Optimal classification of HCI spectra

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Abstract

Energy levels of highly charged ions as a rule cannot be classified using $LS$ coupling due to rapid increase of relativistic effects. It is suggested, for optimal classification of energy spectra, to calculate them in $LS$ coupling and to transform the weights of the wave functions, obtained after diagonalization of the energy matrix, to the other coupling schemes. F-like ions are considered as an example.

1 Introduction

For optimal classification of the energy spectra measured, the collaboration of experimenters and theoreticians is required, because only from calculations it is possible to find the closest to reality sets of quantum numbers. The best way to achieve this is found by calculations of energy spectra in $LS$ coupling and transformation of the weights of the wave functions, obtained after diagonalization of the energy matrix, to the other coupling schemes [1].

Let us consider the energy levels of the configuration $1s^22s^22p^43d$ $J = 5/2$ (F-like isoelectronic sequence, Al V - Ge XXIV) as an example. Let us number them, for Al IV, $J = 5/2$, as follows: $(^3P) 4D_{5/2} - 1$, $(^3P) 4F_{5/2} - 2$, $(^3P) 4P_{5/2} - 3$, $(^3P) 2F_{5/2} - 4$, $(^3P) 2D_{5/2} - 5$, $(^1D) 2F_{5/2} - 6$, $(^1D) 2D_{5/2} - 7$, and $(^1S) 2D_{5/2} - 8$. If, calculating the energy spectra, we start with most realistic coupling scheme, then the intermediate coupling will not differ much from the pure one. In such a case one weight will be much larger compared to the others in the eigenfunction obtained after the diagonalization of the energy matrix. Then the quantum numbers of this largest weight are used to classify the relevant energy level. If there are several almost equal weights, then the initial coupling is not suitable and we have to look for the other coupling schemes. Indeed, e. g., if we look at the classification of the energy levels in Fawcett [2], we shall see that there are cases when the quantum numbers of the $LS$ coupling can be hardly used for this purpose.

Similar conclusions can be derived from the relevant theoretical studies. Table I presents the percentage of the largest weights of the levels 2-5 for F-like ions in $LS$ coupling. It illustrates that with the increase of the ionization degree the accuracy of the $LS$ coupling worsens. There are even cases when it is impossible to ascribe the largest weights to certain levels (e.g. levels 2 and 3 for Cr XVI and Mn XVII as well as the levels 2 and 5 for Cu XXI and Zn XXII). Therefore we need a fairly universal methodology of the classification of the levels of atoms and ions with the most reliable sets of quantum numbers. This is of particular importance for the case of the highly ionized atoms.
Table I. Percentage of largest weights of the levels 2-5 for F-like ions in the configuration 1s^22s^22p^43d in LS coupling.

| Element | Z  | level 2       | level 3       | level 4       | level 5       |
|---------|----|---------------|---------------|---------------|---------------|
| Al V    | 13 | 4F (92%)      | 4P (63%)      | 2F (63%)      | 2D (90%)      |
| Si VI   | 14 | 4F (91%)      | 4P (83%)      | 2F (80%)      | 2D (88%)      |
| P VII   | 15 | 4F (90%)      | 4P (85%)      | 2F (82%)      | 2D (85%)      |
| S VIII  | 16 | 4F (88%)      | 4P (84%)      | 2F (80%)      | 2D (82%)      |
| Cl IX   | 17 | 4F (85%)      | 4P (81%)      | 2F (77%)      | 2D (78%)      |
| Ar X    | 18 | 4F (81%)      | 4P (76%)      | 2F (76%)      | 2D (72%)      |
| K XI    | 19 | 4F (76%)      | 4P (69%)      | 2F (67%)      | 2D (69%)      |
| Ca XII  | 20 | 4F (69%)      | 4P (61%)      | 2F (61%)      | 2D (65%)      |
| Sc XIII | 21 | 4F (62%)      | 4P (53%)      | 2F (56%)      | 2D (61%)      |
| Ti XIV  | 22 | 4F (54%)      | 4P (44%)      | 2F (51%)      | 2D (57%)      |
| V XV    | 23 | 4F (45%)      | 4P (37%)      | 2F (46%)      | 2D (54%)      |
| Cr XVI  | 24 | 4F (37%)      | 4F (42%)      | 2F (43%)      | 2D (51%)      |
| Mn XVII | 25 | 4F (30%)      | 4F (47%)      | 4P (40%)      | 2D (48%)      |
| Fe XVIII| 26 | 2F (27%)      | 4F (51%)      | 4P (42%)      | 2D (46%)      |
| Co XIX  | 27 | 2F (27%)      | 4F (52%)      | 4P (43%)      | 2D (44%)      |
| Ni XX   | 28 | 2F (27%)      | 4F (52%)      | 4P (43%)      | 2D (42%)      |
| Cu XXI  | 29 | 2D (27%)      | 4F (51%)      | 4P (43%)      | 2D (39%)      |
| Zn XXII | 30 | 2D (28%)      | 4F (48%)      | 4P (43%)      | 2D (37%)      |
| Ga XXIII| 31 | 2D (29%)      | 4F (45%)      | 4P (42%)      | 2F (36%)      |
| Ge XXIV | 32 | 2D (29%)      | 4F (41%)      | 4P (41%)      | 2F (39%)      |

2 Methodology

In general we shall follow the methodology of the optimization of the coupling scheme described in [1, 3]. If we calculate the energy matrix in LS coupling and diagonalize it, then we arrive at the eigenfunction in the form

$$\Psi(\beta J) = \sum_{\alpha_i L_i S_i} a(\alpha_i L_i S_i J) \Psi(\alpha_i L_i S_i J),$$  \hspace{1cm} (1)

where $\Psi(\alpha_i L_i S_i J)$ is the wave function in the pure LS coupling and $a(\alpha_i L_i S_i J)$ are the weights of the wave functions of that coupling. Calculations show that for the level 3 of the V XV the wave function of the intermediate coupling has two practically equal weights, namely 0.607 and 0.594. Similar situation is also for the levels 3 - 5. Very close are the weights of the functions $\Psi(2p^4 (3P) 3d^2 F_{5/2})$ and $\Psi(2p^4 (3P) 3d^2 F_{5/2})$ of the level 2 for Cu XXI, namely 0.518 and 0.514. Mn XIV has two practically equal weights for level 4, namely $a(2p^4 (3P) 3d^2 F_{5/2})=0.633$ and $a(2p^4 (3P) 3d^2 F_{5/2})=0.635$.

