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All-Electron *GW* Calculation for Quasiparticle Energies in C_{60}

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By carrying out an all-electron *GW* calculation, we firstly obtain quasiparticle energies of C_{60} molecule without any experimental information. The amount of computation of *GW* calculation is propotional to the order of N^6 (N = number of electrons) far more than the case of the standard LDA of N^3 for such a large system. The *GW* program code has been parallelized using MPI and actual computaions are performed on several supercomputers within the Nanotechnology-VPN under ITBL environment. [doi:10.2320/matertrans.47.2620]

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1. Introduction

It is well-known that the energy gap between the highest occupied molecular orbital (HOMO) (or the top of the valence band) and the lowest unoccupied molecular orbital (LUMO) (or the bottom of the conduction band) is significantly underestimated if one uses the Kohn-Sham eigenvalues within the local density approximation (LDA)[1)] of the density functional theory (DFT).[2)] This is simply because the Kohn-Sham eigenvalues do not represent the quasiparticle energies such as the ionization potential (IP) and the electron affinity (EA). If Koopmans' theorem holds, the absolute values of the quasiparticle energies at the HOMO and LUMO levels should correspond to the IP and EA, respectively. However, Koopmans' theorem does not hold for the DFT. To calculate the quasiparticle energies correctly, one needs to go beyond the DFT.

One possible approach to calculate the quasiparticle energy spectra is to use the *GW* approximation (GWA)[3)] for the self-energy of the one-particle Green's function on the basis of many-body perturbation theory. In this approach, the quasiparticle spectra can be determined from the poles of the one-particle Green's function. It has been demonstrated that the GWA can provide accurate quasiparticle energies of typical semiconductors and insulators.[4–6)] So far, most of the GWA calculations relies on pseudopotentials, not being able to evaluate the absolute values of quasiparticle enegies, *e.g.*, IP and EA. Recently some all-electron GWA calculations have been done for crystals,[7–10)] but not yet applied for clusters to determine the absolute values of IP and EA. Here we use the all-electron mixed basis approach, in which both plane waves (PWs) and atomic orbitals (AOs) are used to represent one-particle wave functions. The LDA part of this code[11–15)] has essentially the same architecture as the TOhoku Mixed-Basis Orbitals *ab initio* program (TOMBO).[16,17)] The GWA calculation using this approach is capable to determine the absolute values of quasiparticle energies. So far, we have carried out the all-electron GWA calculations of alkali-metal clusters[18–20)] and clusters of semiconductor.[21)]

The GWA calculations demand a lot of CPU time compared with the LDA calculations because CPU time of the GWA (LDA) calculations are proportional to N^6 (N^3). Here N denotes the number of electrons. In the present calculation, we have used a GRID super-computing system connecting three supercomputers via SuperSINET. Now this network is called Nanotech Virtual Private Network (Nanotech-VPN). In this system, we used 4 nodes of HITACHI SR8000 each at the Institute for Materialas Research (IMR) of Tohoku University and at the Institute for Solid State Physics (ISSP) of University of Tokyo, and 2 nodes of NEC SX-6 at the Japan Atomic Energy Agency (JAEA). We divided the processes and memories into every supercomputer that is separated in physical space, making it possible to perform large scale computation. We parallelized our GWA code to perform this type of calculations (see Fig. 1).

By using the Nanotechnolgy-VPN, the number of floating point calculation per process became less than 20%, and the use of memories became 65% compared to the original program. The Green's function approach makes it possible to evaluate parallelly and simultaneously each of the quasiparticle energies required to remove one electron from (or aquired to add one electron to) the neutral systems. Here we report on our all-electron GWA calculation of C_{60} by using the Nanotechnology-VPN and also 4 nodes of the HITACHI SR11000 supercomputer in Institute for Molecular Science (IMS) at Okazaki. Although the GWA calculation using pseudopotential approach was already performed by Shirley and Louie[22)] for the fcc C_{60} crystal, they used some experimental parameters when evaluating dielectric function. That is, their calculation was not a perfect *ab initio* GWA calculation. To treat 60 carbon atoms by means of the all-electron GWA calculation is still very demanding even in the large supercomputing facilities described above. Here we present a result, which is the best we can do at the moment.

