[Grant-in-Aid for Specially Promoted Research]
Science and Engineering (Chemistry)


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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.

[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]

[Term of Project] FY2010-2014
[Budget Allocation] 353,500 Thousand Yen
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Figure 1 Examples investigated in this work