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ABSOLUTE VALUE OF QUASIPARTICLE ENERGIES OF Li CLUSTERS BY AN AB-INITIO *GW* APPROXIMATION

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Ab-initio quasiparticle energy calculations are performed for small lithium clusters (Li_2, Li_4, and Li_6) by an all-electron approach within the GW approximation. Electron self-energy is evaluated by using the generalized plasmon-pole model. The quasiparticle energies of the HOMO (highest occupied molecular orbital) level are in very good agreement with available experimental ionization potentials. The absolute values of the quasiparticle energies of the LUMO (lowest unoccupied molecular orbital) levels are much less than those of Kohn-Sham eigenvalues and in good agreement with available experimental data.
Key words: ab initio, GW approximation, Lithium clusters, all-electron approach, ionization potential, and electron affinity

1. INTRODUCTION

In the first-principle calculations, one of the standard methods is the local density approximation (LDA) based on the density functional theory. This theory is a very good approximation for describing the ground state properties of the system. However, many experiments involve excited states that the density functional theory cannot reproduce in principle. For example, it is well known that the LDA underestimates the band gap of semiconductors and insulators typically 30-50%. Therefore, for example, the color of materials by the LDA calculation is very different from the actual one. In order to reproduce the actual color by first-principle calculations, one needs the theory beyond the density functional theory to evaluate the excitation energy correctly. One of them is the GW approximation, which was introduced from the viewpoint of the quantum many-body theory [1].

Ab-initio GW calculation was firstly performed by Hybertsen and Louie for silicon and diamond crystals [2]. The GW approximation has been widely applied for many materials and succeeded in reproducing the experimental band gap. However, there are only few results for clusters. Onida et al. calculated the quasiparticle energies of sodium tetramer within the GW approximation by a pseudopotential approach [3]. Although pseudopotential approaches can calculate relative quasiparticle energies fast, they cannot evaluate the absolute values of the quasiparticle energies. Ishii et al. calculated the absolute value of the quasiparticle energies for small sodium clusters within the GW approximation by an all-electron approach [4]. In the present study, we performed ab-initio GW calculations for small lithium clusters (Li_n, n=2,4, and 6) by an all-electron approach.

2. METHODOLOGY

We employed an all-electron mixed-basis approach [5]. The mixed-basis approach is introduced by Louie, Ho and Cohen [6] in order to treat localized d orbitals within the pseudopotential approach. The present approach is a natural extension of pseudopotential approach. Wave functions are expanded using plane waves and atomic orbitals. The core wave function is mainly represented by atomic orbitals which is evaluated by Herman-Skillman's code [7].

In the GW approximation (GWA), electron self-energy operator Σ is defined by

$$\Sigma(\mathbf{r},\mathbf{r}';E)=\frac{i}{2\pi}\int_{-\infty}^{+\infty}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega)e^{-i\eta\omega}d\omega. \quad (1)$$

Here G denotes the one-particle Green function, W the dynamically screened Coulomb interaction, and η a positive infinitesimal. W is represented by the bare Coulomb interaction and the dielectric response function $\varepsilon_{GG'}(\mathbf{q},\omega)$, which is usually evaluated by the random phase approximation (RPA). **G** (**G'**) and ω represent reciprocal lattice vectors and frequency, respectively. The case of $\mathbf{G}\neq\mathbf{G'}$ corresponds to the local-field effect. We need 645 **G** (**G'**) to achieve a good convergency within 0.1 eV. To evaluate the ω dependence of the dielectric response function, we employed the generalized plasmon-pole (GPP) model [2] which is a standard approximation in the GW calculations. This model assumes that an electron excitation arises only at the frequency of an average

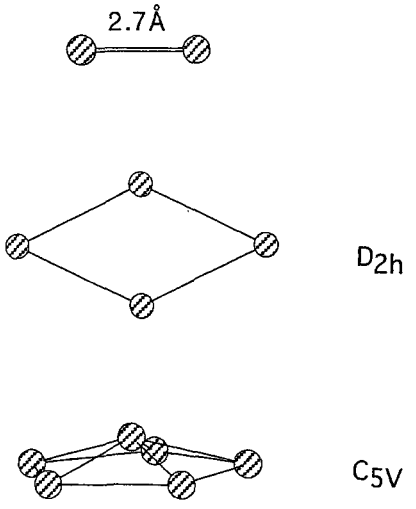

Fig.1. Structures used in the present study. They are referred to in Ref. [8].

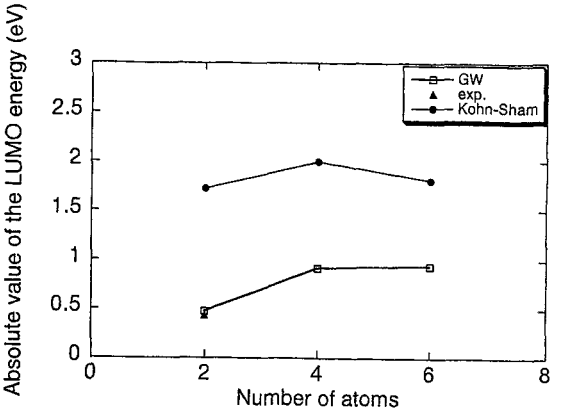

Fig.3. Cluster-size dependence of the absolute value of the LUMO energy obtained by the present GW calculations compared with the Kohn-Sham eigenvalues and available experimental electron affinity.

energy gap and that plasma frequency can be replaced by an effective bare plasma frequency determined by the generalized *f*-sum rule and the Kramers-Kronig relation. By using the GPP model, one can integrate the integrand of self-energy operator with respect to frequency analytically. The validity of this model is discussed in Sec.3.

