

The PNO-based Reduce-scaling MRPT2 Theories based on Orthonormal Local Virtuals

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The multireference second-order perturbation theory (CASPT2) is known to deliver a quantitative description of various complex electronic states. Despite its near-size-consistent nature, the applicability of the CASPT2 method to large, real-life systems is mostly hindered by large computational and storage costs for the 2-external tensors such as two-electron integrals, amplitudes, and residuum. To this end, Menezes and co-workers developed a reduced-scaling CASPT2 scheme by incorporating the local pair-natural orbital (PNO) representation of the many-body wave functions using non-orthonormal projected atomic orbitals (PAOs) into the CASPT theory [F. Menezes et al., J. Chem. Phys. 145, 124115 (2016)]. Alternatively, in this talk, we show a new PNO-based CASPT2 scheme using the orthonormal localized virtual molecular orbitals (LVMOs) and assess its performance and accuracy in comparison with the conventional PAO-based counterpart. Albeit the compactness, the LVMOs were considered to perform somewhat poorly compared to PAOs in the local correlation framework because they caused enormously large orbital domains. We show that the size of LVMO domains can be rendered comparable to or even smaller than that of PAOs by the use of the differential overlap integrals (DOIs) for domain construction. Optimality of the MOs from the CASSCF treatment is key to reducing the LVMO domain size for the multireference case. Owing to the augmented Hessian-based localization algorithm, an additional computational cost for obtaining the LVMOs is relatively minor. We demonstrate that the LVMO-based PNO- CASPT2 method is routinely applicable to large, real-life molecules.