Reduced-Scaling Multireference Perturbation Theories using Orthonormal Localized Virtual Orbitals

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In this talk, we present our recent works on the development and application of the reduced-scaling implementations of the second-order multireference perturbation theories (MRPT2) on the basis of localized orbital basis.[1,2] The MRPT2 schemes such as CASPT2 or NEVPT2 methods are capable of providing accurate results for molecules with complicated electronic structures, recovering dynamic electron correlation effect on top of the CASSCF reference functions. A major drawback of such methods is that floating point operations (FPOs) for generating the electron repulsion integrals scales by $O(N^5)$. Moreover, storage of the perturbative amplitude scales by $O(N^4)$. Therefore, application of the MRPT2 methods to systems involving more than 50 atoms is often quite demanding.

To remove such bottlenecks, Neese[3] and Werner[4] independently developed the reduced-scaling version of the MRPT2 methods (DLPNO-NEVPT2 and PNO-CASPT2 schemes) using the concept of the so-called pair-natural orbitals (PNOs). In both approaches, the projected atomic orbitals (PAOs) are used as an intermediate basis in the virtual space. The PAOs are a set of linearly-dependent and over complete functions. Therefore, in such approaches, the orthonormalization should be performed for each surviving orbital pairs.

To remove such redundancy in the PNO-based schemes, we introduce the localized virtual orbitals (LVOs), which are orthonormal set of functions, instead of PAOs. Previous studies,[5,6] however, claim that (1) to achieve a certain accuracy, more LVOs are needed in an orbital domain than PAOs and (2) standard orbital localization algorithms such as Jacobi rotations often fails for virtual orbitals. To overcome such difficulties associated with use of LVOs, we introduce a new domain construction scheme for LVOs using the so-called differential overlap integrals (DOIs). For an efficient orbital localization, we use augmented Hessian-based localizer for LVOs.

Our LVO-based PNO-CASPT2 and NEVPT2 schemes are shown applicable to systems involving hundreds of atoms. With the DOI-based domain construction scheme, performance of LVOs is shown comparable to that of PAOs in the framework of local correlation schemes. In addition to the state-specific formalisms, we show a multistate extension of the LVO-based methods.

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