Advanced multireference quantum chemistry with large active space

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We will present our recent progress in the development of efficient multireference approaches based on the density matrix renormalization group (DMRG) method and its partner dynamical correlation models. Following Chan's successful adaptation of the DMRG algorithm to *ab initio* quantum chemistry calculations, we use it to describe a substantial amount of static correlation accurately with large active space for multireference calculations, 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. For the latter, we will show some novel findings in spin structures of polycarbenes (orgnaic magntic molecules) and graphene-nanoribbons (future organic semiconductors). These electronic structures associated with complex multireference electron correlation are thought to be a key to understand interesting quantum phenomena arising in organic materials and biomolecules.

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. As an alternative efficient routine to approach the dynamical correlation problems, we have recently developed a novel extension of DMRG which has led to its combination with the CASPT2 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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