An examination of the consistency of the published levels of the p^2, p^3 and p^4 isoelectronic sequences using jj-relativistic expressions

Julio C. Aguiar [a], Héctor O. Di Rocco [b],*

[a] Autoridad Regulatoria Nuclear, Av. del Libertador 8250, C1429BNP Buenos Aires, Argentina
[b] Instituto de Física Arroyo Seco, CIFICEN (CONICET-UNCPBA), Pinto 399, (7000) Tandil, Argentina

ARTICLE INFO

ABSTRACT

We check the consistency of the known energy levels of the p^2, p^3 and p^4 isoelectronic sequences tabulated at the NIST Atomic Spectroscopy Database. We used a screening parameter formulation using the Slater integrals arising from the jj-coupling relativistic expressions for the matrix elements. The general conclusion is that the use of the screening parameters is very adequate to check the consistency of level values along their isoelectronic sequences, more suitable than comparison of Slater integrals or other criteria, such as the widely used difference between theoretical and observed values.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The isoelectronic sequences corresponding to the p^2, p^3 and p^4 configurations have been investigated in detail since long time ago; they are canonical examples in the books about Atomic Spectra [1–3]. In certain cases, the levels were fixed by an observation of $M1$ and $E2$ forbidden transitions; they are important for diagnostic purposes in astrophysical and laboratory plasmas. For some sequences, new theoretical calculations were recently published by Jönsson et al. [4] (Csequence), by Rynkun et al. [5] (Nsequence) and by Rynkun et al. [6] (O sequence); however, these detailed calculations cannot answer, in many cases, the question about the accuracy of the experimental data. In fact, for the purposes of interpolation, extrapolation and checking, semi-empirical methods can be used with success. Such methods, developed by Edlén and by Curtis, are required when one needs to determine the level positions with an uncertainty of the order of a few hundreds of cm^{-1} [2,7].

In all the p^2, p^3 and p^4 sequences, there are five levels and, in the LS coupling scheme, only two Slater parameters: $F^2(pp)$ and ζ_{np}; therefore, the system is overdetermined. In particular, for the p^2 and p^4 cases, Edlén did not use the $^1S_0$ level to find the parameters noted above. The departure from the theory appears to be large for this level, not taken into account in the fitting process. In fact, in this work we found indications that in some cases the experimental $^1S_0$ level is not well established. On the other hand, in the p^3 sequence, the theoretical relations involve the levels $^2P_{3/2}$, $^2P_{1/2}$ and $^2D_{5/2}$; the departure from the theory is now for the $^4S_{3/2}$ level [7]. The introduction of the jj-relativistic coupling approach permits a more complete parameterization, because it introduces more Slater parameters that in the non-relativistic LS case [8].

Although there are extensive calculations using the MCDHF method (cited above), in order to apply the semi-empirical method, it can be useful to develop a simplified model utilizing single-configuration expressions or, at the most, accounting for interactions within the same complex. We used this method to study the $4s\,4p$ configuration of the Zn sequence [9].

The goal of this short paper is to use the semi-empirical jj-relativistic approach to check the consistency of the

* Corresponding author.
   E-mail address: hdirocco@exa.unicen.edu.ar (H.O. Di Rocco).

published experimental levels of the p^2 configurations of the C, Si, Ge and Sn sequences, p^3 configurations of the N, P, As and Sb sequences and p^4 configurations of the O and S sequences [11]. We will use the screening parameter s_F, associated with the Slater integral F^2_{rel} (or s_G associated with the integral G^2_{rel} or s_R associated with R^2_{rel}; we call them, generically, $s_X(Z_c)$) because these screening parameters are sensitive to small changes in the energy levels. Consistently smooth behavior of the screening parameters along isoelectronic sequences can be of interest in searching for and/or classification of forbidden lines. For the above cited purposes we study the behavior of s_X parameters along their respective isoelectronic sequences.

The present approach can be complementary to the use of the well known codes such as the quasi-relativistic code with superposition of configurations by Cowan [1] or fully relativistic codes, such as FAC, by Gu [10].

2. Theory

The theoretical expressions of *relativistic jj-coupling* approach can be found in the book by Johnson for two-electron cases [12] and, more generally, in the book by Rudzikas for more complex ones [8]. It is important to note that in the non-relativistic treatment of the p^2 and p^4 cases, no simple relation can be found between the levels that permits one to extract F^2 and/or ζ_{np} (see the explicit expression for the matrix elements for a p^2 configuration in the book by Curtis [2]). In the case of p^3, an explicit expression for $F^2(pp)$ exists: $F^2(pp) = 25(^2P_{1/2} - ^2D_{5/2})/6$ but ζ_{np} must be found by diagonalizing the $J=3$ submatrix. In the relativistic treatment, something similar happens; for p^2 and p^4 cases, only when ignoring the CI integrals $R^2(p^2_-, p^2_+)$ and $R^2(p_- p_+, p^2_+)$ we can find simple expressions for the Slater integrals. To simplify our parameterization of p^2, we neglect these integrals, although for few-times ionized atoms their value can be important (see Section 2.1). In the p^3 case, similar to the non-relativistic case, $F^2(p_+ p_+) = 25(^2P_{1/2} - ^2D_{5/2})/8$ and $G^2(p_- p_+)$ are linked to $F^2(p_+ p_+)$ through $G^2(p_- p_+) = 1.5F^2(p_+ p_+)$ (see Section 2.2). Here it is important to use the $R^2(p_- p_+, p^2_+)$ term in order to separate $^2D_{5/2}$ from $^2D_{3/2}$ levels. For the procedure of checking consistency along isoelectronic sequences, these simple approximations work adequately, because we fix our attention on the smooth behavior of the screening parameters s_X and not on the behavior of the Slater integrals.

