Multireference Theories for Ground and Excited States Based on the Similarity Renormalization Group

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Despite the enormous progress made in the description of molecules with closed-shell ground states, a general, robust, and systematically-improvable multireference method to treat near-degenerate electronic states is still lacking. The framework of coupled cluster theory is a natural candidate for creating hierachies of multireference approaches that can be made arbitrarily accurate. However, efforts to develop genuine multireference coupled cluster methods have often resulted in computational schemes that suffer from numerical instabilities or that can target only a limited number of active orbitals. To address these issues, we have recently developed a novel approach to multireference theories inspired by renormalization group methods. Our work is based on the similarity renormalization group (SRG)—a many-body formalism to diagonalize operators using a series of infinitesimal transformations. [1,2] Because of its renormalization group structure, the SRG naturally avoids divergences that arise from small energy denominators. Starting from the SRG, we have recently proposed a multireference *driven* SRG (MR-DSRG) scheme for Quantum Chemistry applications. [3,4] The MR-DSRG provides a convenient framework to derive numerically-robust multireference theories with electron correlation treated perturbatively or at a level comparable to that of coupled cluster methods. This talk will give an overview of recent developments, including novel schemes to treat near-degenerate ground and excited states and conical intersections.

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