The structures used in this study are shown in Fig.1. They are obtained by the SCF calculations and referred to in Ref.[8]. We employ an FCC supercell with a cubic edge of 50 a.u. . The cut-off energy is 5 Ry.

3. RESULTS

The self-energy operator breaks into two parts:

$$\Sigma = \Sigma_x + \Sigma_c \qquad (2)$$

Σ_x is bare exchange energy by using the LDA wave functions and Σ_c the rest of the self-energy corresponding to the correlation energy. In evaluating Σ_x one cannot ignore the core contribution. For example, For lithium dimer Σ_x of the HOMO level is –7.0 eV. The core contribution to that value is 0.8 eV. On the other hand, core contribution to Σ_c is less than 0.1 eV. For the evaluation of Σ_c, we used the LDA values for E.

For the check of the validity of the GPP model, we performed a numerical integration with frequency for lithium dimer. The technical details are given in Ref. [4]. Obtained Σ_c of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) by using the GPP model are 0.66 and 0.81 eV, respectively. The corresponding values obtained by performing the full integration are 0.64 and 0.79 eV, respectively. Both methods give same results within the error of 0.1 eV.

The absolute values of the HOMO energies are comparable with the ionization potentials. The cluster-size dependence of the absolute value of the HOMO energies obtained by the present GW calculations are shown in Fig.2 compared with the Kohn-Sham eigenvalues and experimental ionization potentials [9]. Although Kohn-Sham eigenvalue underestimates the experimental ionization potential by about 30-50%, GW quasiparticle energies reproduce the available experimental ionization potentials.

The absolute values of the LUMO energies are comparable with the electron affinities. The cluster-size dependence of the absolute values of the LUMO energies obtained by the present GW calculations are shown in Fig.3 compared with the Kohn-Sham eigenvalues. Absolute values of the present GW quasiparticle energies are less than that of the Kohn-Sham eigenvalues about 200-500%.

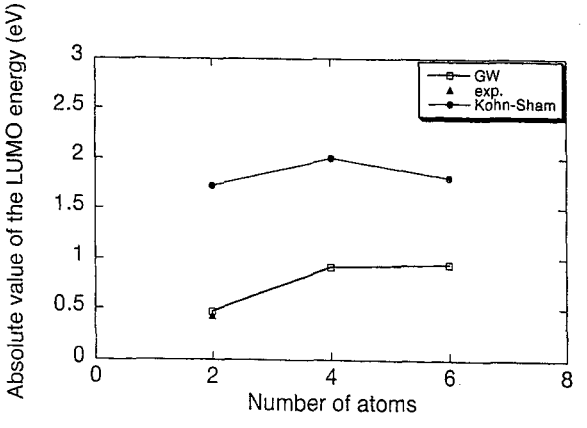

Fig.2. Cluster-size dependence of the absolute value of the HOMO energy obtained by the present GW calculations compared with the Kohn-Sham eigenvalues and experimental ionization potentials [9].

4. SUMMARY

We performed ab-initio quasiparticle energy calculations for small lithium clusters within the GW approximation by using the all-electron mixed-basis approach. The frequency dependence of the dielectric response function is evaluated by using the generalized plasmon-pole model, which is in very good agreement

with the results obtained by performing the numerical integration. The quasiparticle energies of the HOMO level in the present calculations are in good agreement with available experimental ionization potentials. Electron affinities obtained by the GW calculations are much larger than those obtained by the Kohn-Sham eigenvalues and in good agreement with the available experimental value.

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REFERENCES

[1] L. Hedin, Phys. Rev. **139**, A796 (1965).
[2] M. Hybertsen and S. G. Louie, Phys. Rev. **B34**, 5390 (1984).
[3] G. Onida, L. Reining, R. W. Godby, R. D. Sole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
[4] S. Ishii, K. Ohno, Y. Kawazoe, and S. G. Louie, accepted to Phys. Rev. B.
[5] Y. Maruyama, Doctor thesis, Tohoku University (1996).
[6] S. G. Louie, K. Ho, and M. Cohen, Phys. Rev. **B19**, 1774 (1979).
[7] F. Herman and S. Skillman,``Atomic structure Calculations'' (Prentice-Hall, New Jersey, 1963).
[8] I. Boustani et al., Phys. Rev. **B35**, 9437 (1987).
[9] C. H. Wu, J. Phys. Chem. **87**, 1534 (1983); Ph Dugourd *et al*, Chem. Phys. Lett. **197**, 433 (1992); Chem. Phys. Lett. **206**, 521(1993).
[10] H. W. Sarkas *et al*, Z. Phys. D**29**, 209 (1994).

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