Although in all cases, the $R^2(ab; cd)$ integrals are essential in the theoretical calculation, the use of the observed energy-level data empirically accounts to some degree for effects of configuration interaction [2].

2.1. The p^2 case

For a p^2 configuration there are five levels, denoted in LS notation as $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$ and $^1S_0$. Taking into account that, in the non-relativistic approach we must consider the spin–orbit interaction, the eigenvectors with $J=0$ and $J=2$ include contributions from two basis states each. Therefore, the levels should be best denoted as $^3P'_0$, $^3P'_1$, $^3P'_2$, $^1D'_2$ and $^1S'_0$, where the primes indicate that the LS symbols are only nominal [2].[1] Similarly, in the relativistic case, the levels with $J=0$ and $J=2$ are mixed due to the direct and exchange terms [12]. Anyway, with this clarification in mind, we will continue using, only for convenience, the widely used LS notation, where the correlation (*not identity*) indicated by the symbol "↔", is in accordance with the transition from pure LS to pure jj coupling (see Fig. 12 in Ref. [1] or Fig. 5 in Ref. [2]). The *nominal* levels, in the relativistic, pure jj coupling, are given by

$$^3P_0 \longleftrightarrow (1/2, 1/2)_0 = E_0(p_- p_-)$$

$$^1S_0 \leftrightarrow (3/2, 3/2)_0 = E_0(p_+ p_+) + F^2(p_+ p_+)/5$$

$$^3P_1 \leftrightarrow (1/2, 3/2)_1 = E_0(p_- p_+) - G^2(p_- p_+)/5$$

$$^3P_2 \leftrightarrow (1/2, 3/2)_2 = E_0(p_- p_+) - G^2(p_- p_+)/25$$

$$^1D_2 \leftrightarrow (3/2, 3/2)_2 = E_0(p_+ p_+) - 3F^2(p_+ p_+)/25 \qquad (1)$$

therefore,

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

and

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

The $R^2(ab; cd)$ integrals are clearly important for describing theoretically the p^2 level structure in the relativistic approach; however, in order to see the smoothness of trends along isoelectronic sequences, we can simplify the treatment ignoring such Slater integrals. Indeed, calculations made using the complete energy matrix indicate that, for the C I isoelectronic sequence, $R^2(p^2_-, p^2_+) \approx R^2(p_- p_+, p^2_+) \approx 0.84F^2(p_+ p_+)$. Taking into account this fact, the full expressions for $F^2(p_+ p_+)$ and $G^2(p_- p_+)$ differ from Eqs. (2) and (3), but the smoothness of the trends is similar to the case when $R^2 = 0$.

2.2. The p^3 case

For a p^3 configuration there are five levels, denoted in LS notation as $^2P_{1/2}$, $^4S_{3/2}$, $^2D_{3/2}$, $^2P_{3/2}$ and $^2D_{5/2}$. Analogous to the p^2 case, the spin–orbit interaction mixes the $J=3/2$ levels, therefore these levels should be best denoted as $^4S'_{3/2}$, $^2D'_{3/2}$, $^2P'_{3/2}$. The correlation denoted by the symbol "↔" is, as noted above, in accordance with the transition from pure LS to pure jj coupling (see Fig. 12 from Ref. [1]). In this configuration, the ground level is $^4S_{3/2} \leftrightarrow \left(\left(\frac{1}{2}\right)^2 \frac{3}{2} \right) \frac{3}{2}$.

We used the expressions from the book by Rudzikas [8]; additionally, we made verifications with the expressions obtained by Larkins for the average energies [13].

---

[1] Also, we could denote the states as $|a\rangle_0$, $|b\rangle_1$, etc., making clear that the only good quantum number is J.

In the pure jj coupling, the nominal levels are given by

$$^2P_{1/2} \equiv \left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)_{1/2} = E_0(p_- p_+^2) + F^2(p_+ p_+)/5 - G^2(p_- p_+)/5$$

$$^4S_{3/2} \leftrightarrow \left(\left(\frac{1}{2}\right)^2\frac{3}{2}\right)_{3/2} = E_0(p_-^2 p_+) - G^2(p_- p_+)/5$$

$$^2D_{3/2} \leftrightarrow \left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)_{3/2} = E_0(p_- p_+^2) - 3F^2(p_+^2)/25 - G^2(p_- p_+)/5$$

$$^2P_{3/2} \leftrightarrow \left(\left(\frac{3}{2}\right)^3\right)_{3/2} = E_0(p_+^3) - F^2(p_+ p_+)/5$$

$$^2D_{5/2} \equiv \left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)_{5/2} = E_0(p_- p_+^2) - 3F^2(p_+ p_+)/$$
$$\times 25 - G^2(p_- p_+)/5. \qquad (4)$$

From the above equations, an immediate expression arises

$$F^2(p_+ p_+) = \frac{25}{8}\left(\left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)_{1/2} - \left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)_{3/2,5/2}\right); \quad (5)$$

for comparison, the non-relativistic relation is $F^2(p_+ p_+) = 25(^2P_{1/2} - {}^2D_{5/2})/6$. The average energy of a pair of Dirac electrons can be found in a work of Larkins [13]. In this configuration-average model, the general relation between the non-relativistic and relativistic Slater integrals is $F^2(pp) = [2G^2(p_- p_+) + F^2(p_+ p_+)]/3$ and $F^2(pp) = 25(^2P_{1/2} - {}^2D_{5/2})/6$, therefore $G^2(p_- p_+) = 1.5F^2(p_+ p_+)$. In the non-mixing approximation, we cannot separate the $^2D_{3/2,5/2}$ levels, but with the introduction of an effective CI integral we can (see below).

