

# Configuration interaction with separately optimized pair correlation functions

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Variational methods produce one-electron radial functions that minimize the total energy of the system. Independent pair correlation functions (PCFs) designed to represent a specific correlation effect – valence, core-valence, or core-core – can be obtained from multiconfiguration Hartree-Fock (MCHF) or Dirac-Hartree-Fock (MCDHF) calculations [1,2]. These separately optimized and non-orthogonal PCFs may then be coupled by solving the associated generalized eigenproblem. In the present study, the Hamiltonian and overlap matrix elements are evaluated through biorthonormal orbital transformations and efficient counter-transformation of the configuration interaction eigenvectors [3]. The ground state of Be atom has been thoroughly tested by this method for various computational strategies and correlation models. It has been shown that the energy convergence is faster than with the usual SD-MCHF method of optimizing a single, orthonormal, one-electron orbital basis spanning the complete configuration space. Beryllium is a small system for which basis saturation can be achieved through complete active space MCHF expansions. But for larger systems describing electron correlation in all space by optimizing a common orthonormal set becomes hopeless whereas the calculation of additional PCFs is straight forward. Our independent optimization scheme, raises many questions related in the choice of the zero-order model to be used when building the interaction matrix. The present study is the first step in the current development of the extension of the ATSP2K and GRASP2K packages [1,2] that will adopt the biorthonormal treatment for energies, isotope shifts, hyperfine structures and transition probabilities.

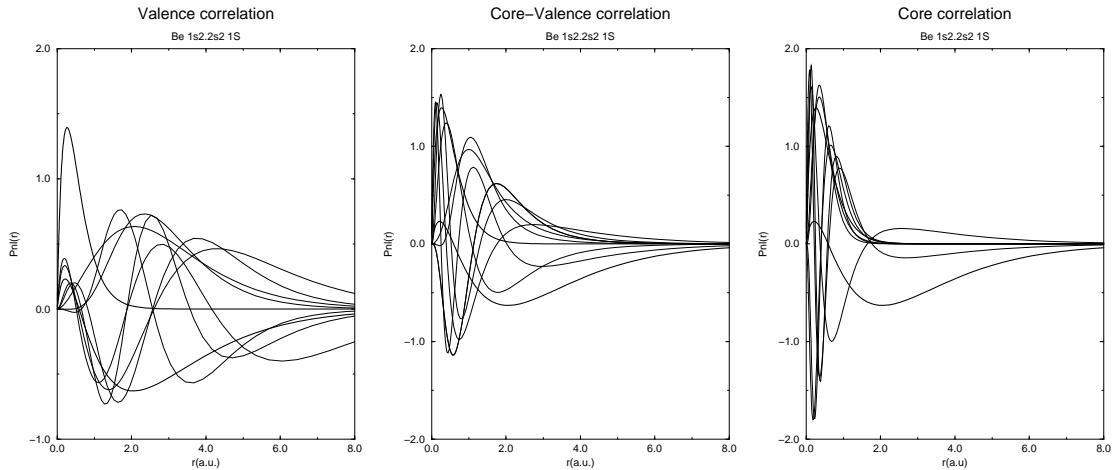


Figure 1: Correlation orbitals for Be  $1s^2 2s^2 \ ^1S$  from MCHF  $n = 4$  active set calculations.

## References

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