

Development of Multistate Multireference Density Function Theory

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Accurately describing strongly correlated systems is an important target for the development of quantum chemical methods. Most excited states, systems with stretched bonds, and most catalytic intermediates are strongly correlated systems. The accurate description of strongly correlated systems requires a balanced treatment of both static and dynamic correlations. One of the accurate and efficient approach to describe strongly correlated systems is the multireference density function theory (MRDFT). Various MRDFT methods have been proposed since the 1990s. However, not all of these MRDFT methods are multistate (MS) methods, which properly consider the interaction between electronic states. When electronic states are nearly degenerate and have the same symmetry, they interact strongly with each other, and should be treated by MS methods that give the correct topography of adiabatic potential energy surfaces. In this representation, the MS treatment based on two MRDFT methods, multiconfiguration pair-density functional theory (MC-PDFT) and hybrid density functional valence bond method (λ -DFVB), is presented. The effective Hamiltonian in the intermediate state basis is constructed and then diagonalized in the MS treatment. Test examples show that the mentioned MS treatment gives similar description of state interaction compared with the high-level quantum chemical method, extended multistate complete active space perturbation theory (XMS-CASPT2).