2.2.1. Comparison with the expressions by Larkins

Each of the configurations $\left(\left(\frac{1}{2}\right)^2\frac{3}{2}\right)$ and $\left(\frac{3}{2}\right)^3$ have only one level: $\left(\left(\frac{1}{2}\right)^2\frac{3}{2}\right)_{3/2}$ and $\left(\frac{3}{2}\right)^3_{3/2}$, respectively. So, their average energies coincide with the energies of these levels, given by the 2nd and 4th lines of Eq. (4). On the other hand, using the approach of Larkins [13], the average energy of the configuration $\left(\frac{3}{2}\right)^3$, is given by $E_{av}\left[\left(\frac{3}{2}\right)^3\right] = 3E_{av}(p_+ p_+)$. Analogously, the average energy of the configuration $\left(\left(\frac{1}{2}\right)^2\frac{3}{2}\right)$ is given by $E_{av}\left[\left(\left(\frac{1}{2}\right)^2\frac{3}{2}\right)\right] = E_{av}(p_- p_-) + 2E_{av}(p_- p_+)$. In both cases, our results coincide with the ones by Larkins. Finally, the configuration $\left(\frac{1}{2}\left(\frac{3}{2}\right)^2\right)$ has three levels, and its average energy calculated using the approach of Rudzikas coincides with the value given by Larkins:

$$\left.\frac{2(^2P_{1/2}) + 4(^2D_{3/2}) + 6(^2D_{5/2})}{12}\right|_{RUD} = E_0(p_- p_+^2) - \frac{F^2(p_+ p_+)}{15}$$
$$- \frac{G^2(p_- p_+)}{5} \qquad (6)$$

$$\left.\frac{2(^2P_{1/2}) + 4(^2D_{3/2}) + 6(^2D_{5/2})}{12}\right|_{RUD} = 2\langle p_- p_+\rangle + \langle p_+ p_+\rangle|_{LAR}. \qquad (7)$$

2.3. Separation of the $^2D_{3/2}$ level from the $^2D_{5/2}$

In the above, non-mixing approximation, the levels $^2D_{3/2,5/2}$ have the same energy; we need the CI matrix elements between the $J = 3/2$ levels in order to break that degeneracy. There exist CI matrix elements linking the states $|^4S_{3/2}\rangle - |^2P_{3/2}\rangle$ and $|^2D_{3/2}\rangle - |^2P_{3/2}\rangle$. The ratio $(^4S - {}^2P)/(^2D - {}^2P)$ is always ≥ 1.6 (it is in the range of ≈ 3 for small values of Z_c and tends to ≈ 1.6 for higher values of Z_c. Therefore, in order to obtain a short, analytic expression, we ignore the first interaction and use only the last one, which has the energy equal to $\sqrt{4/5}[-0.08R_d^2 (p_- p_+, p_+^2) - 0.08R_e^2(p_- p_+, p_+^2)]$. Because, in the hydrogenic limit, $R_d^2(p_- p_+, p_+^2) = R_e^2(p_- p_+, p_+^2)$, and for the purposes of a simple parameterization, we introduce an effective term $-\sqrt{4/5}[0.16R^2(p_- p_+, p_+^2)]$. Then, we can write approximately, with $G^2(p_- p_+) = 1.5F^2(p_+ p_+)$ (see Section 10-6 of Ref. [1])

$$^2D_{3/2} = \left(E_0(p_- p_+^2) - \frac{3F^2(p_+ p_+)}{25} - \frac{G^2(p_- p_+)}{5}\right)$$
$$- \left(\frac{0.02048[R^2(p_- p_+, p_+^2)]^2}{E_0(p_+^3) - E_0(p_- p_+^2) + 0.22F^2(p_+ p_+)}\right) \qquad (8)$$

and, therefore

$$^2D_{5/2} - {}^2D_{3/2} = \frac{0.02048[R^2(p_- p_+, p_+^2)]^2}{E_0(p_+^3) - E_0(p_- p_+^2) + 0.22F^2(p_+ p_+)}; \qquad (9)$$

this will be sufficient in order to test the consistency of the experimental $^2D_{3/2}$ levels.

2.4. The p^4 case

The five levels of the p^4 configuration have, in LS coupling, the same designations as in the p^2 case. However, the transition from pure LS to pure jj coupling is very different to the p^2 configuration, and there is a reordering of the jj designations (see Figures 12.2 from Ref. [1] and Fig. 5 from Ref. [2]).

