WFT-in-DFT Embedding with Coupled-Cluster Wavefunctions

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Coupled-cluster (CC) methods are perhaps the most reliable wavefunction theory (WFT)-based approach currently available for investigating the properties of molecules such as (but not restricted to) electronic spectra. However, unlike density functional theory (DFT)-based approaches such as TDDFT, their steep computational scaling poses rather severe constraints on their application to relatively large systems, such as those one would wish to investigate in most chemically interesting cases (e.g. species in solution, at interfaces or trapped in solid matrices).

Since spectral properties of interest often arise from rather localized phenomena (e.g. electronic transitions predominantly involving orbitals centered on one of a few chromophores), the use of embedding approaches [1] such as frozen density embedding (FDE) [2] is particularly appealing, as it provides an efficient way to incorporate the effect of the surroundings in the WFT calculation.

In this contribution we discuss the formulation and implementation of CC-in-DFT approaches within a framework based on response theory [3], which is general enough as to allow any desired combination of methods (e.g. CC-in-CC [4]) and offers a (formal) path to couple electronic excitations from different subsystems [5] akin to a purely DFT formulation [6]. Furthermore, we discuss computational approximations that allow for efficient CC-in-DFT calculations, and their connection to formulations which do not rely on CC response theory [7].

References

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