

# 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 doping of cage-like molecules and clusters including fullerenes and carbon nanotubes are investigated to develop functional nano-molecular systems. Efficient computational methods are also developed to perform reliable quantum chemistry calculations even for large molecular systems.

## 1. New Parallel Algorithm of Energy Gradient Calculations for Second-Order Møller-Plesset Perturbation (MP2) Theory<sup>1)</sup>

It is an important subject to determine molecular geometries and reaction paths. For this purpose, density functional theory (DFT) is widely used because of its low computational cost. However, the generally used DFT methods fail to describe non-covalent interactions that play an important role in supramolecules, host-guest interactions, self-assembly, molecular recognition, and the folding of proteins, and they tend to underestimate reaction barriers.

Second-order Møller-Plesset perturbation theory (MP2) is the simplest method that includes electron correlation important for non-covalent interactions and reaction barriers. MP2 is also helpful for checking DFT results. Despite these advantages, MP2 calculations are much more time-consuming than DFT calculations and require very large memory and hard disk. These make MP2 geometry optimization difficult for large molecules. Therefore, a new parallel algorithm of MP2 energy gradient calculations is developed using the MP2 energy algorithm that we have developed recently, which is

essential for the determination of molecular geometries and reaction paths. The algorithm decreases highly the FLOP (floating point operation) count as well as memory and disk sizes. Test parallel calculations are performed for taxol (C<sub>47</sub>N<sub>14</sub>H<sub>51</sub>) and luciferin (C<sub>11</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>H<sub>8</sub>) with the 6-31G, 6-31G(d) and aug-cc-pVDZ basis sets. The results demonstrate the high parallel efficiency of the algorithm. In addition, the computational speed per CPU is considerably higher than that of other representative programs. Obviously, these make MP2 calculations feasible for considerably large molecules, and enriches the important applications, especially for molecular systems where DFT is inferior to MP2 in accuracy and reliability.

## 2. Accuracy of the Fragment Molecular orbital (FMO) Method Based MP2 Theory<sup>2)</sup>

The fragment molecular orbital (FMO) method permits high-speed *ab initio* calculations of large molecular systems by dividing them into small fragments. Since the MP2 code applicable to large molecules is developed, it is interesting to calibrate the accuracy of the MP2-based FMO method. Therefore, three-body interactions as well as two-body interactions are considered in the FMO method. These are named FMO2 (two-body) and FOM3 (three-body). Test calculations are carried out with the 6-31G(d) and 6-311G(d) basis sets for (H<sub>2</sub>O)<sub>n</sub> (*n* = 16, 32, 64), (alanine)<sub>n</sub> (*n* = 10, 20, 40), and a small synthetic protein. FMO3-MP2 energies are closer to full MP2 energies than FMO2-MP2 energies. For example, the energy errors for the protein shown in Figure 1 are 4.61 (FMO2-MP2) and 0.81 (FMO3-MP2) mH for the 6-311G (d) basis set.

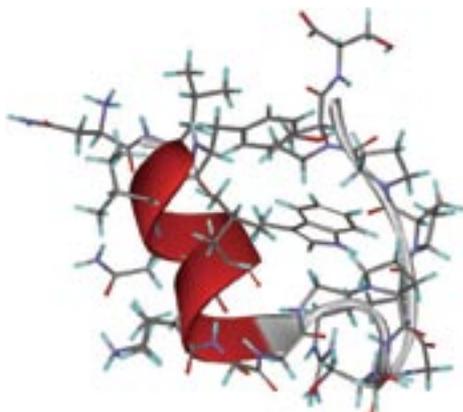


Figure 1. The synthetic protein IL2Y containing 304 atoms.

