Séminaire :

« Toward a molecular theory for large systems. »

Prof. K. HIRAO

Department of Applied Chemistry, School of Engineering,
The University of Tokyo, Japan

Vendredi 4 mai 2007, 11h00

Salle RAPHAEL 2 & 3 – site d’Ivry-sur-Seine

With the emergence of peta-scale computing platforms we are entering a new period of modeling. The computer simulations can be carried out for larger, more complex, and more realistic systems than ever before. DFT may be the only tool that enables us to carry out accurate simulations for larger systems with reasonable computational cost. If practical DFT is developed, which can handle biomolecules and nanomaterials, we can enlarge greatly the scope of computational chemistry.

The evaluation of Coulomb integrals is very often the most time consuming step for DFT with GGA functionals. A new linear scaling method has been developed for the fast evaluation of Coulomb integrals [1]. The Coulomb potential is expanded in the mixed Gaussian and finite-element auxiliary functions that express the core and smooth Coulomb potentials, respectively. Then Coulomb integrals can be evaluated by solving the Poisson equation. The method realizes a linear scaling with system size for both one-dimensional alanine α-helix and three-dimensional diamond pieces. It makes molecular quantum calculations affordable for very large systems involving several thousands of basis functions.

Although hybrid GGA improves the accuracy, it makes the calculation more expensive since the fast algorithms for Coulomb integrals cannot be employed for HF exchange. The hybrid DFT application to large systems is limited. Recently we have developed the dual-level approach to DFT [2]. The scheme is based on the low sensitivity of the electron density to the choice of the functional and the basis set. The dual-level DFT works quite well and the large reduction of the computer resources can be achieved. Hybrid functional can now be applied to very large systems.

The first-order molecular properties are well predicted by GGA functionals. However, induced or response properties require correction for the asymptotic behavior. The failure arises from the wrong long range behavior due to the local character of the approximate exchange-correlation functionals. By splitting the Coulomb interaction into short-range and long-range components following Savin’s idea [3], we have proposed a new hybrid GGA functional with correct long-range electron-electron interactions [4]. Hybrid GGA has good energetics, good Rydberg behavior, good CT predictions, and good optical response. Van der Waals interactions are also described accurately [5]. The scheme was applied to planar aromatic systems (dimers and trimers of coronene, circum coronene, and circum circum coronene) to estimate π-stacking energies.
[Les références bibliographiques sont précisées sur le site Web du laboratoire.]