There exists the following relationship between the weights of the wave functions of two pure coupling schemes [1]:

$$a_{ij} = \sum_k c_{ik} (\Psi_i | \Phi_k).$$  \hspace{1cm} (2)

Here $(\Psi_i | \Phi_k)$ stands for the transformation matrix from one coupling scheme to the other. Their general expressions as well as simplified formulas for special cases may be also found in [1]. Thus, knowing the weights $c_{ik}$ of the wave functions in a certain pure coupling scheme, let us say LS, we are able to find them for the case of any other coupling.
and to choose in this way the optimal one, avoiding the calculation and the diagonalization of the energy matrices in other coupling schemes. The relevant procedure is very simple, particularly when having the necessary computer code. Let us illustrate its practical use for the optimization of the classification of the energy levels 2 and 3 of the F-like ions. The levels of the configuration $2p^4$ are classified using LS coupling whereas four coupling schemes (LS, LK, JK and JJ) are possible for coupling the angular momenta of $2p^4$ electrons with those of $3d$ electron. The energy levels in the LK, JK and JJ coupling schemes may be denoted as $L_1[K]_J$, $J_1[K]_J$ and $[J_1J_2]_J$ correspondingly.

3 Discussion

It turned out that the level 3 for low ionization degrees (Al V - Ar X) may be also classified with LK coupling. However LK coupling is extremely unfit for Ca XII - Fe XVIII. The JK coupling is slightly preferable in the middle of the isoelectronic sequence, whereas JJ coupling at the end. However, for the ionization degrees studied the rather large deviations from all considered pure coupling schemes including LS are observed.

Mean deviation $R$ of the vectors $C$ of intermediate coupling from pure coupling $T$ may be also used as the measure of the applicability of coupling scheme (see [3]):

$$R = \frac{1}{n} \sum_{k=1}^{n} \left( \sum_{i=1}^{n} (c_{ik} - t_{ij})^2 \right)^{1/2} = \frac{1}{n} \sum_{k=1}^{n} \sqrt{2(1 - c_{jk})}.$$  (3)

Second equality in (3) is obtained making use of the orthonormality conditions of the vectors $C$ and $T$ considered in the basis of the same coupling scheme i.e., when $t_{ij} = \delta_{ij}$. Here $j_k$ denotes the largest component of the $k$-th vector and $n = 4$. Using the codes worked out let us calculate $R$ for the levels mentioned above. Considering the weights of separate levels we see that the validity of one or another coupling scheme varies from one level to the other. On the contrary, $R$ is an averaged quantity. It reflects the main features of the whole group of the levels.

Figure 1 illustrates the dependence of $R$ on $Z$ for the levels 2-5. Dotted line and curves with filled squares, triangles and circles respectively correspond to the LS, LK, JK and JJ coupling schemes. We see from Figure 1 that the dependence of $R$ on $Z$ may be devided into three intervals. In the first interval $Z=12 - 20$ LS coupling is the best. Moreover, at the beginning of the isoelectronic sequence ($Z = 12 - 17$) it is valid with high accuracy ($R < 0.5$) but with the increase of the ionization degree its quality worsens. In this interval LK coupling occupies the second place, but with the increase of $Z$ it also worsens whereas the quality of JK coupling improves. Around Sc XIII ion all three coupling schemes (LS, LK and JK) are practically equally valid (their $R$ values are respectively equal to 0.693, 0.686 and 0.692). In the second interval ($Z = 21 - 26$) the JK coupling is the most suitable. Here $R$ value is decreasing (with the increase of $Z$) only for JJ coupling. In the third interval ($Z = 28 - 32$) the JJ coupling is the best. Only for it the $R$ value is decreasing with the increase of $Z$, whereas for the rest three coupling schemes $R$ is practically the same and at the end ($Z = 31, 32$) it reaches 0.880.

4 Conclusion

The levels 1, 6 - 8 for Al V - Ge XXIV in the configuration $1s^22s^22p^43d$ may be fairly accurately identified with the help of LS coupling. However, the identification of the rest levels 2 - 5 based on the LS coupling for some ionization stages is doubtful.
Considering the validity of the various coupling schemes for levels 2 - 5, using the analysis of the structure of the weights of the eigenfunctions or the quantity $R$, we arrive at similar conclusions. In both cases we see that at the beginning of the sequence the $LS$ coupling is valid with high accuracy whereas at its end $JJ$ coupling prevails. Namely, the optimal classification of the levels 2 - 5 would be: $LS$ for Al V - Ca XII, $JK$ for Sc XII - Co XIX and $JJ$ for the more highly ionized atoms.

The methodology of the optimization of the coupling scheme, based on the transformation of the weights of a given pure coupling scheme to other couplings and on the computer codes written, allow us to find the optimal coupling scheme for classification of the energy levels of atoms and ions, multiply charged ions included. The methodology and the codes are fairly universal allowing a study of the complex many-electron configurations. They may be particularly useful when combined with relevant experimental studies.

**References**

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