Theoretical Investigation and Development of a New Method towards Quasi-Degenerate Electronic States in Molecular Systems

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論 文 名　：Theoretical Investigation and Development of a New Method towards Quasi-Degenerate Electronic States in Molecular Systems
（分子系の擬縮退電子状態に向けた理論的調査と新たな方法の開発）

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論 文 内 容 の 要 旨

In this dissertation, I investigated quasi-degenerate systems in solution using transition metal aqua complexes ($[Cu(H_2O)_{4\text{-}6}]^{2+}$ and $[Cr(H_2O)_6]^{3+}$) as examples and developed a new theoretical method for the quasi-degenerate systems, which I call the generalized occupation-restricted-multiple-active-spaces self-consistent field (GORMAS SCF).

In chapter 1, I review and discuss the challenges of the modern quantum chemical theory for complex electronic states as those of the transition metal complexes in solutions.

In chapter 2, I investigate three solvation structures of hydrated Cu^{2+} ion, $[Cu(H_2O)_6]^{2+}$, $[Cu(H_2O)_5]^{2+}$ and $[Cu(H_2O)_4]^{2+}$ by Kohn-Sham density functional theory (KS-DFT) combined with the three-dimensional reference interaction site model self-consistent field (3D-RISM-SCF) method. Here I show that they have a similar solvation structure from radial distribution functions (RDFs) and spatial distribution functions (SDFs), and conclude for the Cu^{2+} ion in aqueous solution, it has 5–6 coordination waters in the first hydration shell, and structures with different coordination numbers may interchange in solution. In separate study of each coordination systems, the six-coordination system $[Cu(H_2O)_6]^{2+}$ has the most stable ground state energy among five different geometries we calculated. For five-, and four-coordination system, the coordination number has averaged 5.2 water ligands in $[Cu(H_2O)_5]^{2+}$ and 5.3 in $[Cu(H_2O)_4]^{2+}$. Moreover, comparing our calculation results with the absorption spectra, the d-d excitation energies also have a good agreement with the experimental data.

In chapter 3, I examine the applicability of DFT and wave function theories (WFT) combined with 3D-RISM-SCF method to the d–d transitions of a transition metal aqua complex using $[Cr(H_2O)_6]^{3+}$ in aqueous solution as an example. I show that DFTs with hybrid functionals, multiconfigurational SCF followed by perturbation theory, and coupled-cluster singles and doubles (CCSD) followed by the equation of motion CCSD give reasonable d–d transition energies.

In chapter 4, I develop an efficient computational method for quasi-degenerate systems. Multiconfigurational self-consistent field (MCSCF) methods are effective for studying chemical systems with strong non-dynamical electron correlation. However, a highly accurate MCSCF method, such as complete active space (CAS) SCF, confronts inefficiency problems when the variational active space is growing larger. Several approaches have been published for the variational space, such as the quasi-CASSCF (QCASSCF) method, the occupation-restricted-multiple-active-space (ORMAS) SCF method, the restricted active space (RAS) SCF method, and the generalized active space (GAS) SCF method. Well-designed active spaces reduce the variational space in MCSCF calculations and save the computational cost without compromising chemical accuracy. I propose a novel construction scheme of variational active space, which I call generalized occupation-restricted-multiple-active-spaces (GORMAS). I apply GORMAS to several molecular systems, e. g. N_2, CH_2O, water dimer molecules, and oxoMn(salen) and show that this new approach performs well showing good agreements with previous studies.

In chapter 5, I summarize the results in the dissertation and draw general conclusions. I also give a future perspective on the theory for quasi-degenerate systems.