

# Study of the $4p^2$ , $5p^2$ and $5s5f$ excited configurations of the Zn and Cd isoelectronic sequences, using relativistic and non-relativistic semiempirical approaches

Héctor O. Di Rocco<sup>1,a</sup>, Mónica Raineri<sup>2</sup>, and Jorge G. Reyna-Almandos<sup>2</sup>

<sup>1</sup> Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional del Centro and CIFICEN (CONICET-UNCPBA), Pinto 399, 7000 Tandil, Argentina

<sup>2</sup> Centro de Investigaciones Ópticas, CIOp, CC 3, 1897, Gonnet, La Plata, Argentina

Received 29 April 2016 / Received in final form 5 September 2016

Published online 10 November 2016 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2016

**Abstract.** The consistency of the energy levels published for configurations  $4p^2$ ,  $5p^2$  and  $5s5f$  belonging to Zn and Cd isoelectronic sequences is studied. Different semiempirical approaches considering the linearity of the Slater integrals for large  $Z_c$ , the smoothness of the  $s_F$  screening parameters, the energy values in terms of  $Z$  (or  $Z_c$ ), and the differences of the  $E_{calc} - E_{exp}$  values are used, where  $E_{calc}$  values are energies calculated with a Hartree-Fock method with relativistic corrections and superposition of configurations (HFR-SOC), and  $E_{exp}$  are the experimental values. For the  $np^2$  configurations both  $LS$  and relativistic  $jj$  expressions are considered. Configuration  $5s5f$  is also analyzed taking into account the Landé's interval rule.

## 1 Introduction

The isoelectronic sequences corresponding to  $p^2$  and  $nsnf$  configurations have been thoroughly studied for a long time; they are canonical examples in those books about atomic spectra [1–3]. For these configurations, theoretical calculations can be carried out using different approaches, as the Hartree-Fock method with relativistic corrections and superposition of configurations (HFR-SOC) due to Cowan [4] or the fully relativistic codes GRASP [5] and FAC [6,7]. However, these detailed calculations cannot answer, in many cases, the question about the accuracy of the experimental level data. In fact, for the purposes of interpolation, extrapolation and checking, semi-empirical methods can be used successfully. Methods of this type, developed by Edlén [8] and Curtis [3], are needed when accuracies in the level positions must be of the order of a few hundreds of  $\text{cm}^{-1}$ . It should be stressed that our aim is to assess the accuracy of the published energy levels from the behavior of the Slater integrals as well as the smoothness of the screening parameters  $s_F$  and/or  $s_G$  previously introduced [9].

In the  $p^2$  configuration, there are five levels (denoted in the  $LS$  coupling as  $^3P_{0,1,2}$ ,  $^1D_2$  and  $^1S_0$  and, in the  $jj$  schema, as  $(1/2, 1/2)_0$ ,  $(1/2, 3/2)_{1,2}$  and  $(3/2, 3/2)_{0,2}$ ). In the  $LS$  coupling scheme there are only two Slater parameters:  $F^2(pp)$  and  $\zeta_{np}$ ; therefore, the system is overdetermined. In particular, for the  $p^2$  case, Edlén did

not use the  $^1S_0$  level to find the parameters mentioned above, therefore the accuracy of that level cannot be assessed. Introduction of the  $jj$ -relativistic coupling approach allows a more complete parametrization, because there appear more Slater parameters than in the  $LS$  non-relativistic case ( $F^2(p_+^2)$ ,  $G^2(p_-p_+)$ ,  $R^2(p_-^2, p_+^2)$  and  $R^2(p_-p_+, p_+^2)$ ; see Refs. [9,10]) and all levels can be subjected to scrutiny. Although we can make extensive calculations using the quasirelativistic superposition-of-configurations method (HFR-SOC), a relativistic semi-empirical method can be used within a simplified model based on single configuration expressions or, at most, interactions within the same complex. Two of us used this method to study the  $4s4p$  configuration of the Zn sequence [11] and  $p^2$ ,  $p^3$  and  $p^4$  ground configurations of several isoelectronic sequences in reference [9]. The disadvantage of using only the non-relativistic approach is that, in the  $p^2$  case, the  $F^2(pp)$  calculation is from levels  $^3P_{0,1}$  and  $^1S_0$ , therefore nothing can be said about the other two levels. Using the relativistic  $jj$  model, the calculation of  $F^2(p_+^2)$  needs  $^1D_2$  and  $^1S_0$  whereas the calculation of  $G^2(p_-p_+)$  needs  $^3P_{1,2}$ ; now, the level  $^3P_0$  remains with no scrutiny. Summing up, to study the correctness of all the five levels, we need both point of views.