2. Methodology

In our mixed-basis approach, AOs are expressed as a product of numerical radial funcions and the analytic spherical harmonics. The radial functions for the core AOs are determined by Herman-Skillman's atomic code[23)] on the logarithmic radial mesh, while those for the valence AOs are

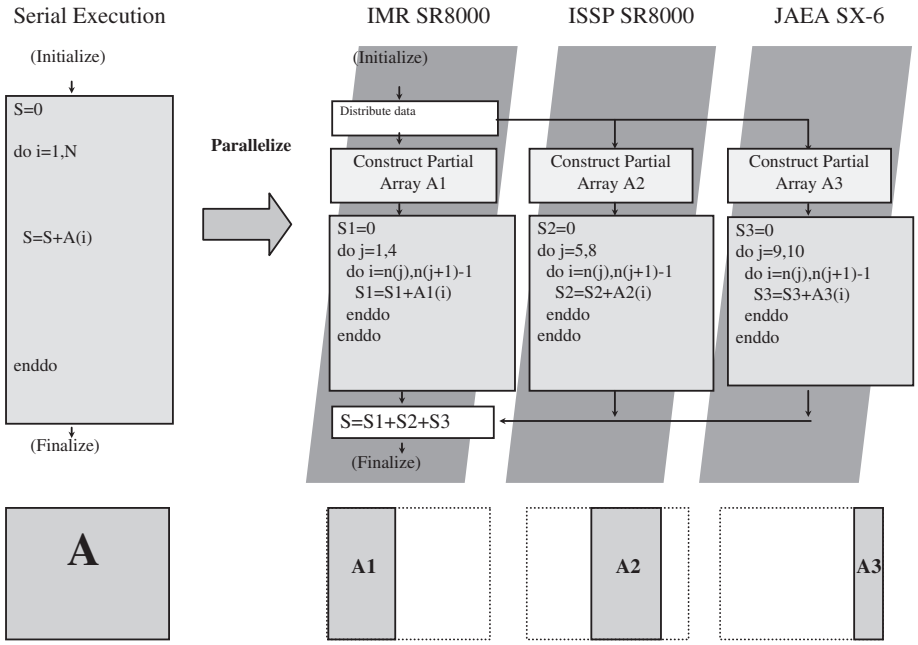

Fig. 1 Wide area distributed execution of GW program.

determined similarly but truncated smoothly within the nonoverlapping atomic sphere.

We start from the Dyson equation,

$$[T + U + \Sigma(E_n^{\mathrm{q}p})]|n\rangle = E_n^{\mathrm{q}p}|n\rangle. \quad (1)$$

Here, T and U denotes the kinetic energy operator and the electron-electron Coulomb interaction plus external potential, respectively. In the GWA, the one-electron self-energy $\Sigma(\omega)$ (defined apart from the Hartree potential $U = \int \rho(\boldsymbol{r}')v(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}'$ of the electron-electron Coulomb interaction v) is given by

$$\Sigma(\omega) = \frac{i}{2\pi}\int G(\omega+\omega')W(\omega')e^{i\eta\omega'}d\omega', \quad (2)$$

where G and W denote, respectively, the one-particle Green's function and the dynamically screened Coulomb interaction; and η is a positive infinitesimal number. [For simplicity, we have suppressed the $(\mathbf{r}, \mathbf{r}')$ dependence of all quantities.] One can divide the self-energy into two parts; one corresponds to the Fock-exchange energy evaluated with the LDA wave functions,

$$\Sigma_{\mathrm{x}} = \frac{i}{2\pi} v\int G(\omega)e^{i\eta\omega}d\omega, \quad (3)$$

which can be evaluated as eq. (9) in Ref. 18). The remaining $\Sigma_{\mathrm{c}}(\omega)$ is related to the correlation energy and represented by eq. (11) in Ref. 18) (it is defined as the residue after Σ_{x} is subtracted from eq. (2)). Writing the dielectric function and polarizability, respectively, as ϵ and P, one can derive $W = \epsilon^{-1}v$ from $\epsilon = 1 - vP$. Usually, the polarizability P is evaluated under the random phase approximation (RPA).

On the other hand, it becomes a question which G and W we should use. In the present study, we use G and W using the LDA wave functions and KS eigenvalues. In determining quasiparticle energies within the GWA we used the equation:

$$E_n^{GWA} = E_n^{LDA} + \langle n|\{\Sigma_x + \Sigma_c(E_n^{LDA}) - \mu_{\mathrm{xc}}^{LDA}\}|n\rangle, \quad (4)$$

where E_n^{LDA} and μ_{xc}^{LDA} is the LDA Kohn-Sham eigenvalue and exchange-correlation potential of the LDA, respectively. Here we neglect the renormalization factor Z in the conventional approach[4,5] since the difference caused by it is small.

In the present study, we used an fcc unit cell with a cubic edge of 3.0 nm (corresponding the rhombus edge of 2.12 nm). We used the cut-off energy of 7.1 Ry for PWs and also for the G and G′ vectors in the evaluation of the correlation part of the self-energy, Σ_c. For the G vectors in the evaluation of the Fock-exchange part of the self-energy, Σ_x, we used the cut-off energy of 15 Ry. When we evaluate the polarizability function and the correlation part of the self-energy, 3000 levels are used in the summations of the states.

The Coulomb potentials are spherically cut at the distance equal to the half of the lattice constant to seclude from the neighboring cells. We use the generalized plasmon-pole (GPP) model[5,19] to evaluate the frequency dependence of the dielectric function $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ and electron self-energy.

