

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. Efficient Parallel Algorithm of Second-Order Møller-Plesset Perturbation Theory with Resolution-of-Identity Approximation (RI-MP2)¹⁾

Density functional theory (DFT) is widely used to calculate large molecules as well as small molecules because of its accuracy and low computational cost. However, the generally used DFT methods fail to describe noncovalent interactions that play an essential role in host-guest molecules, self-assembly, molecular recognition, and three-dimensional structures of proteins, and usually underestimate reaction barriers. Therefore, many attempts have been made to develop new functionals. However, no widely applicable method has emerged yet.

Second-order Møller-Plesset perturbation theory (MP2) is the simplest and effective method that accounts for electron correlation effects important for noncovalent interactions and reaction barriers. MP2 is also helpful for checking DFT results. Despite these advantages, the formal scaling of MP2 calculations is $O(n^5)$ (n is the number of basis functions), much higher than that of DFT calculations. We have recently developed a new parallel algorithm of MP2 calculations. Despite this new algorithm, MP2 calculations of huge mol-

ecules are considerably time-consuming and require very large sizes of fast memory and hard disk. Therefore, we have developed an efficient parallel algorithm of RI-MP2 calculations to reduce highly the computational cost as well as the sizes of memory and disk by employing the resolution-of-identity (RI) approximation for two-electron repulsion integrals. The parallel algorithm aims at reducing I/O overheads and achieving good load balancing.

Test parallel calculations were carried out using 6-31G* and 6-311G basis sets for taxol ($C_{47}H_{51}NO_{14}$), valinomycin ($C_{54}H_{90}N_6O_{18}$), two-layer nanographene sheets ($C_{192}H_{28}$), and the noncovalent complex of C_{60} and $C_{60}H_{28}$. All the RI-MP2 calculations were performed on a Linux cluster of 3.2 GHz EM64T Pentium 4 processors connected by a Gigabit Ethernet network. These calculations confirm the high parallel efficiency of the developed algorithm. For taxol, the speedup, defined as the ratio of elapsed time, was almost linear, 27.0 (6-31G*) and 29.6 (6-311G*) for 32 processors. For valinomycin with the larger number of basis functions, super-linear scaling was achieved, the speedup being 36.6 (6-31G*) and 34.8 (6-311G*) for 32 processors. As the calculations of the noncovalent complex of C_{60} and $C_{60}H_{28}$ show (Figure 1), the high parallel efficiency is kept up to 64 CPU cores. The parallel efficiency depends on the speed of network communication because the amount of network communication increases linearly as the number of processors. It is expected that the high parallel efficiency is kept up to much more processors when more efficient network communication is employed. As shown by the RI-MP2 calculation of two-layer nanographene sheets with the 6-311 G* basis set (3,932 basis functions), only 2.3 GB memory per processor and a total of 228 GB disk are required, unlike the MP2 calculation that requires 14.6 GB memory and a total of 7.9 TB disk. In addition, RI-MP2 energies deviate from MP2 energies only by 1-3 mHartree.

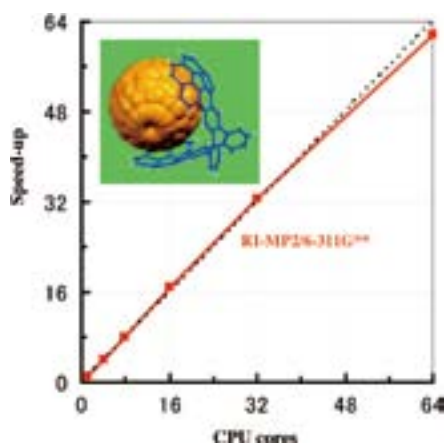
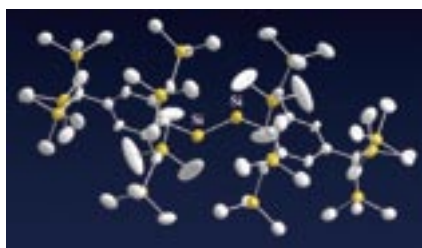


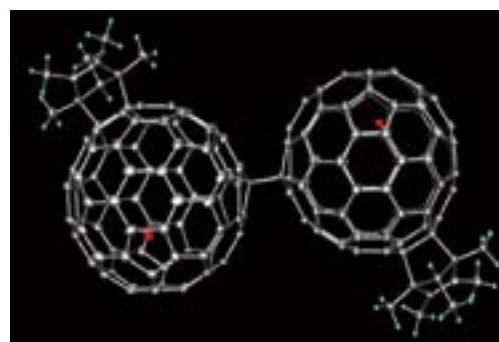
Figure 1. The RI-MP2 parallel calculations of the complex of C_{60} and $C_{60}H_{20}$.

2. Computational Approach to the Structures, Reactions, and Functionalization of Large Molecules

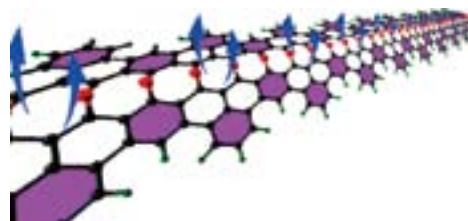
There has been much interest in silicon-silicon triply bonded compounds. Therefore, the structure and properties of 1,2-diaryldisilyne ($ArSi\equiv SiAr$), isolated by introducing bulky aryl groups ($Ar = C_6H_2-2,6\{CH(SiMe_3)_2\}_2-4-C(SiMe_3)_3$), were investigated by theoretical calculations.^{2,3} The mechanisms of unique reactions of $R^{Si}Si\equiv SiR^{Si}$ protected by bulky silyl groups ($R^{Si} = Si^iPr\{CH(SiMe_3)_2\}_2$) were theoretically disclosed.⁴ In addition, neutral organogallium aryl dimers and monomers were investigated to characterize the gallium-gallium bonds in digallenes and digallynes.⁵



Endohedral metallofullerenes are of great interest in developing functional nanomolecules. It is an important task to observe the ^{13}C NMR chemical shifts of metal carbides in $Sc_2C_2@C_{82}$, $Sc_2C_2@C_{84}$, and $Sc_3C_2@C_{80}$ in an attempt to provide insight into its electronic and magnetic properties. The ^{13}C NMR chemical shifts were theoretically predicted and experimentally confirmed using ^{13}C -enriched samples.⁶ In addition, calculations were performed for the radical coupling reactions of paramagnetic endohedral metallofullerenes,⁷ anisotropic behavior of anionic carbene derivatives,⁸ and missing metallofullerenes.⁹



Nanographene (NG) has attracted great interest as the new generation of carbon electronics. We predicted how the oxidation unzipping of stable NG leads to spin-rich fragments in an attempt to realize NG-based molecular magnets.¹⁰



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