The aim of this short paper is to use the semi-empirical  $jj$ -relativistic as well as the non-relativistic approaches to check the consistency of the published experimental levels of the excited  $4p^2$  configurations of Zn sequence and  $5p^2$  and  $5s5f$  of the Cd sequence. In the case of scrutiny of the

<sup>a</sup> e-mail: hdirocco@exa.unicen.edu.ar

5s5f levels, the use of the Landé intervals allows a better approximation as compared with other methods used for the  $np^2$  configurations.

## 2 Theory

As we know,  $LS$  and  $jj$  notations are “nominal” and strictly valid only in the corresponding limits [1]. Anyway, with this in mind, we will continue using, only for convenience, the widely used  $LS$  notation, where the correlation (*not identity*) indicated by the symbol “ $\longleftrightarrow$ ” is in accordance with the transition from pure  $LS$  to pure  $jj$  coupling (see Fig. 12.1 in Ref. [1] or Fig. 5.2 in Ref. [3]). The *nominal* levels, in the relativistic, pure  $jj$  coupling, are given by

$$\begin{aligned} |a\rangle_0 &\equiv {}^3P_0 \longleftrightarrow (1/2, 1/2)_0, \\ |b\rangle_0 &\equiv {}^1S_0 \longleftrightarrow (3/2, 3/2)_0, \\ |c\rangle_1 &\equiv {}^3P_1 \longleftrightarrow (1/2, 3/2)_1, \\ |d\rangle_2 &\equiv {}^3P_2 \longleftrightarrow (1/2, 3/2)_2 \quad \text{and} \\ |e\rangle_2 &\equiv {}^1D_2 \longleftrightarrow (3/2, 3/2)_2. \end{aligned}$$

The theoretical expressions for the levels in the  $LS$ -coupling approach can be found in the book by Curtis [3]. In this case, no simple exact relation can be found between the levels enabling extracting  $F^2$ , due to the presence of spin-orbit integrals  $\zeta_{np}$ . Curtis proposed an approximate relation independent of  $\zeta_{np}$ :

$$F^2(pp) = \frac{25}{15} (E({}^1S_0) + E({}^3P_0) - 2E({}^3P_1));$$

it is interesting to note that, in his classic article, Edlén did not use the  ${}^1S_0$  level [8]. Using either Curtis or Edlén  $LS$ -coupling expressions, we cannot test all the levels.

The theoretical *relativistic jj-coupling* expressions for two electrons outside closed shells can be found in the book by Johnson [12]. In the relativistic treatment, something similar to the  $LS$  case happens; only when ignoring the configuration interaction integrals  $R^2(p_-^2, p_+^2)$  and  $R^2(p-p_+, p_+^2)$  we can find simple expressions. As explained below, neglecting  $R^2(p_-^2, p_+^2)$  and  $R^2(p-p_+, p_+^2)$ ,  $F^2(p_+^2) = 25({}^1S_0 - {}^1D_2)/8$  and  $G^2(p-p_+) = 25({}^3P_2 - {}^3P_1)/4$ . To simplify the parametrization we could neglect  $R^2(p_-^2, p_+^2)$  and  $R^2(p-p_+, p_+^2)$ , although their value can be important for few-times ionized atoms. However, for the checking procedure, simple approximations can work adequately, because we fix our attention on the smooth behavior of the screening parameter  $s_F$  and/or  $s_G$  and not on the behavior of the Slater integrals themselves.

### 2.1 The relativistic $p^2$ matrices

With the nominal levels given above, in the Configuration Interaction approximation, the matrix elements are

given by

$J = 0$	$ a\rangle_0$	$ b\rangle_0$
$ a\rangle_0$	$E_0(p_-^2)$	$2\sqrt{2}R^2(p_-^2, p_+^2)/5$
$ b\rangle_0$	$2\sqrt{2}R^2(p_-^2, p_+^2)/5$	$E_0(p_+^2) + F^2(p_+^2)/5$

$J = 1$	$ c\rangle_1$
$ c\rangle_1$	$E_0(p-p_+) - G^2(p-p_+)/5$

and

$J = 2$	$ d\rangle_2$	$ e\rangle_2$
$ d\rangle_2$	$E_0(p-p_+) - G^2(p-p_+)/25$	$-0.16R^2(p-p_+, p_+^2)$
$ e\rangle_2$	$-0.16R^2(p-p_+, p_+^2)$	$E_0(p_+^2) - 3F^2(p_+^2)/25$

Although the  $R^2(p_-^2, p_+^2)$  and  $R^2(p-p_+, p_+^2)$  parameters are important when describing theoretically the  $p^2$  level structure in the relativistic approach, in order to see the behavior of the  $s$  ( $Z_c$ ) (for example, to check the smoothness of the  $s$  ( $Z_c$ ) curves), we can simplify the treatment by neglecting these Slater integrals.

