【Grant-in-Aid for Specially Promoted Research】
Science and Engineering (Chemistry)

Title of Project : Theoretical Study of Complex Electronic Systems Including d Electron: Fundamental Understanding and Prediction by New Electronic Structure Calculation Method for Large Systems

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Research Area : Fundamental Chemistry (Physical Chemistry)

Keyword : Electronic Structure, Theoretical Chemistry, Chemical Reaction, Coordination Chemistry, Metal Complex/Organometallic Catalysts

【Purpose and Background of the Research】

Molecules which have transition metal, non-transition metal, non-metallic heavy elements, and organic groups exhibit varieties of geometry, chemical bond, physicochemical property, and reactivity. As a result, such molecules play important roles in basic and applied chemistry fields. Also, their complex electronic structures are challenging research target in theoretical/computational chemistry and molecular science. However, these molecules are not always investigated well with DFT method which is often applied to large system, because of the presence of large electron-correlation effects.

In this theoretical/computational study, we wish to propose a new hybrid-electronic structure method by combination of our own frontier-orbital-consistent effective potential (FOC-EP) and high-quality computational methods based on wavefunction. Our main purposes here are to present fundamental understanding of geometries, bonding nature, physicochemical properties, and reactivity of complex systems including transition metal, non-transition metal, and/or non-metallic heavy elements and organic group. Our main targets are multi-nuclear transition metal systems containing multiple-bond, complex systems consisting of transition metal, non-transition metal, heavy non-metallic elements and organic groups, nano-scale carbon materials containing transition metal and/or non-transition metal elements, and catalytic reactions by transition metal systems. Some of our targets are shown in Figure 1.

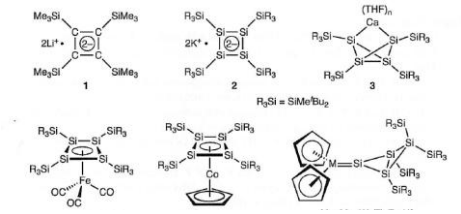

Figure 1 Examples investigated in this work

【Research Methods】

A new hybrid method based on wavefunction is employed here, as well as DFT. The hybrid method is constructed by the combination of FOC-EP and FMO, ONIOM, CASPT2, or SAC/SAC-CI method to perform high-quality calculation with electronic effects of substituent. Also, we will propose an analysis method of complex systems by the linear combination of fragment molecular orbital. Above-mentioned large systems will be investigated with the hybrid electronic structure theory, in which the FOC-EP will be applied to incorporate electronic effects of substituents omitted in model. For instance, multi-nuclear transition metal complexes including multiple metal-metal bond will be investigated by the CASPT2 method combined with the FOC-EP and analyzed.

【Expected Research Achievements and Scientific Significance】

The hybrid electronic structure calculation method presented here can be applied to general large complex systems bearing complicated electronic structure. The theoretical knowledge of metal-metal and metal-non-metal bonds, electronic structures, physicochemical properties, and reactivity of complex systems provides us with non-classical new understanding. We believe that all these findings contribute to new development of molecular science and its application to engineering.

【Publications Relevant to the Project】

・S. Sakaki, Y.-y. Ohnishi, H. Sato, *Chem. Record.*, 10, 29-45 (2010).
・N. Ochi, Y. Matano, Y. Nakao, H. Sato, S. Sakaki, *J. Am. Chem. Soc.*, 131, 10955-10963 (2009).

【Term of Project】 FY2010-2014
【Budget Allocation】 353,500 Thousand Yen

【Homepage Address and Other Contact Information】

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