Now, the ground level is $^3P_2$. In this case, we have the configurations $(p_-^2 p_+^2)$ giving levels with $J = 0(\equiv {}^3P_0)$ and $J = 2(\leftrightarrow {}^3P_2)$, $(p_- p_+^3)$ giving levels with $J = 1(\equiv {}^3P_1)$ and $J = 2(\leftrightarrow {}^1D_2)$ and (p_+^4) with $J = 0(\equiv {}^1S_0)$. The expressions for the matrix elements are calculated using the expressions of Rudzikas [8] and verified with the expressions of Larkins [13]. In the pure jj coupling, the nominal levels are given by

$$^1S_0 \equiv (1/2, 1/2)_0 = E_0(p_+^4) - \frac{2}{5}F^2(p_+ p_+)$$

$$^3P_1 \equiv (1/2, 3/2)_1 = E_0(p_- p_+^3) - \frac{3}{15}F^2(p_+ p_+) - \frac{2}{5}G^2(p_- p_+)$$

$$^1D_2 \leftrightarrow (1/2, 3/2)_2 = E_0(p_-p_+^3) - \frac{3}{15}F^2(p_+p_+) - \frac{6}{25}G^2(p_-p_+)$$

$$^3P_0 \equiv (3/2, 3/2)_0 = E_0(p_-^2 p_+^2) + \frac{1}{5}F^2(p_+p_+) - \frac{2}{5}G^2(p_-p_+)$$

$$^3P_2 \leftrightarrow (3/2, 3/2)_2 = E_0(p_-^2 p_+^2) - \frac{3}{25}F^2(p_+p_+) - \frac{2}{5}G^2(p_-p_+)$$

$$(10)$$

giving the subconfiguration averages

$$\langle p_-p_+^3 \rangle = E_0(p_-p_+^3) - \frac{3}{15}F^2(p_+p_+) - \frac{3}{10}G^2(p_-p_+) \quad (11)$$

and

$$\langle p_-^2 p_+^2 \rangle = E_0(p_-^2 p_+^2) - \frac{1}{15}F^2(p_+p_+) - \frac{2}{5}G^2(p_-p_+), \quad (12)$$

as given by Larkins.

Therefore, in the non-mixing approximation, we have, from Eqs. (10)

$$G^2(p_-p_+) = \frac{25}{4}\left[(1/2, 3/2)_2 - (1/2, 3/2)_1\right] \quad (13)$$

and

$$F^2(p_+p_+) = \frac{25}{8}\left[(3/2, 3/2)_0 - (3/2, 3/2)_2\right], \quad (14)$$

that can be compared with Eqs. (3) and (2), respectively.

3. Experimental material and theoretical calculations

All experimental values were taken from the NIST compilations [11]. In a few cases, the values are given in this database with the symbol "+x" indicating no experimental connection with other levels. In other cases, levels given in parentheses are theoretical; levels given in square brackets are semi-empirical. The latter may be based on interpolations, but may also be from some other kind of semi-empirical calculation, such as a parametric fitting with Cowan's codes [1]. We have checked the p^2 configuration of the C, Si, Ge and Sn sequences, the p^3 configuration of the N, P, As and Sb sequences and the p^4 configuration of the O and S sequences. In a few cases, notably the As sequence, we also used published level values not critically evaluated at NIST.

Extensive new MCDHF calculations were made by Jönsson et al. [4] (p^2, the C sequence) and by Rynkun et al. [5] (p^3, the N sequence); total energies of ground state configurations, which can be used to calculate the ionization potentials if required, were published by Rodrigues et al. [14].

4. The semi-empirical method

Although in many cases, the analysis of the experimental levels and/or the Slater parameters along isoelectronic sequences, using the net charge Z_c as the variable, can detect level inconsistencies, in other cases the erroneous levels can be sufficiently near the correct one, so that better parameterizations are needed. It is verified that Slater parameters increase linearly with Z_c, for sufficiently high Z_c, but deviations are noticeable in the beginning of each sequence. Therefore, they can be fitted by expressions of the type (using F^2 only as an example): $F^2_{\exp} = aZ_c + b + c(Z_c + d)^{-1}$. In some type of configurations, a tends to

the unit-charge hydrogenic value F^2_H,[2]

$$F^2_{\exp} = F^2_H Z_c + b + c(Z_c + d)^{-1}. \quad (15)$$

On the other hand, with the scaling relation (using F^2 only as an example)

$$F^2_{\exp} = F^2_H \times (Z - s_F) \quad (16)$$

valid, in principle, for large Z_c values, we can define a screening parameter s as

$$s_F = Z - F^2_{\exp}/F^2_H \quad (17)$$

when necessary, the integrals F^2_H (or similar ones) were computed using relativistic wave-functions from the book by Mizushima [15]. It is important to highlight that, due to the behavior of Slater integrals, the screening parameters tend to a constant value for high Z_c.

The screening parameters are very sensitive to small errors in the determination of energy levels. For example, for the C sequences, in the non-mixing approximation, $F^2(p_+p_+) = 25(^1S_0 - {}^1D_2)/8$, and we can see a strong departure of s_F from smoothness for $Z_c = 23$ (see Fig. 1). Numerical interpolation procedures indicate that $^1S_0$ could be in error more probably than $^1D_2$. Possibly, also $^1S_0$ values for $Z_c = 16, 18$ can be suspicious. It is important to take into account that, using the method of Edlén, it is not possible to find errors in the determination of the $^1S_0$ values, because this level is not used in the parameterization. A similar study using $s_G = Z - G^2_{\exp}/G^2_H$, with $G^2_{\exp} = 25(^3P_2 - {}^3P_1)/4$ indicates that these two levels are determined sufficiently well.

Analogously, in the cases of the p^3 configuration, the use of the screening approach permits one to say that, in the As sequence some of the NIST values need to be corrected (see the detailed discussion below).

