Multiconfigurational self-consistent field theory for large active space and spin-orbit coupling

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To treat systems that require large active spaces, various approximate full configuration interaction (FCI) methods have been developed, including selected CI, density matrix renormalization group (DMRG) and FCI quantum Monte Carlo (FCIQMC) theories. In the present talk, we would like to introduce a configuration state function (CSF) based multiconfigurational self-consistent field method, iCISCF [1]. The success of iCISCF stems from three ingredients: (1) efficient selection of individual configuration state functions spanning the active space while maintaining full spin symmetry; (2) the use of Jacobi rotation for optimization of the active orbitals in conjunction with a quasi-Newton algorithm for the core/active–virtual and core–active orbital rotations; (3) a second-order perturbative treatment of the residual space left over by the selection procedure (iCISCF(2)). The iCISCF has been further extended to consider spin-orbit coupling (SOC) effects. The extended method is referred to as SOiCISCF [2]. In SOiCISCF, SOC induced orbital relaxation effect is treated on an equal footing as that by electron correlation. Interesting applications using iCISCF and SOiCISCF methods are presented.

[1] Y. Guo, N. Zhang, Y. Lei, W. Liu, *J. Chem. Theory Comput.* 17, (2021) 7545

[2] Y. Guo, N. Zhang, W. Liu, *in preparation*