1936.118 (130.)
$D^2(n_0s5d, 5d5d)P^{10}(n_0s, 6s)$	1936.122 (130.)	$D^2(5dn's, 6s6s)P^{01}(5d, n'd)$	0
$D^2(n_0s5d, 6s6s)P^{01}(n_0d, 5d)$	0	Electric-quadrupole <i>hfs</i> interactions	
$b_{5d}^{02}$	231.511 (4.1)	$b_{5d}^{02}$	180.111 (1.7)
$b_{5d}^{13}$	32.039 (3.1)	$b_{5d}^{13}$	32.039 (3.1)
$b_{5d}^{11}$	-4.061 (1.6)	$b_{5d}^{11}$	-4.061 (1.6)
$D^0(n_0d5d, 5d5d)P^{02}(n_0d, 5d)$	-19.206 (7.1)	$D^0(5d5d, 5dn'd)P^{02}(5d, n'd)$	19.206 (7.1)
$D^2(n_0d5d, 5d5d)P^{02}(n_0d, 5d)$	11.207 (3.5)	$D^2(5d5d, 5dn'd)P^{02}(5d, n'd)$	-11.206 (3.5)
$D^4(n_0d5d, 5d5d)P^{02}(n_0d, 5d)$	7.292	$D^4(5d5d, 5dn'd)P^{02}(5d, n'd)$	-7.292
$E^2(n_0d6s, 6s5d)P^{02}(n_0d, 5d)$	73.450 (2.1)	$E^2(5d6s, 6sn'd)P^{02}(5d, n'd)$	-73.449 (2.1)
$D^2(n_0s5d, 5d5d)P^{02}(n_0s, 5d)$	0	$D^2(5d5d, 5dn's)P^{02}(5d, n's)$	0
$b_{5d,6s}^{02}$	-2.874 (8.5)	$b_{5d,6s}^{12}$	-35.858 (1.3)
$D^2(n_0d5d, 5d6s)P^{02}(n_0d, 5d)$	-2.674 (12.)	$D^2(5dn'd, 5d6s)P^{02}(5d, n'd)$	2.670 (12.)
$E^2(n_0d5d, 6s5d)P^{02}(n_0d, 5d)$	56.384 (18.)	$E^2(5dn'd, 6s5d)P^{02}(5d, n'd)$	-56.388 (18.)
$D^2(n_0s5d, 6s6s)P^{02}(n_0d, 5d)$	0	$D^2(5dn's, 6s6s)P^{02}(5d, n'd)$	0

**Table 7.** Values of the one-body hyperfine structure parameters [MHz] and effective radial integrals [a.u.] obtained from the experimental data

Parameter	Configurations				
	(5d+6s) <sup>3</sup>	5d 6s <sup>2</sup>	5d <sup>2</sup> 6s	5d <sup>3</sup>	
spin-orbit :					
$\zeta_{5d}$	(c-o)	596.425	490.260	451.455	377.915
	(o-e)	525.024	490.260	451.482	377.940
magnetic-dipole :					
$a_{5d}^{01}$	(c-o)	218.970	168.971	146.604	110.526
	(o-e)	182.791	169.079	146.713	110.635
$a_{5d}^{12}$	(c-o)	175.074	122.432	99.716	65.446
	(o-e)	139.040	122.435	99.721	65.451
$a_{6s}^{10}$	(c-o)	3897.652		3897.652	
	(o-e)	3749.025		3749.025	
$\langle r^{-3} \rangle_{5d \text{ eff}}^{01}$			2.226	1.932	1.456
$\langle r^{-3} \rangle_{5d \text{ eff}}^{12}$			1.614	1.316	0.865
$\langle r^{-3} \rangle_{6s \text{ eff}}^{10}$				77.060	
electric-quadrupole :					
$b_{5d}^{02}$	(c-o)	231.511	150.730	141.697	103.285
	(o-e)	180.111	150.731	141.699	103.287
$\langle r^{-3} \rangle_{5d \text{ eff}}^{02}$			3.208	3.015	2.198