5. Detailed discussion of the critically evaluated data in the NIST Atomic Spectra Database

5.1. The general methodology; determination of uncertainties

The first step was to use the experimental data found in the NIST ASD database plotting, for each isoelectronic sequence, the screening parameter s_F in terms of Z_c, to determine if the departure of the "smoothness" is sufficiently clear to doubt about the tabulated values of some energy levels. However, because in the NIST compilations about energy levels are not published the uncertainties $\delta\sigma$, we consulted the diverse compilations due to Edlén [16–18] where the energy levels and their uncertainties were derived from the uncertainties of the measured wavelengths. Knowing that the relation between λ (in Ångströms) and the wavenumber σ (in cm^{-1}) is given by $\lambda = 10^8/\sigma$, it follows that for each spectral line we write $\sigma = \sigma_0 \pm d\sigma$ with $d\sigma = 10^8\lambda^{-2}d\lambda \equiv 10^{-8}\sigma^2 d\lambda$. These works

---

[2] In fact, for the p^2 configurations, the F^2 integrals do show a nearly linear behavior but the G^2 ones do not; for the p^4 cases, the inverse is true.

of Edlén were used in the compilation of forbidden lines made by Kaufman and Sugar [19].

In the case of the configuration $2s^2 2p^2$ (C sequence), the intervals $^1D_2 - ^3P_{1,2}$ were accurately determined by forbidden $M1$ transitions observed in celestial sources and in tokamaks. This determines accurate values for the interval $^3P_2 - ^3P_1$ and, therefore, for the Slater integral $G^2(p_- p_+)$ (see Eq. (3)). The observed data for $^1S_0$ are less accurate and, in most cases, the values were derived via transitions from $2s2p^3$ ^1P to $2s^2 2p^2$ $^1D_2$ and $^1S_0$. As a consequence, whereas we can consider that the levels $^1D_2$ are well determined, the $^1S_0$ levels are less accurate. Precisely, in the doubtful cases to be discussed below, there are no measured forbidden transitions starting from the $^1S_0$ levels (see Section 5.2).

On the other hand, the calculation of the Slater integrals $F^2(p_+ p_+)$ and $G^2(p_- p_+)$ involves the difference $\Delta\sigma$ between ground levels. For our example, we use Eq. (2): $F^2(p_+ p_+) = 25(^1S_0 - ^1D_2)/8 = 25(\Delta\sigma \pm \delta\sigma)/8$. Then, $\delta F^2 (p_+ p_+) = (25/8)\delta\sigma$ and, using Eq. (17), $|\delta s_F| = \delta F^2 (p_+ p_+)/F_H^2$. Putting it all together,

$$|\delta s_F|_{exp} = \frac{\delta F^2(p_+ p_+)}{F_H^2} = \frac{25}{8}\frac{\delta\sigma}{F_H^2},\qquad(18)$$

and similarly for the other cases (the subscript "exp" indicates that $|\delta s_F|$ was evaluated from the experimental wavenumbers uncertainties, see Refs. [16–18] etc.). As an example, for the CI sequence, $Z=26$, the level $2s^2 2p^2$ $^1S_0$ has the value $(298,241 \pm 210)$ cm^{-1} [18]; with $F_H^2 = 19,290$ cm^{-1}, it follows that $|\delta s_F|_{exp} \approx 0.034$. Because in this case, $s_F \approx 5.358$, then $|\delta s_F|_{exp}/s_F \approx 0.006$. In the C sequence, $|\delta s_F|_{exp}$ is in the range $0(Z=6)$ to 0.0486 ($Z=29$). Another contribution to the uncertainty is due to the interpolation process in which the values of s_F for the doubtful levels are estimated from the s_F values calculated from the levels considered as well established. This uncertainty (indicated with the subscript "int") depends on the polynomial degree used to interpolate. After studying all sequences, it is verified that $|\delta s_F|_{int}/s_F \approx 0.003$. Summing up, the values of $|\delta s_F|$ corresponding to the maxima values of s_F of each sequence are C: 0.016, Si: 0.030, Ge: 0.081, Sn: 0.120, N: 0.033, P: 0.051, As: 0.085, Sb: 0.132, O: 0.051 and S: 0.066.

For determination of uncertainties of new recommended values for the energy levels from $|\delta s_F|_{int}$, we start from Eq. (18) interpreted now as

$$|\delta\sigma|_{int} = \tfrac{8}{25} F_H^2 |\delta s_F|_{int};\qquad(19)$$

as an example, when $n=2$, $F_H^2 = 19,290$ cm^{-1} and $|\delta s_F|_{int} \approx 0.01$, $|\delta\sigma|_{int} \approx 60$ cm^{-1}. When $n=5$, $F_H^2 = 2784$ cm^{-1} and $|\delta s_F|_{int} \approx 0.11$, $|\delta\sigma|_{int} \approx 100$ cm^{-1}. Alternatively, in terms of the tabulated $\Delta\sigma$, and remembering that $|\delta s_F|_{int}/s_F \approx 0.003$, it follows that

$$|\delta\sigma|_{int} \approx 0.003[(8/25)ZF_H^2 - \Delta\sigma].\qquad(20)$$

An analogous process can be made using the Slater integral $G^2(p_- p_+)$; in this case, it should be noted that the

corresponding change in the coefficient multiplying G_H^2:

$$|\delta\sigma|_{int} \approx 0.003[(4/25)ZG_H^2 - \Delta\sigma].\qquad(21)$$

The calculations indicate that the largest values (practically, the same as the typical ones) of $|\delta\sigma|_{int}$ for the different sequences are C I: 100 cm^{-1}, Si I: 70 cm^{-1}, Ge I: 150 cm^{-1}, Sn I: 110 cm^{-1}, N I: 265 cm^{-1}, P I: 130 cm^{-1}, O I: 175 cm^{-1} and Si I: 130 cm^{-1}. The corresponding values for the Slater integral F_H^2 are 12,290 cm^{-1}($n=2$), 7898 cm^{-1} ($n=3$), 6004 cm^{-1}($n=4$) and 2784 cm^{-1} ($n=5$).

