

## VARIATIONAL PAIR-CORRELATION FUNCTIONS FOR ATOMIC PROPERTIES

S. Verdebout<sup>1</sup>, P. Jönsson<sup>2</sup>, G. Gaigalas<sup>3</sup>, C. Froese Fischer<sup>4</sup> M. Godefroid<sup>1</sup>

<sup>1</sup>Chimie Quantique et Photophysique, CP160/09, Université Libre de Bruxelles,  
Av. F.D. Roosevelt 50, B-1050 Brussels, BELGIUM

<sup>2</sup>Center for Technology Studies, Malmö University, 205-06 Malmö, SWEDEN

<sup>3</sup>Vilnius University, Institute of Theoretical Physics and Astronomy,  
A. Goštauto 12, Vilnius, LT-01108, LITHUANIA

<sup>4</sup>National Institute of Standards and Technology, Gaithersburg, USA

It is well known that variational methods produce one-electron radial functions that minimise the total energy of the system. By tailoring the configuration expansion we are able to target a specific correlation effect. The multiconfiguration Hartree-Fock [1] method (MCHF) is used to produce independent variational pair-correlation functions (PCFs) each one representing the correlation for a given electron pair. These nonorthogonal PCFs are coupled to each other through the small size, associated generalised eigenvalue problem. The Hamiltonian and overlap matrices are produced using biorthonormal orbital transformations and efficient counter-transformation of the configuration interaction eigenvectors [2]. The complete many-electron wave function, in the PCF basis, is then tested through different sensitive electronic properties computed using the same biorthonormal algorithm.

Using this methodology we describe the lowest  $^1S$ ,  $^1P^o$ ,  $^3P^o$  states of the beryllium atom. We show that the energy convergence is faster for our pair correlation function interaction method (PCFI) than with the usual SD-MR-MCHF scheme. The resulting wave function is tested with the expectation value of the specific mass shift operator, the hyperfine structure parameters and with the transition probabilities. These properties illustrate the importance of keeping a representation with enough variational degrees of freedom.

Beryllium atom constitutes a perfect benchmark for the PCFI method since it is possible to saturate a common orthonormal basis for complete active space expansions. On contrary for larger systems, it is hopeless to describe the electron correlation in the entire space by optimising a common orthonormal basis. The PCF calculation offers a good alternative for these. This methodology could also be used for coupling different and independently optimised physical states with their own representation. The present study fits in the framework of contemporary developments of the ATSP2K and GRASP2K packages [1,3].

### References

- [1] C. Froese Fischer *et al.*, *Comp. Phys. Commun.* **176**, 559 (2007)
- [2] J. Olsen *et al.*, *Phys. Rev. E* **52**, 4499 4 (1995)
- [3] P. Jönsson *et al.*, *Comp. Phys. Commun.* **176**, 597 (2007)