

Optical properties of $M^+@C_{60}$ ($M = H, Li, Na, \text{ and } K$): All-electron GW +Bethe-Salpeter method

Yoshifumi Noguchi

Institute for Solid State Physics, The University of Tokyo,

5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.

Tel: +81-4-7136-3291, E-mail address: y.noguchi@issp.u-tokyo.ac.jp

All-electron mixed basis approach, in which one-particle wave function is expanded as a linear combination of atomic orbitals (AOs) and plane waves (PWs), is efficient and powerful in treating the isolated systems such as molecules and clusters and extended systems such as crystals. This tactic is required in particular in Green's function method based on the many-body perturbation theory beyond the framework of the density functional theory (DFT) because the perturbation theory needs all the information from core electron states localizing nuclear and free electron states above the vacuum levels. Our all-electron method can fully respond to this high-level demand owing to the use of both PWs and AOs.

We have implemented GW [1], T -matrix [2,3], Bethe-Salpeter [4,5], and 2nd order Møller-Plesset perturbation theory (MP2), etc., into an all-electron mixed basis program. As already known, these Green's function methods are accurate however require much more expensive computational cost than that of the DFT-base methods. Therefore, there is a strong limitation in treatable system size. A straightforward way to overcome this problem is to develop a message passing interface (MPI) program because the Green's function method is perfectly suitable for the massively parallel calculations and there is neither difficulty to write the MPI program code nor a factor to hinder the parallel efficiency. Figure 1 shows the parallel efficiency in weak scaling measured on Fujitsu FX10 supercomputer installed at Information Technology Center, the University of Tokyo. The parallel efficiency of GW calculation is almost scalable and about 97 % at 1,536 MPI parallel execution.

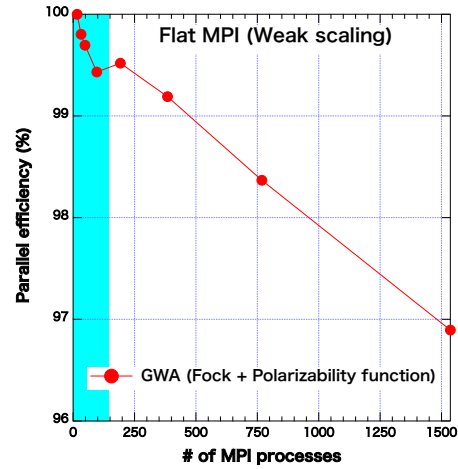


FIG. 1. MPI parallel efficiency in weak scaling of GW calculation.

Recently, we applied our program to $M^+@C_{60}$ (where $M = H, Li, Na,$ and K) and calculated the optical properties by using GW +Bethe-Salpeter method. Figure 2 shows the metastable atomic geometries optimized by B3LYP (note that the atomic geometries where M^+ is located outside C_{60} is the most stable). In order to investigate the bonding properties between M^+ and a carbon atom, we calculated the electron localization function (Fig. 3). It is clear that all the alkali-metal ions we studied here are weakly bound to C_{60} and only H^+ is chemically bonded to the carbon atom and distorts the local frame of C_{60} . This difference in bonding properties between M^+ and carbon atom is also seen in the HOMO-LUMO gap and photoabsorption spectra. In this talk, we will compare the present results with the available experiments and discuss the effect of the insertion of M^+ in detail.

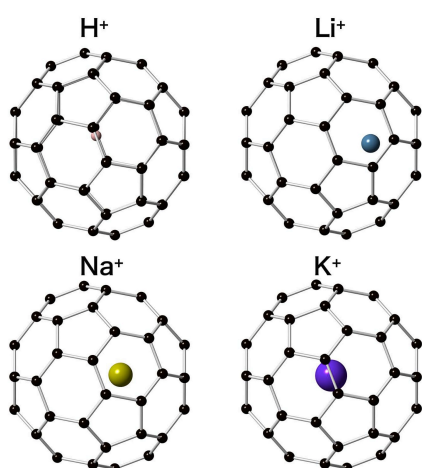


FIG. 2. Metastable atomic geometries of $M^+@C_{60}$ (where $M = H, Li, Na,$ and K) optimized by B3LYP.

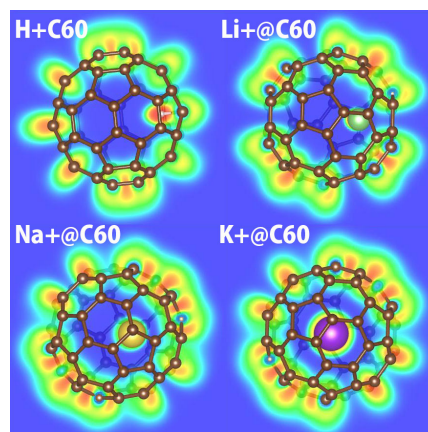


FIG. 3. Electron localization function calculated for $M^+@C_{60}$. The electron localization function localizes around alkali-metal ions and delocalizes between H^+ and a carbon atom.

References:

- [1] [Y. Noguchi](#), S. Ishii, K. Ohno, and T. Sasaki, *J. Chem. Phys.*, **129**, 104104 (2008).
- [2] [Y. Noguchi](#), S. Ishii, K. Ohno, I. Solovyev, and T. Sasaki, *Phys. Rev. B* **77**, 035132 (2008).
- [3] [Y. Noguchi](#), K. Ohno, I. Solovyev, and T. Sasaki, *Phys. Rev. B* **81**, 165411 (2010).
- [4] [Y. Noguchi](#) and K. Ohno, *Phys. Rev. A* **81**, 045201 (2010).
- [5] [Y. Noguchi](#), O. Sugino, M. Nagaoka, S. Ishii, and K. Ohno, *J. Chem. Phys.*, **137**, 024306 (2012).
- [6] [Y. Noguchi](#), O. Sugino, H. Okada, and Y. Matsuo, *J. Phys. Chem. C*, DOI: 10.1021/jp4041259 (2013).