Theoretical Study and Design of Functional Molecules: New Bonding, Structures, and Reactions

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In theoretical and computational chemistry, it is an important goal to develop functional molecules prior to or in cooperation with experiment. Thus, new bonds and structures provided by heavier atoms are investigated together with the reactivities. In addition, chemical modification and properties of nanocarbons are investigated to develop functional nanomolecular systems. Efficient computational methods are also developed to perform reliable quantum chemistry calculations for small and large molecular systems.

1. Two-Level Hierarchical Parallelization of Second-Order Møller-Plesset Perturbation Theory in Divide-and-Conquer Method

Electron correlation plays an important role in the accurate description of the energies, structures, and properties of molecules. Density functional theory (DFT) is widely used to calculate large molecules because of its low computational cost. However, frequently used DFT methods have several shortcomings. For example, they fail to describe non-covalent interaction energies and reaction barriers. Second-order Møller–Plesset perturbation (MP2) theory is the simplest method to account for electron correlation at an *ab initio* level. However, the computational cost is considerably high and the applications are limited to molecules of moderate size. We have developed an efficient parallel algorithm to reduce the computational cost as well as the requited sizes of memory and disk by employing the resolution-of-identity (RI) approximation.[1,2] Despite the high performance, the computational cost is still too high for MP2 calculations to be applicable to very large molecules.

To make MP2 applicable to nanosystems and biological systems, we have developed a two-level hierarchical parallelization scheme in the divide-and-conquer (DC) method.[3] In the DC-MP2 method, the total system is divided into small non-overlapping subsystems and its energy is obtained as a sum of the energies of subsystems. The two-level hierarchical parallelization scheme is a combination of coarse-grain parallelization assigning each subsystem to a group of processors, with fine-grain parallelization, where the computational tasks for evaluating MP2 correlation energy of the assigned subsystem are distributed among processors in the group.

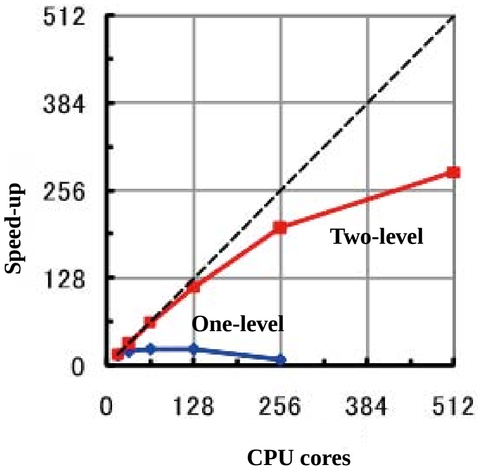

Figure 1. One-level and two-level parallelization of DC-MP2/6-31G* calculations of (β-alanine)$_{20}$.

Several test calculations on PC clusters show the high efficiency of the two-level hierarchical parallelization. Large scale parallel calculations of (β-alanine)$_{20}$ with the 6-31G* basis set are also performed using the T2K-Tsukuba massively parallel supercomputer. The results obtained using up to 512 CPU cores are summarized in Figure 1, which demonstrate that two-level parallelization becomes more effective for the larger number of CPU cores than single-level parallel calculations. It is noticeable that the two-level parallel calculation is 22 times faster even for 256 CPU cores than the single-level calculation. The parallel efficiency makes DC-MP2 calculations feasible for very large molecules in massively parallel computers.

2. A New Sampling Method for Projector Monte Carlo Calculations Based on Slater Determinants

In the next-generation computational chemistry, exact solutions of the Schrödinger equation are highly desired. For this purpose, we have developed a projector Monte Carlo method based on Slater determinants (PMC-SD) for the ground and excited sates.[4,5] Unlike the conventional method, no additional information such as nodes of trial wave functions is required. The accuracy of the PMC-SD method is improved systematically by increasing the number of walkers and the full-CI energies are obtainable as a limit for a given basis set. To make PMC-SD effective, we have proposed a new sampling method by using the symmetry of α and β electron configurations.[6] The advantages of the new sampling methods have been confirmed by several test calculations.

3. Examples of Computational Approaches to Interesting Molecular Systems

Endohedral metallofullerenes have attracted interest as building blocks of future nanoscale electronic devices because they have low oxidation and reduction potentials. Although endohedral metallofullerenes do not crystallize in general, chemical derivatization allows for the efficient crystallization. Thus, a single crystal is formed, in which the adamantylidene (Ad) derivative of La@C_{82} is aligned in an orderly fashion, as shown in Figure 2.[7]

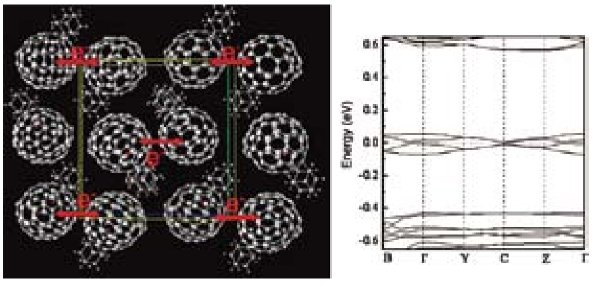

Figure 2. Single crystal of the La@C_{82} derivative and its band structure.

Density functional calculations confirm that the single crystal of La@C_{82}Ad is semi-metallic with a small band gap of 0.005 eV: the effective mass of electron of the conduction-band bottom and hole of the valence-band top is 0.97 and 0.97m_0 (m_0 is the mass of free electron), suggestive of nearly free-electron behavior. Accordingly, a high electron mobility of $\mu \geq 10$ cm^2 V^{-1} s^{-1} is observed by flash-photolysis time-resolved microwave conductivity measurements. The observed mobility is the highest of reported organic conductors. It is expected that the derivatization of endohedrtal metallofullerenes will open up a new field related to tunable organic conductors for molecular electronics.

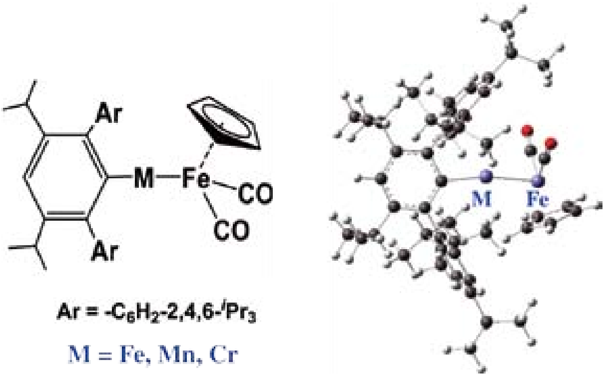

Figure 3. Two-coordinate transition metal complexes.

In collaboration with experiment, we have also performed calculations for (a) two-coordinate transition metal complexes with unusually short metal-metal bonds (Figure 3),[8] (b) planar four-membered aromatic systems protected by pentaary[60] fullerene,[9] (c) ferromagnetic spin coupling between La@C_{82} and cyclodimeric copper porphyrin upon inclusion,[10] and (d) covalently linked porphyrin-La@C_{82} hybrids.[11]

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