Then, in the single-configuration approximation, for both  $LS$  and  $jj$  couplings, we can use the following equations [9]:

$$F^2(pp) = \frac{25}{15} (E({}^1S_0) + E({}^3P_0) - 2E({}^3P_1)), \quad (1)$$

$$F^2(p_+^2) = 25(E(3/2, 3/2)_0 - E(3/2, 3/2)_2)/8 \quad (2)$$

and

$$G^2(p-p_+) = 25(E(1/2, 3/2)_2 - E(1/2, 3/2)_1)/4. \quad (3)$$

This is the only way to study all five levels of the  $p^2$  configuration, because the  $jj$  approach does not inform us about the  ${}^3P_0$  level, whereas the  $LS$  one deals only with  ${}^1S_0, {}^3P_0$  and  ${}^3P_1$ .

## 3 Experimental material and theoretical calculations

All experimental values were taken from the National Institute of Standards and Technology-Atomic Spectra Database (NIST-ASD) as well as from the references indicated there (NIST-Bibliographic Database) [13,14]. We checked the excited  $p^2$  configuration of Zn and Cd sequences and 5s5f configuration of Cd sequence using, as first criterion, the behavior of the screening parameters  $s_F$  and/or  $s_G$  [9]. To check them, a posteriori, we made extensive calculations by mainly using Cowan codes, comparing the calculated values with the experimental ones in order to verify the smoothness of the difference  $E_{calc} - E_{exp}$ . It is known empirically that computed energy-level intervals will better agree with experiment if Coulomb parameter values are smaller than those theoretical. The calculations were made by scaling the theoretical values of the parameters  $F^k(l_i, l_i)$ ,  $\zeta_i$ ,  $F^k(l_i, l_j)$ ,  $G^k(l_i, l_j)$  and  $R^k(l_i, l_j; l'_i, l'_j)$ . These scale factors were 1.00 for  $\zeta_i$  in all cases; for Coulomb parameters were 0.80 for neutral

atoms, 0.90 for 5– or 10– fold ionized atoms and 0.95 for very highly ionized atoms [1].

## 4 The semi-empirical method

Although in many cases the analysis of the experimental levels and/or Slater parameters along isoelectronic sequences, using net charge  $Z_c$  as variable, can detect level inconsistencies, in other cases the erroneous levels can be so close to the correct one that a better parametrization is needed. It is verified that in most cases Slater parameters show a linear increase with  $Z_c$ , but deviations are noticeable at the beginning of each sequence. Therefore, they can be fitted by expressions of the type (using  $F^2$  only as an example):  $F_{exp}^2 = aZ_c + b + c(Z_c + d)^{-1}$ , where  $a$  is the unit-charge hydrogenic value  $F_H^2$  and  $Z_c \equiv Z - N + 1$  is the net charge of the nucleus plus the  $N - 1$  electrons of the ion core. Therefore

$$F_{exp}^2 = F_H^2 Z_c + b + c(Z_c + d)^{-1}. \quad (4)$$

On the other hand, using the scaling relation

$$F_{exp}^2 = F_H^2 \times (Z - s_F) \quad (5)$$

valid in principle for large  $Z_c$  values, we can define a screening parameter  $s$  as (using  $F^2$  only as example)

$$s_F = Z - F_{exp}^2 / F_H^2; \quad (6)$$

from equations (4) and (5) we deduce that, for large  $Z_c$  the  $s_F$  values tend to a constant:

$$s_F \rightarrow (Z - Z_c) - b/F_H^2 \equiv (N - 1) - b/F_H^2.$$

In each case, the integrals  $F_H^2$  or similar ones were computed using the relativistic wave-functions from the book by Mizushima [15]. The screening parameters are very sensitive to small errors in the determination of energy levels [9].

## 5 Detailed discussion about the critically evaluated data in the NIST atomic spectra database and the literature in the NIST bibliographic database

### 5.1 $4p^2$ sequence of Zn

Data in the NIST-ASD are in the range  $Z = 30$ – $54$  with some gaps for low and medium  $Z_c$  values ( $Z = 31$ – $38$ ). For higher  $Z_c$  there are no critically evaluated values for the ranges  $Z = 39$ – $41$  and  $Z = 43$ – $53$  and we must appeal to the Bibliographic Database.

In short:

- (a) For  $Z = 30$ , levels  $4p^2 \ ^3P_{0,1,2}$  were firmly identified in experimental spectra, but the strongly autoionizing  $^1D_2$  and  $^1S_0$  levels were not observed in optical spectra. Martin and Kaufman noted that  $^1D_2$

could strongly interact with the  $4d^{10}4snd \ ^1D_2$  series and should be repelled upwards from the ionization limit [16]. We made extensive calculations as explained in Section 3 and verified the conclusions by Martin and Kaufman with respect to the  $^1D_2$  level; additionally, the level  $4p^2 \ ^1S_0$  strongly interact with the  $4s^2 \ ^1S_0$  and the  $4p5p \ ^1S_0$  levels. Therefore, our approach, based on the single-configuration approximation, is not useful for this case.

