

The Partitioned Correlation Function Interaction approach applied to B I, C II and more complex systems

Simon Verdebout*, Pavel Rynkun[†], Per Jönsson[§], Gediminas Gaigalas^{†,‡},
Charlotte Froese Fischer^{||} and Michel Godefroid*¹

* Chimie Quantique et Photophysique, Université Libre de Bruxelles, B-1050 Brussels, Belgium

[†] Vilnius Pedagogical University, Studentų 39, Vilnius, LT-08106, Lithuania

[§] School of Technology, Malmö University, S-205 06 Malmö, Sweden

[‡] Vilnius University Research Institute of Theoretical Physics and Astronomy, LT-01108 Vilnius, Lithuania

^{||} Atomic Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Synopsis The Partitioned Correlation Function Interaction (PCFI) approach has been proposed recently as a promising method for capturing efficiently electron correlation in many-electron atoms. In the present work, we apply this method to study five-electron systems (B I and C II) and more complex atoms.

The traditional multiconfiguration Hartree-Fock and configuration interaction methods are based on a single orthonormal orbital basis. For atoms with many closed core shells, or complicated shell structures, a large orbital basis is needed to saturate the different electron correlation effects such as valence, core-valence correlation and correlation within the core shells. The large orbital basis leads to massive configuration state function (CSF) expansions that are difficult to handle, even on large computer systems. In a recent paper [1], we have shown that it is possible to relax the orthonormality restriction on the orbital basis and break down the originally very large calculations to a series of smaller calculations that can be run in parallel. Each calculation determines a partitioned correlation function (PCF) that accounts for a specific correlation effect. The PCFs are built on optimally localized orbital sets and are added to a zero-order multireference (MR) function to form a total wave function. The expansion coefficients of the PCFs are determined from a low dimensional generalized eigenvalue problem. The interaction and overlap matrices are computed using a biorthonormal transformation technique [2]. The new method, called partitioned correlation function interaction (PCFI), converges rapidly with respect to the orbital basis and gives Li I and Be I total energies that are lower than the ones from ordinary multiconfiguration calculations.

No intercombination lines are observed in B I. The position of the quartets relative to the ground state is therefore obtained from extrapolation along the iso-electronic sequence. Edlén *et al.* [3] estimated the energy difference $2s^2 2p^2 P_{3/2}^o - 2s 2p^2 {}^4P_{5/2}$ to be $28866 \pm 15 \text{ cm}^{-1}$ while Kramida and Ryabtsev [4] revised the esti-

mate to $28643.11 + x \text{ cm}^{-1}$ with an uncertainty of 1.8 cm^{-1} , where x represents the error in the extrapolation. The difference in the two extrapolated values is 223 cm^{-1} . We apply the PCFI method to investigate this discrepancy. The same strategy is applied to the other terms $2s 2p^2 {}^2P$, 2D , 2S whose excitation energies are well known and to the $2s^2 2p^2 P^o - 2s 2p^2 {}^4P$ energy separation in the isoelectronic ion C II, also known experimentally. This study reveals the importance of choosing correctly-balanced zero-order MR in order to claim the spectroscopic accuracy on a predicted excitation energy. To achieve this balanced description of the desired levels, the selection of the CSFs defining the MR is done on the basis of the accumulated percentage of a valence CAS expansion. Fixing the same threshold for all the levels we are interested in, we get MR spaces capturing the most important components and satisfying the level-specificity requirements.

Some PCFI calculations on excitation energies, hyperfine structures and isotope shifts in Mg I and Al I will be presented. These systems are indeed interesting for learning how the PCFI method should be explored to describe core-correlation effects.

References

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¹E-mail: mrgodef@ulb.ac.be