Title of Project : Development of Density Functional Theory

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Research Area : Theoretical Chemistry

Keyword : electronic structure theory, density functional theory (DFT), LC functional

【Purpose and Background of the Research】

Density functional theory (DFT) has emerged as a powerful computational tool for the chemical systems. However, there is no means of systematically improving DFT energies. Our long-range corrected density functional theory (LC-DFT) solves many problems of the conventional DFT. The purpose of this project is to establish LC-DFT as the standard of the electronic structure theory.

There are two approaches in the electronic structure theory, the wave function method and the density functional theory. For wave function method, a huge and very successful effort has been done in the last 30 years leading to accepted state-of-the-art methodology. Accurate results can be obtained for small systems but it is rather difficult to handle very large systems due to the steep N-dependence. DFT is not reached such a mature stage as wave function method but DFT is simple, conceptual, and applicable to large systems. However, the accuracy depends on the xc functional employed. DFT fails to describe induced/response properties. The failures arise mainly from the wrong long-range behavior due to the local character of the approximate xc functionals. We have developed new functionals based on the long-range correction scheme. The exchange functional is partitioned with respect to the interelectronic separation into long-range and short-range parts using a standard error function

$$\frac{1}{r_{12}} = \frac{1 - erf(\mu r_{12})}{r_{12}} + \frac{erf(\mu r_{12})}{r_{12}}$$

LC solves many of the conventional DFT problems. Very recently we have demonstrated that LC satisfies DFT-Koopmans' theorem. This implies that the orbitals and the orbital energies of the LC-Kohn-Sham theory do have a strict physical meaning.

In this project, we will further develop LC-DFT theoretically. We will extend LC-DFT to more practical one by collaborating with experimental and other field theoretical investigators. Using this new theory, we will clarify the mechanisms of significant photo- and electro-chemical reactions and suggest new functional materials. LC-DFT will be established as the standard of the electronic structure theory.

【Research Methods】

In this project, we feature new developments of photo- and electro-chemical reaction theories and its high-speed computational algorithms for using on next-generation supercomputer "K", and the eludations of significant reaction mechanisms and the designs of new functional materials in photo- and electrochemistry:

1. New developments of photo- and electro-chemical reaction theories:
・A nonadiabatic interaction calculation theory on time-dependent DFT (TDDFT)
・A multiconfigurational DFT
・An open-shell TDDFT with spin-orbit effects
・A new reaction analysis method on orbital

2. Developments of high-speed computational algorithm of DFT used on K supercomputer:
・An order-N algorithm of LC-DFT
・An order-N algorithm of LC-TDDFT

3. Reaction mechanism analyses and new functional material designs on:
・Electron transfers in fuel cell
・Photosynthetic reactions of purple bacteria

【Expected Research Achievements and Scientific Significance】

Our LC will evolve DFT into the higher stage. As the accomplishments of this project, we will obtain new photo- and electro-chemical reaction theories and an analysis method on orbital, and a new software with high-speed computational algorithms of DFT adapted to the K supercomputer architecture. This software enables us to analyze photochemistries of several thousands atoms and charge transfers in the interfaces, which cannot be treated even by the state-of-the-art method.

【Publications Relevant to the Project】

・Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai and K. Hirao, "A long-range- corrected time-dependent density functional theory", *J. Chem. Phys.* 120, 8425 – 8433 (2004).
・T. Tsuneda, J. Song, S. Suzuki, and K. Hirao, "On Koopmans' theorem in density functional theory", *J. Chem. Phys.*, 133, 174101(1-9) (2010)

【Term of Project】 FY2011-2015

【Budget Allocation】 165,500 Thousand Yen

【Homepage Address and Other Contact Information】

http://www.aics.riken.jp/