Abstract

Iron phthalocyanine (FePc) has strongly correlated electronic configurations, which is essential for its various applications. However, even the ground state of FePc has not been established for more than 50 years. The previous works predicted different groud states for isolated FePc, which hampers to know which electronic state realizes in more realistic situations. Recently, ligand-field model is used to predict the energy level of each electronic state. However, a work based on this model give an inconsistent conclusion against most of the *ab initio* works, which makes the problem more complex.

The electronic state of FePc is characterized by the *3d* electronic configuration of the central iron. The ground state is known as triplet state, in which these four configurations are considered as the promising candidates: A_{2g}, B_{2g}, E_g(a), and E_g(b). We applied diffusion Monte Carlo (DMC) method to get the relative energies of the configurations. DMC is known as one of the most accurate *ab initio* methods. In the case of the density functional theory (DFT) [conventional, generally used], its prediction sometimes changes due to the choice of exchange correlation functionals, which represent the electronic correlation approximately. On the other hand, DMC can evaluate it accurately based on projection operation towards the true ground state, without exchange correlation functionals. The projection method can optimize the amplitude of the wave function, but the nodes of the wave function remain to be fixed. The fixed nodes are generally given by *ab initio* methods other than DMC. Aspuru-Guzik used Hartree Fock method to generate the fixed nodes and succeeded to represent the electron excitation energy of metal-free phthalocyanine. In the case of FePc, the correlation among the electronic configurations of the iron's *3d*-shell are strong, so single determinant methods like Hartree Fock would not work well. We employed 'complete active space self-consistent field' (CASSCF) to make trial wave functions in this work. The wave function of CASSCF consists of Slater determinants for energetically degenerated electronic configurations. There are two types of CASSCF, Specific-State CASSCF and State-Averaged CASSCF. We used the latter one, since Boubca *et al.* established that Stated-Averaged CASSCF is suitable to evaluate an electron excitation energy, applying DMC to acrolein. Finally, our DMC specified that A_{2g} is the electronic ground state for isolate FePc, agreeing with most of the previous DFT works.

It is also interesting to study why DFT works gave different predictions. The predictions seem depending on exchange correlation functionals. The Liao *et al.*'s work is a useful reference to think about this matter. They applied DFT calculations using different functionals to iron porphyrin, and they showed that ratio of exchange effect significantly affects prediction of the energy levels. To know more detaily how exchange effect works for the prediction, we applied DFT calculations with Minessota functional family, which provides functionals with different exchange ratio. Comparing the DFT predictions with our DMC results, it is found that a sufficient amount of short-ranged exchange should be contained to reproduce A_{2g} ground state.

In the above part, we have explained that DMC supports the A_{2g} ground state, and DFT can reproduce it, when sufficient amount short-ranged exchange effect is included in the functional. However, this conclusion is appearently denied by the Kuz'min *et al.*'s work that applied ligand-field theory to get the energy levels: Their model includes 2 arbitrary parameters, and they have shown that the A_{2g} ground state does not appear for any choice of the parameters. On the other hand, the other works using ligand-field theory accepts a possibility of A_{2g} ground state. We found that the Kuz'min *et al.* used superposition model in their modeling, causing a denial of the A_{2g} ground state possibility. Roughly speaking, superposition model considers just the

nearest-neighbor ions of the central iron affects its electronic configuration, reducing the number of arbitrary parameters 3 (original ligand-field theory) to 2 (superposition model). Comparing the calculated orbital shapes with the ones expected by superposition model, we concluded the superposition model cannot wel describe the actual situation, and leading the A_{2g} electronic state unreasonably unstabilized.

Keywords: Diffusion Monte Carlo, Iron Phthalocyanine, Density Functional Theory,
Electron Ground State Identification, CASSCF