### 3. Multiple Bonds between Heavier Group 14 Elements: Structure and Reactivity<sup>3,4)</sup>

Multiple bonds between heavier elements are of wide interest in main-group chemistry. Among these, heavier group 14 element analogues of alkynes, RMMR (M = Si, Ge, Sn, Pb), have attracted special interest as challenging synthetic targets. We have theoretically predicted that bulky substituent groups play an important role in making RMMR synthetically accessible and isolable as stable compounds. Accordingly, the Si, Ge, Sn, and Pb analogues of alkynes have been synthesized and isolated by introducing very bulky aryl and silyl groups. As shown by X-ray crystal structural analysis, the Si, Ge, and Sn analogues of alkynes have a multiply bonded structure, while the heaviest Pb analogue, Ar<sup>\*</sup>PbPbAr<sup>\*</sup> (Ar<sup>\*</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-*i*Pr<sub>3</sub>)<sub>2</sub>), takes a singly bonded structure. Form theoretical calculations, however, we have revealed that even the heaviest analogue has a multiply bonded structure in solution, unlike the singly bonded structure found by X-ray crystal analysis. The different structures in solution and the crystal state are ascribed to packing forces. In addition, it is general that crystallization is significantly affected by the bulk of substituent groups. These have been also demonstrated for the recently synthesized tin analogues, Ar<sup>\*</sup>SnSnAr<sup>\*</sup> and Ar<sup>\*\*</sup>SnSnAr<sup>\*\*</sup> (Ar<sup>\*\*</sup> = C<sub>6</sub>H<sub>2</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>-4-SiMe<sub>3</sub>).

To provide insight to the unique reactivity of the silicon–silicon triple bond, the reactions of R<sup>Si</sup>SiSiR<sup>Si</sup> (R<sup>Si</sup> = Si<sup>*i*</sup>Pr [CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>) with 2-butenes (cis and trans) and alkynes are investigated. The cycloaddition of R<sup>Si</sup>SiSiR<sup>Si</sup> to 2-butenes proceeds in a stereospecific way, while its cycloaddition to phenylalkyne leads to an isolable aromatic 1,2-disilabenzene derivative. The reaction mechanisms are disclosed by theoretical calculations.

### 4. Structures and Functionalization of Endohedral Metallofullerenes<sup>5,6)</sup>

From MEM/Rietveld analysis of synchrotron X-ray powder diffraction data of Sc<sub>2</sub>C<sub>84</sub>, it was once believed that two Sc atoms are encaged inside the C<sub>84</sub> fullerene. From theoretical calculations and experiment, however, we have disclosed that two C atoms as well two Sc atoms are encapsulated inside the C<sub>82</sub> fullerene, forming Sc<sub>2</sub>C<sub>2</sub>@C<sub>82</sub>.

We have predicted theoretically that the three-dimensional random motion of two La<sup>3+</sup> cations in La<sub>2</sub>@C<sub>80</sub> can be restricted to the circular motion in a plane by attaching an electron-donating molecule such as disilirane on the outer surface of the C<sub>80</sub> cage. This has been beautifully verified, as shown in Figure 2. Such circular motion in a plane is expected to induce unique electronic and magnetic fields in the direction perpendicular to the plane.

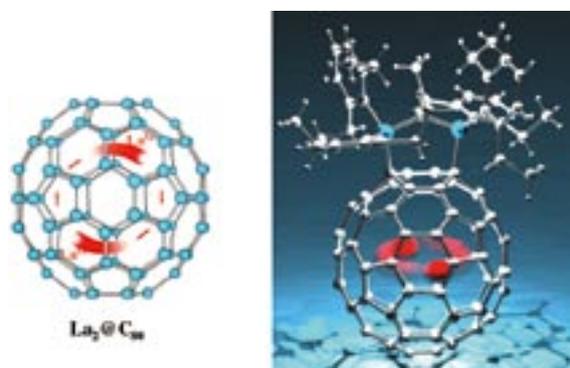


Figure 2. Random and two-dimensional circular motions of two La<sup>3+</sup> cations in La<sub>2</sub>@C<sub>80</sub> and its derivative.

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