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

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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.

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] (*C*sequence), by Rynkun et al. [5] (*N*sequence) 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

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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 "$\leftrightarrow$", 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

$$\begin{aligned}
&{}^3P_0 \longleftrightarrow (1/2,1/2)_0 = E_0(p_-p_-)\\
&{}^1S_0 \leftrightarrow (3/2,3/2)_0 = E_0(p_+p_+) + F^2(p_+p_+)/5\\
&{}^3P_1 \leftrightarrow (1/2,3/2)_1 = E_0(p_-p_+) - G^2(p_-p_+)/5\\
&{}^3P_2 \leftrightarrow (1/2,3/2)_2 = E_0(p_-p_+) - G^2(p_-p_+)/25\\
&{}^1D_2 \leftrightarrow (3/2,3/2)_2 = E_0(p_+p_+) - 3F^2(p_+p_+)/25 \qquad (1)
\end{aligned}$$

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 "$\leftrightarrow$" 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].

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[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*.