Relativistic Calculations in the Arsenic Sequence: Fine-Structure Transitions

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1 Introduction

One of the properties of highly ionized atoms that is a subject of considerable interest for many fields, such astrophysics and fusion plasma research, is the transition probability between different electronic levels or the oscillator strength. One of the isoelectronic series of the heavier species which has not been studied so far, to our knowledge, is that of the arsenic atom. As I has itself been the object of great interest in the last few years ([4]), given the detection of its $4p^2 \; 5s \; ^4P_{3/2} - 4p^3 \; ^4S_{3/2}$ line in the spectrum of Chi Lupi, a HgMn type star, with a spectrometer on board the Hubble Space Telescope. Other atomic systems that have been found to exist in different ionization degrees in Chi Lupi are Sr, Y, Zr, Ru and Pd [5], which are potencially members of the As I isoelectronic sequence, although there are so far no reports on the existence of these elements in As-like form.

For many years we have applied the Quantum Defect Orbital method, both in its non-relativistic (QDO) [1] and its relativistic (RQDO) [2] versions, to the calculation of oscillator strengths and photoionization cross sections of a rather large number of atomic species, including several isoelectronic sequences ([3]). Nevertheless, for the reasons given above, we have undertaken the study of the intensities of all the allowed lines of the $4s^2 \; 4p^3 - 4s^2 \; 4p^2 \; 5s$ transition array in a number of As-like ions ranging from Br III (Z = 35) to La XXV (Z = 57). Two methodologies have been followed: the aforementioned RQDO method and the multiconfiguration Dirac-Fock (MCDF) formalism with the GRASP code written by Grant et al. [6] .

2 Relativistic Quantum Defect Orbital Method

The RQDO method has been described in detail [2] . We shall thus only mention here those aspects of the formalism which are relevant to this study.

The relativistic quantum defect orbitals are the analytical solutions of a quasirelativistic second-order Dirac-like equation with a model Hamiltonian that contains the quantum defect as a parameter. This model Hamiltonian allows for an effective variation of the screening effects with radial distance and, as a consequence, the radial solutions behave approximately correctly in the core region of space, and display a correct behaviour at large radial distances. These have been found to be, in many cases, the most relevant regions contributing to the transition integral. The RQDO's lead to closed-form analytical expressions for the transition integrals, which allows us to calculate transition probabilities with simple algebra and little computational effort.

The RQDO Hamiltonian accounts for core-valence polarization only implicitly, through the inclusion of the quantum defect. However, it is our experience that the explicit inclusion of the above effect is often important. As in some previous works (see, e.g., [3]) we have performed

two types of RQDO f-value calculations: one with the standard dipole-length transition operator, $Q(r) = r$, and another with a core-polarization corrected form of the former [7]:

$$Q(r) = r \left[1 - \frac{\alpha}{r^3} \left[1 - \exp(-r/r_c) \right]^3 \right],$$ (1)

where α is the core polarizability and r_c is a cut-off radius, chosen to be in these calculations the mean radius of the outermost orbital of the core, calculated in accord with an expression given by Chichkov and Shevelko [8]. The core has been considered in all cases to be Ar $3d^{10}$ $4s^2$. For the core polarizabilities we have taken the values supplied by Fraga et al [9], which do not go beyond Nb IX (Z = 41). For the higher ions in the sequence we have found the core polarizabilities in atomic units from the following expression

$$\ln \alpha = 38.838 - 10.615 \ln Z,$$ (2)

which has been obtained through a fitting of the α-values of Fraga et al. [9] from As I (Z = 33) to Nb IX (Z = 41), with a correlation factor of 0.9967. Z is the atomic number.

In the RQDO context, energy level data are required in order to obtain the quantum defects. For Br III we have been employed the data provided from a compilation by Kelly [10]. For the quartet levels of the $4s^2$ $4p^2$ $5s$ configuration we have taken the experimental energy values of O'Sullivan [11] for Rb V and O'Sullivan and Maher [12] for Sr VI. No experimental energies have been found for the remaining levels of these two ions and we have employed the energies obtained with our MCDF calculations. For the ions Y VII to Mo X we have used experimental energies by Reader and Acquista [13]. Early energy data measured by Rahimullah et al.[14] for these ions are in good agreement with those of Reader and Acquista [13].

All the above experimental data have relied on theoretical predictions and observed intensities for the identification of the lines, as well as an analysis of the systematic trends followed by the level energies along the isoelectronic sequence [11, 12, 13, 14]. O'Sullivan [11] and O'Sullivan and Maher [12] rely on MCDF calculations. Reader and Acquista [13] employ Hartree-Fock (HF) calculations. These authors estimate uncertainties in the range from 0.6 cm^{-1} to 15 cm^{-1} for the levels of the $4s^2$ $4p^3$ and $4s^2$ $4p^2$ $5s$ configurations, the uncertainties increasing from the ground to the excited configurations, and also from Y VII to Mo X.

In order to have a basis on to which test the quality of the energies employed, we have plotted the energies of the ground and excited configurations, respectively. They present a regular behaviour, in all cases, along the isoelectronic sequence, and the connection between the present MCDF and the experimental energies [13] is smooth.

