

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. Application of Second-Order Møller-Plesset Perturbation Theory with Resolution-of-Identity Approximation to Periodic Systems

Electron correlation plays an important role in the accurate description of the conductive, optical, and magnetic properties of periodic systems. Second-order Møller-Plesset perturbation theory (MP2) is the simplest method to account for electron correlation at an *ab initio* level. Periodic boundary condition (PBC) calculations by the MP2 method (PBC MP2) have been developed. However, the computational cost is considerably high and practical applications are limited to small periodic systems. A promising approach to reduce the computational cost is resorting to the resolution-of-identity (RI) approximation of four-center two-electron atomic integrals (ERIs). However, no attempt has been made to incorporate the RI approximation with the PBC MP2 method because the lattice sums of long-range AO ERIs show extremely slow r^{-1} decay.

Therefore, we have developed an efficient PBC RI-MP2 method in the crystal orbital framework, which is applicable to large periodic systems.¹⁾ In this method, the slow convergence of lattice sum of long-range AO ERIs is avoided using Poisson and Gaussian mixed auxiliary basis functions. To assess the accuracy and computational efficiency of the developed PBC RI-MP2 code, test calculations were performed for trans-polyacetylene using the 6-31G** basis sets. PBC RI-MP2 is

98 times faster than PBC MP2, and the energy difference between PBC RI-MP2 and PBC MP2 is only 0.4 mH. In addition, the required memory and disk sizes for PBC RI-MP2 are much smaller than those for PBC MP2. To calculate much larger periodic systems, we plan to develop an efficient parallel code of PBC RI-MP2.

2. Molecular Tailoring Approach to Very Large Molecules

Several divide-and-conquer approaches have been developed to overcome the high scaling problem of *ab initio* calculations. The molecular tailoring approach (MTA) was interfaced with the efficient MP2 and RI-MP2 codes developed in our group.^{2,3)} The performance was extensively benchmarked for a variety of large molecular systems and critically compared with the popular fragment molecular orbital (FMO) method. It was found that FMO2-MP2 is superior to FMO3-MP2 and MTA-MP2 in terms of computational costs. However, the errors of FMO2-MP2 are considerably large and beyond chemical accuracy. FMO3-MP2 is accurate for biological systems, while it is unsuccessful for water clusters. The errors of MTA-MP2 are within 1 kcal/mol for all systems with reasonable time advantage. The accuracy of FMO decreases for the basis sets that include diffuse functions. In contrast, MTA performs well regardless of basis sets.

3. Application of Projector Monte Carlo Method Based on Slater Determinants to Excited States

A projector Monte Carlo method based on Slater determinants (PMC-SD) is expanded to excited state calculations.⁴⁾ Target excited states are calculated state-by-state by eliminating the components of the lower states from the imaginary time propagator. As the test calculations of excited states of

H₂O show, 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. The avoided crossing of covalent and ionic states in the dissociation of LiF is well reproduced using the PMC-SD method.

4. New Bonds Provided by Heavier Main Group Elements and Functionalization of Endohedral Metallofullerenes and Nanographenes

Silicon behaves like carbon in forming covalent bonds to four neighboring atoms. These bonds form the framework of many organosilicon compounds and crystalline silicon. Silicon can also form a pentacoordinated anionic structure, a so-called silicate. No compounds containing a direct bond between two silicate moieties (disilicates), where two silicate structures are combined in one species, have been reported because of the electronic repulsion between the anionic halves and difficulty preventing the release of anions. However, we have developed a stable compound containing the linkage of two pentavalent silicon atoms, as shown in Figure 1.⁵⁾ The unique electronic properties are promising for the construction of functional materials with silicon wire made up of silicate chains.

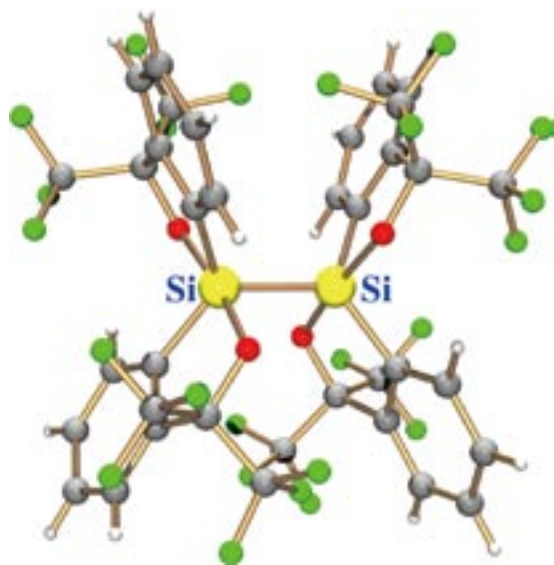


Figure 1. The stable bond between pentavalent silicon atoms.

The concept of aromaticity has long played an important role in carbon chemistry since the discovery of benzene in 1825. To determine that the heavier group 14 elements can sustain aromaticity, silicon, germanium, and tin analogs of carbocyclic aromatic compounds have been synthesized, most of these showing considerable aromaticity. However, there has

been no clear evidence of whether the concept of aromaticity can be expanded to the ring incorporating the heaviest lead atom. Very recently, dilithioplumbole has been successfully synthesized and isolated in collaboration with our research group.⁶⁾ Relativistic theoretical calculations show that its cyclic compound has considerable aromatic character as a result of the important overlap between 2p (C) and 6p (Pb) orbitals. The present results highlight the future possibility of introducing heavier elements including Pb into a broader range of carbon frameworks.

Chemical functionalization of endohedral metallofullerenes regulates the positions and movements of the encapsulated metal atoms.⁷⁾ This control of metal positions and movements within fullerene cages can be valuable for designing functional molecular devices with new electronic or magnetic properties. Also investigated are graphene oxides and monovalency defects in graphene.^{8,9)}

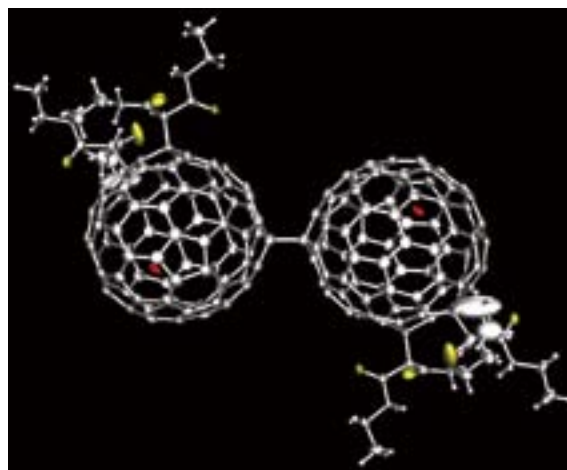


Figure 2. Functionalization of endohedral metallofullerenes.

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