Exact Subsystem Time-Dependent Density-Functional Theory

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Frozen-Density Embedding (FDE-) TDDFT [1,2] and subsystem TDDFT [3] are powerful tools to investigate excited states of large systems of molecules in complex environments or chromophore aggregates. Combined with "exact" embedding strategies, accurate results for excitation energies of embedded molecules can be achieved [4,5,6]. Here, we present a new, open-source implementation [6,7] of FDE-TDDFT and subsystem TDDFT that includes (i) a generalization to unrestricted reference orbitals and open-shell cases, (ii) a combination with potential-reconstruction techniques of top-down and bottom-up type, and (iii) a combination with projection-based exact embedding schemes. In connection with the latter topic, we identify an implicit approximation made in Ref. [5] that led to small numerical deviations from reference results and demonstrate that with the correct setup of the response kernel, conventional TDDFT results can exactly be reproduced with subsystem TDDFT even in challenging situations involving covalent bonds between subsystems [8].

References

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