Other input data that are also needed in the RQDO calculations were the ionization energies of the atomic systems. The corresponding values from As I to Kr IV are supplied by Kelly [10] and a few more by Fraga et al. [9]. For the remaining ions we have employed an extrapolation formula obtained by fitting the ionization energies in cm^{-1} of the previous ions. This formula is

$$E_i = 86.96 \, Z^3 - 2806.66 \, Z^2,$$ (3)

where, again, Z is the atomic number. The correlation factor was 0.9998.

3   Multiconfiguration Dirac-Fock Method

The MCDF method, as implemented in the GRASP code [6], is a generalization of the Dirac-Fock formalism. For details of the atomic MCDF model we refer to a review by Grant [15].

The extended average level (EAL) mode with the Breit and QED corrections [6] has been employed. The following configurations have been introduced: $4s^2\ 4p^3 + 4p^5$ to describe the ground configuration, and $4s^2\ 4p^2\ 5s + 4s^1 4p^4 + 4s^2 4p^2 4d^1$ to describe the excited configuration. The choice of these configurations has been made on the grounds of the comments by Bieroń and Migdalek [16] and O'Sullivan [11] and by observing that this configuration mixing leads to a good accord between dipole-length (Babushkin gauge) and dipole velocity (Coulomb gauge) MCDF oscillator strengths for most of the transitions studied.

4   Results and Analysis

For each transition, two RQDO sets of f-values are given, one obtained with the standard dipole-length transition operator, $Q(r) = r$, and the other with the core-polarization corrected transition operator, Eq. (2.1). The two sets of MCDF oscillator strengths correspond to calculations in the dipole-length and dipole-velocity forms, respectively. The experimental f-values reported by O'Sullivan [11] and O'Sullivan and Maher [12] up to Mo X have been considered for comparative purposes. In all the transitions, our MCDF calculations did not reach convergence both for Br III and Kr IV. For Rb V, all theoretical as well as experimental f-values are anomalously low in magnitude. This feature is explained by O'Sullivan [11] in terms of a large configuration mixing taking place in this particular ion that leads to a major re-distribution of intensity between the $4p - 5s$ and $4p - 4d$ transitions. In all studied transitions both our RQDO and MCDF f-values are in good accord with experiment. As we go down in the sequence, a greater similarity between the dipole-length and dipole velocity MCDF oscillator strengths is observed. In most transitions, the effects of correcting the RQDO f-values for core polarization are sizable and bring them closer to the MCDF oscillator strengths, in particular to those corresponding to the dipole-length calculation. A sharp increase that occurs in most transitions of Sr VI is apparent both in our calculations and experiment. O'Sullivan [11] refers to it as "array quenching" and explains it in terms of a sudden change in eigenvector composition of the $4p^2\ 5s$ term.

In all transitions, the RQDO f-values are generally greater in magnitude than the MCDF results, the differences increasing with atomic number, except for the $^2D_{3/2} - {}^2P_{3/2}$ transition. Nevertheless, the RQDO-MCDF relative difference of 96% occurring at La XXV (Z = 57) for the $^4S_{3/2} - {}^4P_{5/2}$ transition is certainly an exception. For the other transitions, the largest RQDO-MCDF relative differences in the heaviest of the ions studied range from 15% in Sn XVIII (Z = 50) for the $^2P_{3/2} - {}^2S_{1/2}$ transition and Cs XXIII (Z = 55) for the $^2D_{3/2} - {}^2P_{3/2}$ transition to 33,5% for La XXV (Z = 57) for the $^4S_{3/2} - {}^4P_{5/2}$ transition. Apart from the more correct wavefunctions supplied by the MCDF approach, as compared to the RQDO wavefunctions, a possible reason for the discrepancies might be the fact that the LS coupling scheme has been adopted for all the ions in the RQDO procedure, unlike Biémont and Hansen [17] who adopted an intermediate coupling scheme in their calculations of magnetic dipole and electric quadrupole transitions in the ground state of the germanium and arsenic isoelectronic sequences.

In summary, RQDO and MCDF oscillator strengths for the $4s^2\ 4p^3 - 4s^2\ 4p^2\ 5s$ transition array of a number of As-like ions are presented. When experimental data are available, our results are in good accord with them. Some discrepancies between the RQDO and MCDF f-values are apparent, particularly for the heavier ions, for which we consider the MCDF results to be superior in quality. Nevertheless, the RQDO procedure has once more proved to be a very useful tool for estimating transition probabilities. It is particularly adequate in the cases where mass-production of data is needed, given its cost-efficiency and reasonable correctness. It offers also the advantage of its analyticity and lack of convergence problems from which elaborate ab initio calculations often suffer.

One drawback of the RQDO formalism is that it needs quantum defects from other sources as input. But this can be, in many cases, circumvented by making use of the regularities presented by the quantum defects both along spectral series and isoelectronic sequences, which allow for inter- or extrapolations.

5   Acknowledgements

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Tables and figures are available upon request to the authors.