Iterative Configuration Interaction with Selection

Wenjian Liu[a] and Mark R. Hoffmann[b]

[a]College of Chemistry and Molecular Engineering, Peking University, China

[b]University of North Dakota, Grand Forks, USA

Email: liuwj@pku.edu.cn

Abstract:

According to when the static and dynamic components of electron correlation are treated, the available wavefunction-based correlation methods can be classified into three families, viz., "static-then-dynamic", "dynamic-then-static", and "static-dynamic-static (SDS)" [1]. Herewith we report a *restricted* SDS framework [2], which employs *the same number* (Np) of primary, secondary and external states for describing the static, dynamic, and again static components of correlation. That is, the secular equation to be diagonalized is of dimension 3Np, irrespective of the numbers of correlated electrons and orbitals. Even the lowest-order realization of this seemingly *restricted* SDS framework, i.e., SDSPT2, is already very accurate for classic test problems of variable degeneracies [2,3], whereas a high-order realization, i.e., iCI (iterative Configuration Interaction), can converge monotonically and quickly to full CI from above, even when a rather poor reference is taken as the start [1]. The efficiency of iCI can greatly be enhanced when combined with the selection of important configurations and the table-CI technique for evaluation of Hamiltonian matrix elements [4]. It is also of interest to see that the micro-iteration of iCI can be reformulated as an iterative Vector Interaction (iVI) method for exterior or interior roots of large matrices[5,6].

1. W. Liu and M. R. Hoffmann, iCI: iterative CI toward full CI, J. Chem. Theory Comput. 2016, 12, 1169; (E) 2016, 12, 3000.
2. W. Liu and M. R. Hoffmann, SDS: the `static-dynamic-static' framework for strongly correlated electrons, Theor. Chem. Acc. 2014, 133, 1481.
3. Y. Lei, W. Liu, and M. R. Hoffmann, Further development of SDSPT2 for strongly correlated electrons, Mol. Phys. 2017, 115, 2696.
4. W. Liu, M. R. Hoffman, and N. Zhang, making iCI work with selection (unpublished).
5. C. Huang, W. Liu, Y. Xiao, and M. R. Hoffmann, iVI: an iterative vector interaction method for large eigenvalue problems, J. Comput. Chem. 2017, 38, 2481; (E) 2018, 39, 338.
6. C. Huang and W. Liu, iVI-TD-DFT: an iterative vector interaction method for exterior/interior roots of TD-DFT (DOI:10.1002/jcc.25569).