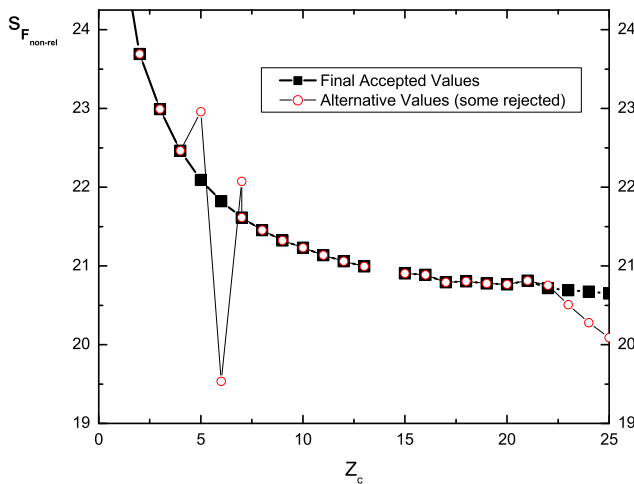
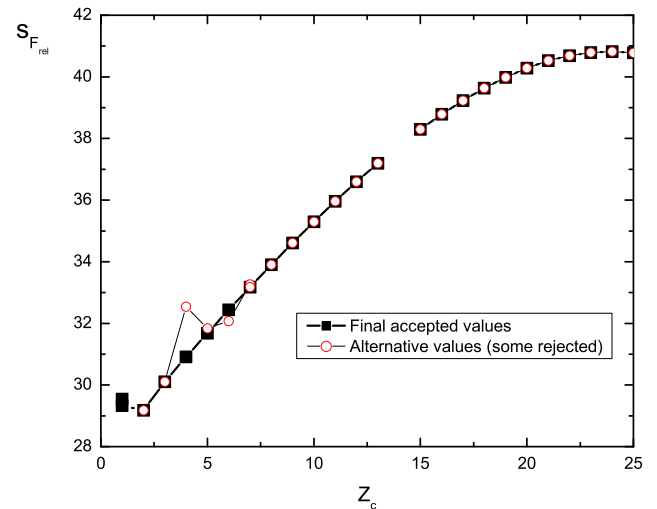
It is important to mention that Gomonai, gathering diverse experimental and theoretical estimations [17], locates the level  $4p^2 \ ^1S_0$  at approximately  $93\,513 \text{ cm}^{-1}$  and the level  $4p^2 \ ^1D_2$  at approximately  $83\,255 \text{ cm}^{-1}$ .

- (b) The levels for  $Z = 31, 32$  in the NIST-ASD are critically evaluated and are the useful ones.
- (c) For  $Z = 33$ , according to the behavior of the sequence, it is verified that the level  $^1D_2$ : 204 658 (NIST-ASD) must be changed to 179 575, as in the reference [18].
- (d) For  $Z = 34$  ( $Z_c = 5$ ), the levels  $^1D_2$  and  $^1S_0$  have not been critically evaluated by NIST and are quoted from reference [19]. According to the isoelectronic comparisons, we verified the analysis of [19] for the level  $^1S_0$ , changing the value of reference [20].
- (e) For  $Z = 35$  the values of references [13] and [20] had to be changed to the levels of reference [21]. It is important to mention that the levels of *As IV*, *Se V*, and *Br VI* given in the NIST-ASD have not been critically evaluated by NIST and are quoted from Kelly [22].
- (f) For  $Z = 36$ , the behavior of  $s_F$  indicates that the level  $^1S_0$  of  $Kr^{6+}$ , previously known as  $321\,794 \text{ cm}^{-1}$  [23] must be changed to approximately  $(323\,025 \pm 50) \text{ cm}^{-1}$ . Indeed, in an unpublished work cited in an Internal Review of the Lund University, Litzen and Sugar located the  $^1S_0$  level at  $323\,049 \text{ cm}^{-1}$  [24].
- (g) For  $Z = 37, 38$  the critically evaluated data [13] have been confirmed.
- (h) For the interval  $Z = 39$ – $42$  the values of reference [25] should be used. Up to now, the level values of reference [25] for  $Z = 39$ – $41$  have not been critically evaluated by NIST.
- (i) For  $Z = 43$  ( $Tc$ ) there are no published data for  $Z_c \geq 3$ , due to the trace nature of that chemical element.
- (j) For  $Z = 44$ – $50$  the values of reference [26] should be used. Up to now, these level values have not been critically evaluated by NIST.
- (k) For  $Z = 51$ – $54$  there are two sets of data from the same group [27,28], published in years 1993 and 1994. Up to now, the levels for  $Z = 51$ – $53$  have not been critically evaluated by NIST whereas for  $Z = 54$  the values given in the NIST-ASD are from reference [28]. According to the behavior of  $s_F$  the set of reference [27] produces a smooth curve as opposed to the data of reference [28]; therefore, we selected the data of reference [27].

