Ab Initio Density Matrix Renormalization Group and Associated Dynamic Correlation Methods: Theory and Applications

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We will present our recent progress in the multireference electronic structure methods based on the density matrix renormalization group (DMRG) theory and its partner dynamical correlation models. Ab initio DMRG is used to describe a substantial amount of static correlation for multireference systems requiring large active space, e.g. CAS(28e,32o) or even larger. Developing our efficient implementation of the DMRG method, we recently demonstrated its significant applicability to challenging multireference chemistry, involving strongly-correlated electronic states of transition metal complexes and π-conjugated molecules. My presentation will show applications of DMRG for quantum chemical studies of graphene nanoribbons (future organic semiconductors) and Mn_4Ca cluster (oxygen evolution center in photosystem II).

Dynamic correlation needs be taken into account to deliver a quantitative accuracy in calculations, and is regarded as weak correlation that should be handled perturbatively in light of efficiency. We have developed a joint theory of the DMRG method and a canonical transformation (CT) idea to calculate the dynamic correlation on top of multireference description with large active space. Our CT theory constructs a renormalization structure of the high-level dynamic electron correlation in an effective Hamiltonian where the bare Hamiltonian is transformed by the unitary exponential correlation operator. We recently developed a further incorporation of the explicit correlation F12 factor into the transformation. As an alternative efficient routine to approach the dynamical correlation problems, we have developed a combination of DMRG with the CASPT2 (multireference second-order perturbation) method. We will discuss some theoretical aspects of the DMRG-CT and DMRG-CASPT2 theory and their applications to quasi-degenerate electronic states in chemistry.

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