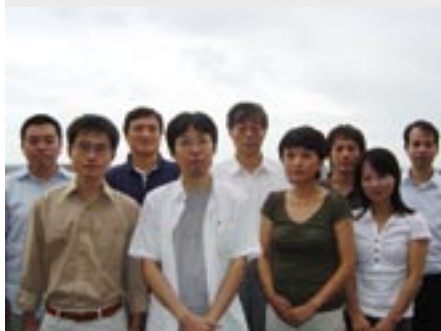# Theoretical Study and Design of Functional Molecules: New Bonding, Structures, and Reactions

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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 large molecules 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. Projector Monte Carlo Method Based on Configuration State Functions. Test Applications to the H_4 System and Dissociation of LiH[1)]

The diffusion Monte Carlo (DMC) method, also called the projector Monte Carlo (PMC) method, has attracted a lot of attention because of its high accuracy and high parallel efficiency. The parallel DMC programs have been developed and applied to various systems. However, the DMC method has an important fermion sign problem because electrons are treated as particles, and the accuracy depends strongly on the nodes of trial wave functions because the fixed-node approximation is generally used to avoid the fermion sign problem. In addition, the accuracy is not always improved systematically even if the nodes of trial functions are generated at high levels of theory. It has been shown that the trial nodes are improved using variational Monte Carlo techniques. However, it is also important to develop a quantum Monte Carlo method that does not require the nodes of trial wave functions.

Thus, we have developed a new PMC method by using configuration state functions (CSFs), spin-adapted linear combinations of Slater determinants, as walkers, to avoid the fermion sign problem (the name "PMC" is used instead of "DMC" because the diffusion equation is not used apparently in the PMC-CSF method). In the PMC-CSF method, new theory and effective calculation algorithm are developed and tested by making a simple program that can treat up to 4 electrons. The accuracy of the PMC-CSF method depends on the basis sets constructing CSFs, but is systematically improved, regardless of trial functions, by increasing the number of walkers. As verified by test applications to the H_4 and LiH systems, full-CI (configuration interaction) energies are obtainable as a limit for a given basis set (Figure 1).
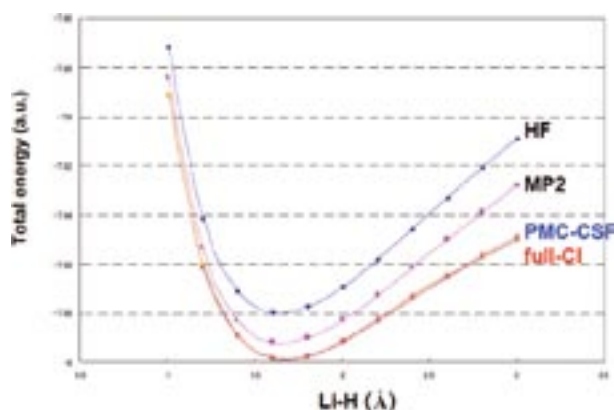

Figure 1. The dissociation of the LiH moilecule.

Obviously, the PMC-CSF method becomes highly accurate by enhancing the quality of basis sets. Unlike conventional CI calculations, no diagonalization of matrices is necessary and important CSFs are effectively selected for the PMC-CSF method. In addition, the PMC-CSF method shows good parallel efficiency, as shown in Table 1.

Table 1. Elapse time (in second) and speedup of the PMC-CSF parallel calculations of the H_4 system.

CPU	1	2	4	8
Time	3999	2010	1008	511
Speedup	1.00	1.99	3.97	7.82

We are now developing a general program suitable high parallel calculations and applicable to large molecules.

## 2. Chemical Modification of Endohedral Metallofullerenes[2–5]

The reactivities and chemical modification of endohedral metallofullerenes are of considerable interest in developing functional nanomolecules. Addition of adamantylidene to $La_2@C_{78}$ takes place at the [5,6] and [6,6] positions around the pole and equator of $La_2@C_{78}$. The Addition to $M_2@C_{80}$ (M = La and Ce) makes the two metal atoms collinear with the spiro carbon of the 6,6-oen adduct. Bissilylation of $Ce_2@C_{78}$ affords regioselectively the 1,4-adduct in which the two Ce atoms stand still by facing toward the hexagonal rings at the equator. Addition of adamantylidene to $La_2@C_{72}$ (that does not satisfy the isolated pentagon rule) mainly takes place at the fused pentagons because of the high surface curvature.

3. Nanographenes and BN Analougues: Ground Electronic States and Energy Gap Engineeering[6]

Graphene has attracted great interest as the new generation of carbon electronics. The lack of an energy gap prevents using graphene in carbon nanoelectronics. It is very important to engineer the band gap by patterning and cutting the graphene sheet into rectangular shapes. Thus, carbon nanographenes (CNGs) were theoretically investigated together with boron nitride nanographenes (BNNGs). As the size of CNGs increases, the HOMO–LUMO energy gaps decrease with a direct inverse dependence on the length of zigzag edges, CNGs with long zigzag edges having open-shell singlet ground states. In contrast, the energy gaps of BNNGs have a weak size-dependence; all BNNGs have closed-shell singlet ground states and those with long zigzag edges have slightly larger energy gaps. CNGs with long zigzag edges are less favorable energetically than their structural isomers with long armchair edges, while BNNGs have the opposite preference. Chemical modifications that change the long zigzag edge into armchair type can efficiently stabilize the kinetically unstable CNGs (with open-shell singlet ground states) and modify their energy gaps.
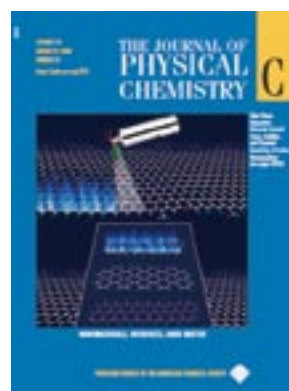
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