On the Concept of Reduced-Scaling Explicitly Time-Dependent Coupled Cluster

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To circumvent the well-known exponential scaling of coupled-cluster theory, many approaches that introduce greater sparsity in the wavefunction have been devised to effectively reduce the method's scaling, with varying degrees of success. For properties related to ground-state energies, *e.g.*, reaction enthalpies and other thermodynamic constants, for which the response or derivative of the wave function is not needed, such methods have proven to be invaluable for treating large systems with little loss of accuracy compared to canonical approaches. Even for properties such as excitation energies, much progress has been made, and a number of reduced-scaling schemes have been introduced. However, the application of localization methods to higher-order response properties is significantly more complex and thus has been much more limited. It has been shown that, in a response theory framework, an electric-field perturbation shifts the statistical distribution of the ground-state double-excitation (T_2) amplitudes upward by about one order of magnitude, *i.e.*, the perturbation significantly reduces the wave function's sparsity, thereby preventing robust application of the existing local correlation methods—as presently formulated—for large-scale response property calculations.

We present here an explicitly time-dependent coupled-cluster approach, in which time propagation is performed directly on the coupled cluster wavefunction while keeping the underlying orbitals constant. An arbitrarily small electromagnetic field is added to the Hamiltonian, and time evolution of the t and λ amplitudes are used to compute any desired property in a time-dependent fashion. Preliminary results are shown with strong indications that the ground state sparsity is preserved through the time evolution, offering the opportunity to develop a novel time-dependent reduced scaling approach for response properties. Additionally, the stability of the time propagation is discussed and results are shown for multiple time integrators.