Analogous to the $2s^2 2p^2$ case, many of the intervals in the ground configurations $2s^2 2p^3$ and $2s^2 2p^4$ are accurately determined by forbidden transitions [16,17]. In general, the four sequences with ground configuration $2s^2 2p^3$ are well established (see below). The same applies to the S sequence ($2s^2 2p^4$); therefore, we fix our attention to the O sequence, where the most difficult level to analyze is the $^1S_0$ one. The line $^1S_0 \rightarrow ^3P_1$ has been observed for $Z = 23 - 24$ (with uncertainties of $\delta\lambda \approx 0.02$ Å) and $Z=26$ (with $\delta\lambda \approx 0.02$ Å). The lines for $Z = 27 - 30$ have $\delta\lambda \approx 0.25 - 0.17$ Å, equivalent to $\delta\sigma \approx 160 - 190$ cm^{-1}. All values were taken from Ref. [17]. Our suggestions, for $Z \geq 24$, are in Section 5.4.

5.2. The p^2 sequences

Sequence C: Data are in the range $Z = 6 - 29$ with no gaps. The behavior of s_F seems to indicate that the NIST values of the $^1S_0$ level for Sc^{15+}, V^{17+} and Ni^{22+} are doubtful, according to the uncertainties calculated as was explained above. Following the tendencies of both $s_F(Z_c)$ and the level values $E_{nlj}(Z_c)$, the tabulated values should be changed as follows. For Sc^{15+}, from 218,720 cm^{-1} to $(218,588 \pm 100)$ cm^{-1}; this is in accordance with the *unpublished* measurement of a forbidden line at 511.2 Å $(^3P_1 - ^1S_0)$ [20], implying a value $^1S_0 = 218,577$ cm^{-1}. This line at 511.2 fits both our energy levels and NIST ones, because of its large uncertainty implied by the small number of significant figures. Anyway, it is interesting to note that our level values fit this line better than the NIST ones. For V^{17+}, from 269,000 cm^{-1} to $(268,728 \pm 100)$ cm^{-1} (there are no measured forbidden lines in the NIST ASD arising from the $^1S_0$ level). For Ni^{22+}, from 463,900 cm^{-1} to $(464,500 \pm 100)$ cm^{-1} (there are no measured forbidden lines in the NIST ASD arising from the $^1S_0$ level). It is important to note that, from the theoretical calculations of Jönsson et al. [4], for Ni^{22+} there occurs the greatest discrepancy between the calculated and observed $^1S_0$ level (465,043 cm^{-1} vs the NIST value, 463,900 cm^{-1}; with our new recommended value, the difference is of the order of only 500 cm^{-1}). See Fig. 1.

Sequence Si: Data are in the range $Z = 14 - 42$ with a few gaps. The $^1S_0$ level for $Z=28$ is missing in the NIST data. We estimate it to be at $(111,710 \pm 70)$ cm^{-1}. All levels for $Z = 37 - 38$ were determined by interpolation, but the behavior of s_F indicates that $^1D_2$ and $^1S_0(Z = 37, 38)$
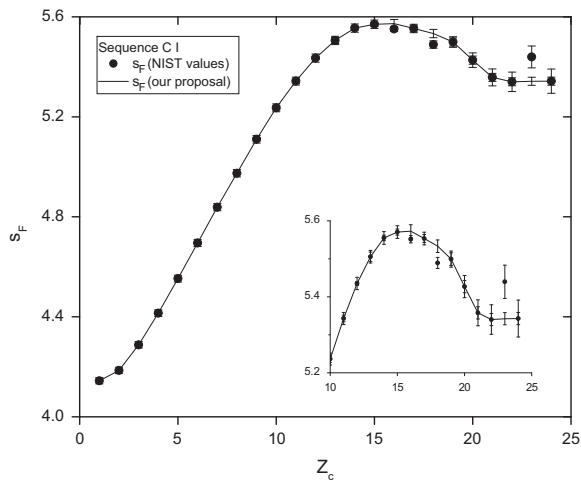
Fig. 1. Isoelectronic sequence of $C\ I$; note the non-smoothness of s_F (*NIST*) for $Z_c = 16$, 18 and 23 ($Z=21$, 23 and 28). Inside are shown details showing s_F for $Z_c = 10$–24. In all cases, the error bars attached to the filled circles come from the experimental level uncertainties; the error bars attached to the full line arise from the relation $|\delta s_F|_{int}/s_F \approx 0.003$ (see Section 5.1).

should be revised. With our calculations, the estimated level values for $Z=37$ are $^1D_2 = (210,984 \pm 70)$ cm^{-1}, $^1S_0 = (282,400 \pm 70)$ cm^{-1}; for $Z=38$ we recommend the following values: $^1D_2 = (239,297 \pm 70)$ cm^{-1}, $^1S_0 = (313,000 \pm 70)$ cm^{-1}. We must consider that the forbidden lines tabulated in the NIST ASD were not measured but interpolated by Sugar et al. [21], using as a guide the difference between observed and calculated values.

Sequence Ge: Data are in the range $Z = 32$–38 with no gaps, except for the level $^1S_0$ for $Z=34$, where the NIST ASD gives $28,430+k$. In the work of Tauheed and Hala [22], these authors established this level at $28,129$ cm^{-1}; from the behavior of s_F, we have estimated $(28,138 \pm 150)$ cm^{-1}. Thus, we confirm the value of Ref. [22] and, therefore, $k = -292$ cm^{-1}.