The energy level values for this sequence are given in Table 1. The corresponding values of  $s_F$  using these levels and equations (1) and (2) are shown in Figures 1 and 2.

**Table 1.** Rounded experimental level values in  $\text{cm}^{-1}$  for the  $4p^2$  configuration of the Zn isoelectronic sequence. The data sources are specified in Section 5.1.

$Z$	$Z_c$	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
31	2	114 695	115 224	116 140	107 720	135 639
32	3	147 685	148 640	150 372	144 975	174 114
33	4	179 937	181 475	184 402	179 575	211 686
34	5	211 794	214 091	218 615	213 203	248 787
35	6	243 419	246 688	253 178	246 473	285 819
36	7	274 932	279 414	288 190	279 715	323 049
37	8	306 401	312 379	323 776	313 112	360 665
38	9	337 890	345 682	360 052	346 804	398 856
39	10	369 367	379 366	397 097	380 850	437 726
40	11	400 998	413 551	435 058	415 381	477 442
41	12	400 998	448 244	473 993	450 413	518 102
42	13	464 439	483 549	514 034	486 036	559 827
43	14	–	–	–	–	–
44	15	528 356	556 205	597 781	559 310	646 912
45	16	560 454	593 613	641 627	596997	692 398
46	17	592 868	631 937	687 168	635 676	739 610
47	18	625 293	671 127	734 179	675 156	788 252
48	19	657 783	711 164	782 812	715 502	838 635
49	20	690 470	752 160	833 140	756 771	890 693
50	21	723 614	794 616	885 922	799 558	945 055
51	22	756 615	837 923	940 155	843 271	1 001 649
52	23	789 876	882 549	996 831	888 240	1 060 429
53	24	823 337	928 423	1 055 686	934 468	1 121 484
54	25	856 975	975 725	1 117 092	982 143	1 185 240

**Fig. 1.** The behavior of the parameter  $s_F$  (non-relativistic) for the final accepted values compared with the alternative values (some rejected) for the  $4p^2$  isoelectronic sequence of Zn.**Fig. 2.** The behavior of the parameter  $s_F$  (relativistic) for the final accepted values compared with the alternative values (some rejected) for the  $4p^2$  isoelectronic sequence of Zn.

## 5.2 $5p^2$ sequence of Cd

Data are in the range  $Z = 48$ – $60$ , with several gaps. In short:

- (a) For  $Z = 48$ , there occurs something similar to the case of ZnI: the levels  $5p^2 \ ^3P_{0,1,2}$  were firmly identified in experimental optical spectra, but not the strongly autoionizing  $^1D_2$  and  $^1S_0$  [29]. We made extensive calculations as explained in Section 3 and verified that the level  $5p^2 \ ^1S_0$  strongly interacts with  $5p^2 \ ^3P_0$ ,  $5p6p \ ^1S_0$

and  $5d^2 \ ^1S_0$  whereas the level  $5p^2 \ ^1D_2$  interacts with  $^3P_2$ ,  $5s5d \ ^1D_2$  and  $5s6d \ ^1D_2$ . Therefore, our approach, based on the single-configuration approximation, is not useful for this case. It is interesting to mention that Gomomai, quoting diverse experimental and theoretical estimations [17], locate the level  $5p^2 \ ^1S_0$  at approximately  $90\,508 \text{ cm}^{-1}$  and the level  $5p^2 \ ^1D_2$  at approximately  $82\,035 \text{ cm}^{-1}$ .

- (b) The levels in the range  $Z = 49-53$  are complete either in the NIST-ASD or in the Bibliographic Database.
- (c) For  $Z = 54$ , the analysis of the isoelectronic sequence for the level  $^1S_0$  indicates a linear behavior; therefore, an estimated value  $(276\,858 \pm 200) \text{ cm}^{-1}$  is suggested. This value shows that it is necessary to check the energy level at  $273\,208 \text{ cm}^{-1}$  [13] (based in Ref. [30]).
- (d) For  $Z = 55, 56$  the levels in the NIST-ASD are critically evaluated and they are useful [13].
- (e) For  $Z = 57$  the latest analysis is from Ryabtsev et al. [31], although the value for  $^1S_0$  at  $369\,690 \text{ cm}^{-1}$  is based on a single transition  $5s5p^1P_1 - 5p^2^1S_0$ . Anyway, that value follows the isoelectronic trend.
- (f) For  $Z = 58$  ( $Z_c = 11$ ), the level  $^1S_0$  at  $395\,301 \text{ cm}^{-1}$  given by Joshi et al. [32] implies abrupt jumps in the behavior of  $F^2(pp)$  and  $F^2(p_+^2)$ . However, the  $5p^2^1S_0$  level is mixed with 36% of  $4f^2^1S_0$ ; so, the single-configuration approach is inapplicable.
- (g) For  $Z = 59$ , Churilov and Joshi give the value for  $^3P_0$  at  $333\,380 \text{ cm}^{-1}$  [33]; the non-smoothness in the behavior of Slater integrals and/or the screening parameters is evident. However, our calculations using Cowan codes indicate that the level composition is

