Multireference Configuration Interaction Beyond Singles and Doubles

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While Multireference Configuration Interaction including single and double excitations (MRCISD) remains a method of choice, or in some cases the only option, for accurate descriptions of reactions on excited state surfaces, the slow convergence of electron correlation for variational calculations and the lack of rigorous size-extensivity are hindrances. Efforts to extend the approach to beyond the single- and double-electron replacement approximation have been challenged by the loss of powerful graphical implementations for greater replacements than two. Although first-order perturbative approximations to MRCISD (i.e., MRCISD(TQ)) can be accomplished relatively efficiently using nongraphical techniques to evaluate e.g. a Löwdin partitioning of the Hamiltonian [1,2]

$$\begin{pmatrix} \mathbf{H}_{MM} & \mathbf{H}_{MQ_1} \\ \mathbf{H}_{Q_1M} & \mathbf{H}_{Q_1Q_1} \end{pmatrix} \begin{vmatrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{vmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{V}_{Q_1Q_1}(E_p^{SDTQ}) \end{pmatrix} \begin{vmatrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{vmatrix} = E_p^{SDTQ} \begin{vmatrix} \mathbf{C}_M^{(p)} \\ \mathbf{C}_{Q_1}^{(p)} \end{vmatrix}$$

efforts to go beyond first-order are less straightforward. Particularly problematic is the selection of determinants (or configuration state functions (CSF)), which hold the promise of a relatively straightforward way of approaching the fully variational solution (or full CI) [3,4]. Using extensions of concepts originally developed for representing macroconfigurations, and in particular short macroconfigurations, it will be shown that a connected graph (or tree) in which vertices are representations of electron distributions (or configurations) using a non-standard positional numeral system provides sufficient structure to make arbitrarily high accuracy calculations feasible. As an example, calculations within 1 μH of full CI for a system of 10 electrons distributed over 24 orbitals can be run on a PC using pilot code. Moreover, since the large scale structure is organized by electron configurations, spin algebra can be implemented efficiently using a unitary group theoretical treatment with the proviso that Yamanouchi-Kotani states are used in lieu of the more familiar Gelfand-Tsetlin basis.

References

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