Sequence Sn: The NIST data are in the range $Z=50$–56. However, a work of Tauheed et al. [23] was published in 2008 for $Z=57$ (La^{7+}). The only gap in the NIST ADS was the level $^1S_0$ for Te^{2+}; however, Tauheed and Naz found this level at $30,398$ cm^{-1} [24]. Our analysis indicates that this value fits in the behavior of s_F.

5.3. The p^3 sequences

In all these sequences, the introduction of an effective CI term given by

$$\frac{0.02048[R^2(p_-p_+, p_+^2)]^2}{[E_0(p_+^3) - E_0(p_-p_+^2) + 0.22F^2(p_+p_+)]}, \tag{22}$$

for the difference $^2D_{5/2} - D_{3/2}$, indicates that the NIST values for the $D_{3/2}$ levels can be considered well founded.

Sequence N: Data are in the range $Z = 7$–32 with no gaps. Our analysis indicates that, in this sequence, all levels can be considered well established.

Sequence P: Data are in the range $Z = 15$–34 with several gaps. For the level $^2P_{3/2}$ of Ni^{13+}, our interpolated value is $(96,564 \pm 130)$ cm^{-1}, whereas the NIST value is $96,630 + x$, therefore $x = -66$ cm^{-1}. For the level $^2P_{1/2}$ of $Z = 29(Cu^{14+})$ the NIST ASD gives an interpolated value $91,106$ cm^{-1}. Our analysis using the behavior of $s_F = 15.801 \pm 0.005$ implies that $^2P_{1/2} = (91,160 \pm 130)$ cm^{-1}, corroborating the NIST proposal. For Ti^{7+} and V^{8+} the NIST ADS adds a "$+x$" to the values. Our analysis indicates that, with our calculated uncertainty of ± 130 cm^{-1} as was explained above, "x" ≈ 0 cm^{-1}.

Sequence As: Data are in the range $Z=33$–42, although the level values for Ru^{11+} and Rh^{12+} were proposed by O'Sullivan et al. [25]. The analysis of s_F indicates that for Br^{2+} the NIST levels should be revised to the values proposed by Persson et al. [26] whereas the values of O'Sullivan et al. follow the isoelectronic trend.
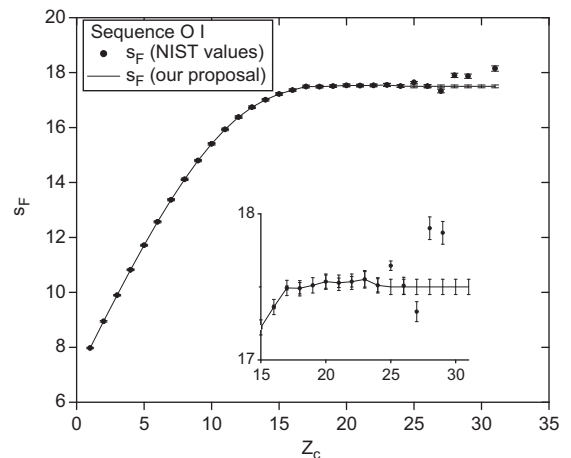

Fig. 2. Isoelectronic sequence of $O\ I$; note the non-smoothness of s_F (*NIST*) for $Z_c \geq 24$. Inside are shown details showing s_F for $Z_c = 15$–31.
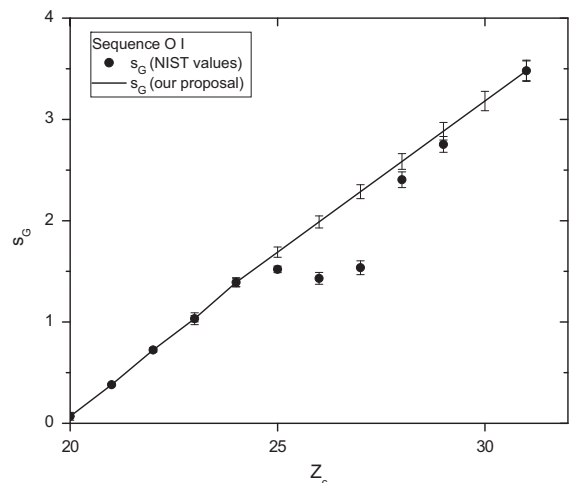

Fig. 3. Analogous to Fig. 2 for s_G, for $Z_c = 20$–31.

Sequence Sb: The NIST data are in the range $Z = 51$–56. However, Gayasov et al. [27] published in 1998 a work on La^{6+}. Our analysis indicates that the values of the NIST ASD and of Gayasov et al. follow a smooth isoelectronic trend.

5.4. The p^4 sequences

Sequence O: The behavior of both s_F and s_G indicates that for $Z_c \geq 24$, the levels should be revised; the worst case occurs for Br^{27+}, and clearly, the values that appear in the NIST webpage should be discarded; as stated there, these data are not critically evaluated by NIST. Thus, the values from Feldman et al. [28] were here to construct Figs. 2 and 3.

Sequence S: The behavior of both s_F and s_G indicates that all NIST levels can be considered well founded.

