Selected configuration interaction for transcorrelated methods

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Selected configuration interaction (SCI) methods allows to reach near full CI (FCI) energies of the standard electronic Hamiltonian $\hat{\mathbf{H}}$ by selecting the most relevant Slater−determinants in the FCI space scaling exponentially with the system size.

Being constrained by the strong computational scaling of SCI with the size of the one−electron functions set, one can improve the convergence of the wavefunction results with respect to the basis by introducing a correlation factor τ depending explicitly on the inter−electron distances. This can be accomplished effectively by incorporating the correlation factor into the Hamiltonian via a similarity transformation, and the usual Hamiltonian is then replaced by the TransCorrelated (TC) Hamiltonian defined as $\hat{\mathbf{H}}_{\mathbf{TC}} = e^{-\hat{\tau}}\hat{\mathbf{H}}e^{\hat{\tau}}$. The TC Hamiltonian $\hat{\mathbf{H}}_{\mathbf{TC}}$ differs from $\hat{\mathbf{H}}$ by being non−Hermitian, holding a three−electron interaction term and if the correlation factor is being properly chosen, it contains a non divergent effective two−electron interaction.

Because of these drastic changes with respect to the usual Hamiltonian, the important Slater determinants are not in general those selected in standard hermitian SCI. In this contribution, we extend the SCI algorithm for TC Hamiltonians and demonstrate its feasibility on atomic and molecular systems. After investigating the impact of different selection criteria on the convergence of the CI wavefunction, we propose a modified perturbative selection criterion which is adapted to handle the non−Hermiticity of $\hat{\mathbf{H}}_{\mathbf{TC}}$. The obtained CI wavefunctions corresponding to the adapted importance criterion appear to be more compact and converge faster to the FCI limit. Moreover, we design a proper second−order perturbative scheme in order to further improve the convergence of the energy, as usually done in standard hermitian SCI.

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