Natural Correlation Orbitals in Local Laplace Transformed Triples (T) Correction

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The coupled cluster (CC) singles and doubles method (CCSD) with perturbative triples correction (CCSD(T)) [1] became the most successful tool for routine and accurate calculations of dynamical correlation effects in medium-sized molecules. It is size consistent, almost variational, and captures the most of the dynamical correlation energy.

The $O(N^7)$ scaling of CCSD(T) makes it difficult to apply it routinely to large molecules. Recent advances in parallel computation (e.g., [2]) has extended its applicability to systems with more than 100 correlated orbitals but the steep scaling precludes applications, for instance, to macromolecules of biological interest. For large systems, most computational effort is spent on the $O(N^7)$ scaling triple substitutions; CCSD scales formally as $O(N^6)$. Local correlation methods, leading to linear scaling, were very successful for CCSD [3]. The triples part is more challenging, as it based on Møller-Plesset perturbation theory, and the noniterative (T) formula uses canonical, i.e., delocalized Hartree-Fock orbitals. An impractical iterative procedure is required in localized orbital basis.

An elegant alternative to the latter, the Laplace transform method [4] enables separate unitary transformations within the occupied and virtual spaces while preserving the simplicity of the canonical formulation. Localizing the occupied MOs reduces the scaling of the triples calculation in two ways: (1) it allows the elimination of triplets *ijk* where the occupied orbitals are distant, and, more importantly, (2) it makes it possible to reduce the dimension of the local virtual space. Methods which truncate the virtual space at the canonical level [5] can diminish the computational effort of the triples significantly but do not affect the scaling.

Localization of virtual space is difficult. In our 2010 program [6] we used a set of optimized virtual orbitals for each occupied MO *i*, obtained as the pseudonatural orbitals (PNOs, [7,8]) of the *diagonal* pair *ii*. These are not as efficient, particularly for dispersion, as PNOs but require many fewer orbital transformations. These orbitals were also used by Schütz *et al.* [9] under the name of Orbital-Specific Virtuals. In a program under development we use Natural Correlation Orbitals (NCOs) which combine the advantages of OSVs and PNOs, by using a hierarchy of virtual spaces (two or three levels) for each occupied orbital.

We demonstrate the efficiency and scaling of our current code which uses only a single virtual space per occupied orbital. Although it requires (a) numerical quadrature at 4-5 points in the Laplace transformation and (b) overlap matrices and transformations between different virtual spaces, it is very efficient. It can recover a very high fraction of the triples correlation energy which is important to avoid artifacts on energy surfaces.

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