6. Conclusions

In this short paper we show that the use of the semi-empirical jj-relativistic approach for the p^2 configuration (the C, Si, Ge and Sn sequences), the p^3 configuration (the N, P, As and Sb sequences) and the p^4 configuration (the O and S sequences), permits one to check the consistency of the published experimental levels in the NIST Atomic Spectra Database. Although, in general, the level values are well established, in a few cases the behavior of $s_X(Z_c)$ casts doubt on the published values. Additionally, the smooth behavior of the screening parameters allows interpolation of unknown levels in a number of elements. Summing all, we consider that the use of the screening parameters allows one to check the consistency of level values in isoelectronic sequences, and it is complementary to the use of numerical codes. This fact can be of interest for the search or classification of forbidden lines important for diagnostic purposes of astro-physical and laboratory plasmas.

Acknowledgments

References

[1] Cowan RD. The theory of atomic structure and spectra. Berkeley: University of California Press; 1981.

[2] Curtis LJ. Atomic structure and lifetimes. Cambridge: Cambridge University Press; 2003.

[3] Sobelman II. Atomic structure and radiative transitions. Berlin: Springer-Verlag; 1979.

[4] Jönsson P, Rynkun P, Gaigalas G. Energies, E1, M1 and E2 transition rates, hyperfine structures and Landé g_J factors for states of the $2s^2 2p^2$, $2s2p^3$ and $2p^4$ configurations in carbon-like ions between F IV and Ni XXIII. At Data Nucl Data Tables 2011;97:648–91.

[5] Rynkun P, Jönsson P, Gaigalas G, Froese-Fischer Ch. Energies and E1, M1 and E2 transition rates, hyperfine structures and Landé g_J factors for states of the $2s^2 2p^3$, $2s2p^4$ and $2p^5$ configurations in nitrogen-like ions between F III and Kr XXX. At Data Nucl Data Tables 2014;100:315–402.

[6] Rynkun P, Jönsson P, Gaigalas G, Froese-Fischer Ch. Energies and E1, M1, E2, and M2 transition rates for states of the $2s^2 2p^4$, $2s2p^5$, and $2p^6$ configurations in oxygen-like ions between F II and Kr XXIX. Astron Astrophys 2013;557:A136.

[7] Edlén B. Atomic spectra. In: Handbuch der Physik, vol. 27; 1964. p. 80–220.

[8] Rudzikas Z. Theoretical atomic spectroscopy. Cambridge: Cambridge University Press; 1997.

[9] Aguiar JC, Raineri M, Di Rocco HO. The study of the 4s 4p config-uration of the Zn isoelectronic sequence using the relativistic jj-coupling approach. Eur Phys J D 2013;67:158–67.

[10] ⟨http://sprg.ssl.berkeley.edu/~mfgu/fac/⟩.

[11] Kramida A, Ralchenko Yu, Reader J, NIST ASD Team. NIST atomic spectra database (version 5.1). National Institute of Standards and Technology, Gaithersburg, MD. Available: ⟨http://physics.nist.gov/asd⟩; 2013 [Online].

[12] Johnson WR. Atomic structure theory. Berlin: Springer Verlag; 2007.

[13] Larkins FP. Relativistic LS multiplet energies for atoms and ions. J Phys B 1976;9:37–46.

[14] Rodriguesa GC, Indelicatoa P, Santos JP, Pattéc P, Parentec F. Systematic calculation of total atomic energies of ground state configurations. At Data Nucl Data Tables 2004;86:117–233.

[15] Mizushima M. Quantum mechanics of atomic spectra and atomic structure. New York: W.A. Benjamin; 1970.

[16] Edlén B. Comparison of theoretical and experimental level values of the $n = 2$ complex in ions isoelectronic with Li, Be, O and F. Phys Scr 1983;28:51–67.

[17] Edlén B. Comparison of theoretical and experimental level values of the $n = 2$ configurations in the nitrogen isoelectronic sequence. Phys Scr 1984;30:135–45.

[18] Edlén B. Comparison of theoretical and experimental level values of the $n = 2$ configurations in the carbon isoelectronic sequence. Phys Scr 1985;31:345–58.

[19] Kaufman V, Sugar J. Forbidden lines in $ns^2 np^k$ ground configurations and $nsnp$ excited configurations of beryllium through molybdenum atoms and ions. J Phys Chem Ref Data 1986;15:321–426, http://dx.doi.org/10.1063/1.555775.

[20] Hinnov E. Private communication to the NIST ASD team (see Ref. [11]).

[21] Sugar J, Kaufman V, Rowan WL. Spectra of the P I isoelectronic sequence from Co XIII to Mo XXVIII. J Opt Soc Am B 1991;8:22–6.

[22] Tauheed A, Hala. Revised and extended analysis of doubly ionized selenium: Se III. Phys Scr 2012;85:025304.

[23] Tauheed A, Joshi YN, Marshall A. Revised and extended analysis of La VIII. Phys Scr 2008;77:045301.

[24] Tauheed A, Naz A. Revision and extension to the analysis of the third spectrum of tellurium: Te III. J Kor Phys Soc 2011;59:2910–6.

[25] O'Sullivan G, Dunne P, Costello JT. 4s to 4p transitions in As I like Ru XII, Rh XIII and Pd XIV. J Phys B 1990;23:L575–81.

[26] Persson W, Pettersson SG. $4s^2 4p^3$ and $4s4p^4$ Configurations in Kr IV, Rb V and Sr VI. Phys Scr 1984;29:308–11.

[27] Gayasov RR, Joshi YN, Tauheed A. Seventh spectrum of lanthanum: La VII. Phys Scr 1988;57:562–5.

[28] Feldman U, Seely JF, Behring WE, Cohen L, Richardson MC, Gold-smith S. Transition of the type 2s–2p in fluorine-like and oxygen-like As, Se, Br and Rb. J Opt Soc Am B 1985;2:1658–60.