$$\begin{aligned} |333\,380 \text{ cm}^{-1}\rangle &\simeq 0.75 |5p^2^3P_0\rangle + 0.40 |5p^2^1S_0\rangle \\ &+ 0.20 |4f^2^3P_0\rangle - 0.49 |4f^2^3P_0\rangle; \quad (7) \end{aligned}$$

therefore, this strong configuration mixing indicates that our approach, based on the single-configuration approximation does not work in this case.

- (h) The values for  $Z = 60$  are correct [13].
- (i) It is interesting to note the change in the percentage composition for the level  $5p^2^1D_2$  along this sequence. Percentage of the dominant component increases from 36% ( $Z = 49$ ) up to 60% ( $Z = 57$ ).

The energy level values for this sequence are in Table 2.

### 5.3 5s5f sequence of Cd

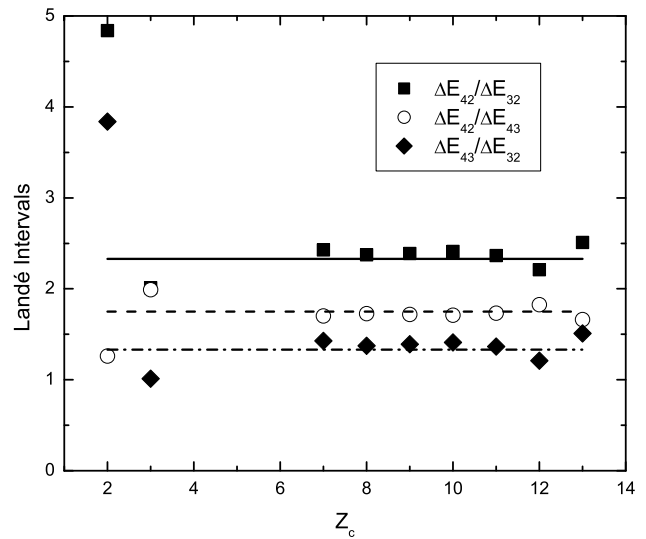
If  $LS$  coupling is adequate for a particular term, the fine structure splitting is given by the Landé interval rule: the energy interval between two levels of a term with consecutive values of  $J$  is proportional to the largest of the two values of  $J$ , so  $E_{\gamma LSJ} - E_{\gamma LS, J-1} = J \cdot \zeta(\gamma LS)$ , where  $\zeta(\gamma LS)$  is an effective spin-orbit splitting factor [1]. Therefore,  $E(^3F_3) - E(^3F_2) = 3\zeta(\gamma LS)$  and  $E(^3F_4) - E(^3F_3) = 4\zeta(\gamma LS)$ . From these relations, it is easy to see that  $E(^3F_4) - E(^3F_2) = 7\zeta(\gamma LS)$ .

From the above equations, the following ratios can be derived

$$\frac{E(^3F_4) - E(^3F_3)}{E(^3F_3) - E(^3F_2)} \equiv \frac{\Delta E_{43}}{\Delta E_{32}} = \frac{4}{3} \approx 1.333, \quad (8)$$

as well as

$$\frac{E(^3F_4) - E(^3F_2)}{E(^3F_3) - E(^3F_2)} \equiv \frac{\Delta E_{42}}{\Delta E_{32}} = \frac{7}{3} \approx 2.333 \quad (9)$$



**Fig. 3.** The Landé intervals for the  $5s5f$  sequence of Cd; the lines are the  $LS$  theoretical values. See Section 5.3 where we explain the selection made for  $Z = 54$  ( $Z_c = 7$ ).

and

$$\frac{E(^3F_4) - E(^3F_2)}{E(^3F_4) - E(^3F_3)} \equiv \frac{\Delta E_{42}}{\Delta E_{43}} = \frac{7}{4} = 1.75. \quad (10)$$

Available experimental data are in the range  $Z = 49-60$  with a gap for  $Z = 51-53$ . Irregularities of the fine-structure intervals of the  $5s5f^3F$  term for the smaller  $Z_c$  values were explained by interaction with the configurations  $5s4f$ ,  $5s5d$  and  $5s6d$ . The ratios given by equations (8)–(10) are not satisfactory for  $Z = 49, 50$  [35,36], but are satisfied for  $Z = 54-60$ . Based on the comparison between experimental and calculated values through the sequence and the Figure 3, it is inferred that for  $Z = 54$ , energy values estimated in  $(461\,800 \pm 200) \text{ cm}^{-1}$ ,  $(462\,000 \pm 200) \text{ cm}^{-1}$  and  $(462\,300 \pm 200) \text{ cm}^{-1}$  for the  $^3F_2$ ,  $^3F_3$  and  $^3F_4$  levels respectively, are in better agreement than those reported in references [13,30]. Surely, the explanations for the singular experimental intervals of  $InII$  [35] are due to the configuration interaction as mentioned above. The energy level values for this sequence are in Table 3.