3. Parallelization

GW program consumes huge amount of computations and requires large memory. We have parallelized GW program using Message Passing Interface (MPI) and performed wide area distributed execution to distribute the computation and memory to enable larger calculation of GW program than before.

The main parts of GW program are huge integrals along pairs of node in the fourier space. We adopted two kinds of parallelizations, coarse grain parallel and fine grain parallel. The former is to distribute the computation and memory by coarse unit, and the latter is to gain efficiency on each computer. Figure 1 shows this situation. We executed using three computers at the same time on Nanotech-VPN,

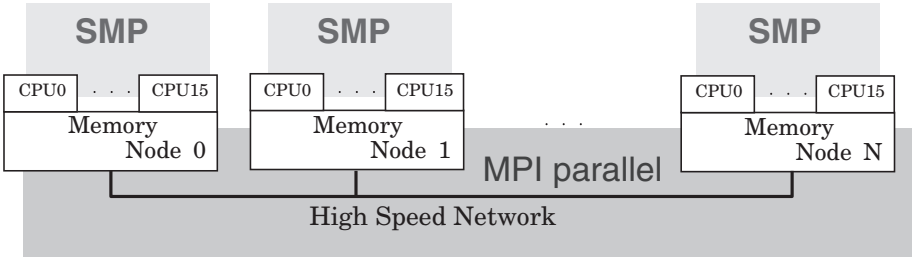

Fig. 2 Single supercomputer execution of GW program.

Table 1 The contributions to the quasiparticle energies (in eV) for the HOMO and LUMO are shown compared with the negatives of the experimental ionization potential and experimental electron affinity ($-E^{\mathrm{EXP}}$).[25,26] Here, $E_n^{\mathrm{LDA}} = \langle n|H^{LDA}|n\rangle$, $\mu_{xc,n}^{\mathrm{LDA}} = \langle n|\mu_{xc}^{LDA}|n\rangle$, $\Sigma_{\mathrm{x},n}$ and $\Sigma_{\mathrm{c},n}$ represent the Kohn-Sham eigenvalue, the Kohn-Sham exchange correlation energy, the exchange part, and the correlation part of the self-energy Σ, respectively. The first column, N_{level}, denotes the number of levels taken into account in the caluculation of $\Sigma_{\mathrm{c},n}$. The corresponding results for the quasiparticle energies are E^{GWA}.

	E_n^{LDA}	$\mu_{xc,n}^{\mathrm{LDA}}$	$\Sigma_{\mathrm{x},n}$	$\Sigma_{\mathrm{c},n}$	E^{GWA}	E^{EXP}
HOMO	−6.61	−14.06	−14.90	0.0 ± 1.0	-7.45 ± 1.0	−7.6[a]
LUMO	−5.26	−11.18	−7.80	-0.7 ± 1.0	-2.58 ± 1.0	−2.6[b]

[a]Ref. 25), [b]Ref. 26)

SR8000(4 nodes) at IMR, SR8000(2 nodes) at ISSP and SX-6(2 CPUs) at JAEA. The total performance of 3 computers is 98 GFLOPS (giga floating operations per second) theoretically. In this case, the amount of floating operations became less than 20% and memory size became less than 65% (less than 50% for practical case) compared to original serial execution. We consumed 7 days for one continuous execution at the most.

Also we used up-to-date supercomputer HITACHI SR11000 model HI (4 nodes) at IMS as a single supercomputer by adopting the parallelized GW program on it. The performance of SR11000 model HI (4 nodes) is 435 GFLOPS theoretically. Figure 2 describes this architecture. The coarse grain parallel is performed between 4 nodes using MPI and the fine grain parallel is performed using Shared Memory Parallel (SMP) by 16 CPUs within each node. The execution time of 4 nodes is 27% of 1 node execution. We consumed 13.5 days for one continuous execution at the most.

4. Results and Discussion

Table 1 shows the HOMO and LUMO quasiparticle energies of C_{60} obtained in the present study. For comparison, the LDA energy eigenvalues (E_n^{LDA}) and the other contributions to the quasiparticle energies in eq. (4) (the LDA exchange-correlation energy, and the exchange and correlation parts of the self-energy) are lised together with the experimental IP and EA with negative sign (E^{EXP}).[25,26] Since the correlation part of the self-energy ($\Sigma_{\mathrm{c},n}$) is not yet converged well with $N_{level} = 3000$, the result has an error of 1.0 eV. Although the error of estimation is large, the present result agrees the experimental data. It is now desirable to extend present calculation to, *e.g.*, metal encapsulated fullerene molecules.

In sammary, we have carried out the all-electron GWA calculations for C_{60} by using a GRID supercomputing system 'Nanotech-VPN' that connects three supercomputers via SuperSINET as well as a single supercomputer SR11000. Although Kohn-Sham eigenvalues underestimate experimental ionization potentials and overestimate electron affinities, the *GW* quasiparticle energies obtained in this study are in good agreement with the experimental data.

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