Until now, all discussion in this section concerned the triplet levels. With respect to  $^1F_3$  levels, the interaction with configuration  $5p5d$  remains significant at least up to  $Z = 60$  ( $Z_c = 13$ ). The comparison  $E_{calc} - E_{exp}$  with calculations made using the configurations  $5s4f + 5s5f + 5p5d + 5p6d$  [4] indicates that we can accept the values for  $Z = 49, 50, 55$  and  $57-60$ , because of the approximately linear variation of the Slater integral  $G^1(5s, 5f)$ . For  $Z = 54$  it is difficult to establish the appropriate number, although in reference [30] the value is  $467\,700 \text{ cm}^{-1}$ . For  $Z = 56$  such linearity as well as smoothness of the difference  $E_{calc} - E_{exp}$  is broken abruptly; therefore the value  $593\,082 \text{ cm}^{-1}$  [37] is suspicious.

**Table 2.** Rounded experimental level values in  $\text{cm}^{-1}$  for the  $5p^2$  configuration of the Cd isoelectronic sequence. The data sources are specified in Section 5.2; for the estimation of the level  $^1S_0$  ( $Z = 58$ ) see this paragraph (N.A.: not experimentally available).

$Z$	$Z_c$	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
49	2	101 608	103 249	105 565	113 885	121 290
50	3	127 309	130 120	134 567	128 205	154 203
51	4	152 076	156 388	163 524	155 956	184 430
52	5	176 255	182 421	192 597	182 804	215 061
53	6	200 085	208 475	221 984	209 432	245 659
54	7	223 673	234 685	251 853	236 100	N.A.
55	8	247 101	261 163	282 348	262 959	308 058
56	9	270 415	287 998	313 571	290 088	338 208
57	10	293 616	315 245	345 362	317 412	369 690
58	11	316 514	342 733	378 129	345 018	(404 000 $\pm$ 2000)
59	12	333 380	370 526	411 631	373 945	443 348
60	13	362 100	398 244	446 132	402 542	479 469

**Table 3.** Rounded experimental level values in  $\text{cm}^{-1}$  for the  $5s5f$  configuration of the Cd isoelectronic sequence. For references and explanation of the estimation of the levels  $^3F_{2,3,4}$  ( $Z = 54$ ) see Section 5.3 (N.A.: not experimentally available).

$Z$	$Z_c$	$^3F_2$	$^3F_3$	$^3F_4$	$^1F_3$
49	2	133 940	133 944	133 960	133 984
50	3	202 040	2024 79	202 923	203 296
51	4	–	–	–	–
52	5	–	–	–	–
53	6	–	–	–	–
54	7	(461 800 $\pm$ 200)	(462 000 $\pm$ 200)	(462 300 $\pm$ 200)	N.A.
55	8	524 726	524 999	525 374	531 193
56	9	587 740	588 102	588 605	N.A.
57	10	652 870	653 325	653 967	667 740
58	11	715 017	715 535	716 242	731 523
59	12	780 048	780 718	781 529	798 083
60	13	843 152	844 019	845 328	864 285

## 6 Conclusions

This paper demonstrates the use of the semi-empirical  $jj$ -relativistic and non-relativistic approaches to check the consistency of the published experimental levels belonging to the  $p^2$  and  $5s5f$  configurations in the Zn and Cd isoelectronic sequences. Clearly, our method is not useful for the strongly autoionizing  $^1D_2$  and  $^1S_0$  levels of Zn I and Cd I, not having been observed in optical spectra (see above, Sects. 5.1 and 5.2). Our analysis suggests that, with respect to the NIST Atomic Spectra Database or the references there indicated, several energy levels should be revised: six in the  $4p^2$  sequence, two in the  $5p^2$  sequence and three in the  $5s5f$  sequence. Tentative revised values are suggested. Furthermore, for  $Z = 54$ , the values for the levels  $5s5f$   $^3F_{2,3,4}$  were estimated using the behavior of  $E_{\text{calc}} - E_{\text{exp}}$  as well as the Landé interval rule. For the  $5s5f$  sequence, the discrepancy from the general trend of the  $^1F_3$  level for  $Z = 54$  and 56 must be noted.

## Author contribution statement

All authors contributed equally to the paper.

The support of Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (where M.R. and J.R.A. are researchers), Consejo Nacional de Investigaciones Científicas y Técnicas and the Universidad Nacional del Centro, Tandil, Argentina, are gratefully acknowledged. Careful reading of the first version by an anonymous referee is gratefully acknowledged.

## References

1. R.D. Cowan, *The Theory of Atomic Structure and Spectra*, 4th edn. (University of California Press, Berkeley, 2001)
2. I.I. Sobelman, *Atomic Spectra and Radiative Transitions*, 2nd edn. (Springer, Berlin, 1996)
3. L.J. Curtis, *Atomic Structure and Lifetimes* (Cambridge University Press, Cambridge, 2003)
4. A. Kramida's version for Windows is from <http://das101.isan.troitsk.ru/COWAN>
5. I.P. Grant, *Relativistic Quantum Theory of Atoms and Molecules* (Springer, New York, 2007)
6. M.F. Gu, AIP Conf. Proc. **730**, 127 (2004)
7. M.F. Gu, Can. J. Phys. **86**, 675 (2008)
8. B. Edlén, *Atomic Spectra*, Handbuch der Physik **27** (Springer, Berlin, 1964)
9. J.C. Aguiar, H.O. Di Rocco, J. Quantit. Spectr. Rad. Transf. **149**, 1 (2014)

10. Z. Rudzikas, *Theoretical atomic spectroscopy* (Cambridge University Press, Cambridge, 1997)
11. J.C. Aguiar, M. Raineri, H.O. Di Rocco, Eur. Phys. J. D **67**, 158 (2013)
12. W.R. Johnson, *Atomic structure theory* (Springer-Verlag, Berlin, 2007)
13. A. Kramida, Yu. Ralchenko, J. Reader, NIST ASD Team, NIST atomic spectra database (version 5.3), National Institute of Standards and Technology, Gaithersburg, MD, available: <http://physics.nist.gov/asd>; 2015
14. A. Kramida, Atomic Energy Levels and Spectra Bibliographic Database (version 2.0), (2010) available: <http://physics.nist.gov/Elevbib> (2016, September 27), National Institute of Standards and Technology, Gaithersburg, MD
15. M. Mizushima, *Quantum mechanics of atomic spectra and atomic structure* (W.A. Benjamin, New York, 1970)
16. W.C. Martin, V. Kaufman, J. Opt. Soc. Am. **60**, 1096 (1970)
17. A.N. Gomonai, J. Appl. Spectrosc. **82**, 13 (2015), and references therein
18. S.S. Churilov, Y.N. Joshi, J. Opt. Soc. Am. B **13**, 11 (1996)
19. S.S. Churilov, Y.N. Joshi, Phys. Scr. **51**, 196 (1995)
20. Y.N. Joshi, Th.A.M. van Kleef, Phys. Scr. **34**, 135 (1986)
21. A. Riyaz, A. Tauheed, K. Rahimullah, J. Quant. Spectrosc. Radiat. Transfer **113**, 2072 (2012)
22. R.L. Kelly, J. Phys. Chem. Ref. Data **16**, Suppl. 1, 1 (1987)
23. E.B. Saloman, J. Phys. Chem. Ref. Data **36**, 215 (2007)
24. U. Litzén, J. Sugar, Annual Report Atomic Spectroscopy, Department of Physics, University of Lund, 32 (1989)
25. U. Litzén, J. Reader, Phys. Rev. A **36**, 5159 (1987)
26. S.S. Churilov, A.N. Ryabtsev, J.-F. Wyart, Phys. Scr. **38**, 326 (1988)
27. J.F. Seely, A. Bar-Shalom, At. Data Nucl. Data Tables **55**, 143 (1993)
28. C.M. Brown, J.F. Seely, D.R. Kania, B.A. Hammel, C.A. Back, R.W. Lee, A. Bar-Shalom, W.E. Behring, At. Data Nucl. Data Tables **58**, 203 (1994)
29. C.E. Moore, Nat. Stand. Ref. Data Ser. **35**, Vol. III (Reprint of NBS Circ. 467, Vol. III, 1958), 245 pp. (Nat. Bur. Stand., US, 1971)
30. S.S. Churilov, Y.N. Joshi, Phys. Scr. **65**, 35 (2002)
31. A.N. Ryabtsev, S.S. Churilov, Y.N. Joshi, Phys. Scr. **65**, 227 (2002)
32. Y.N. Joshi, A.N. Ryabtsev, S.S. Churilov, J. Opt. Soc. Am. B **18**, 1935 (2001)
33. S.S. Churilov, Y.N. Joshi, Phys. Scr. **68**, 128 (2003)
34. V. Kaufman, J. Sugar, J. Opt. Soc. Am. B **4**, 1919 (1987)
35. A. Kramida, J. Res. Nat. Institut. Stand. Technol. **118**, 52 (2013)
36. K. Haris, A. Tauheed, Phys. Scr. **85**, 055301 (2012)
37. S.S. Churilov, Y.N. Joshi, Phys. Scr. **62**, 282 (2000)