

ABSOLUTE VALUE OF *GW* QUASIPARTICLE ENERGIES OF A METHANE USING AN ALL-ELECTRON MIXED-BASIS APPROACH

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An *ab-initio GW* calculation is performed for an isolated methane molecule. In the calculation, we employ an all-electron mixed-basis approach, where a wave function is expanded using both plane waves and atomic orbitals. The present *GW* quasiparticle energy of the highest occupied molecular orbital (HOMO) energy is in good agreement with experimental quasiparticle energies and previous *GW* calculations, although the absolute value of the local density approximation (LDA) eigenvalue is much smaller than the experimental value. The lowest unoccupied molecular orbital (LUMO) energy of the present *GW* calculation is much larger than the LDA eigenvalue. We also discuss the self-energy corrections to the LDA eigenvalues.

Key words: *ab initio*, *GW* approximation, methane, all-electron approach, ionization potential, and electron affinity

1. INTRODUCTION

In the first-principles calculations, one of the standard methods is the local density approximation (LDA) based on the density functional theory (DFT). The LDA is a very good approximation for the description of ground state properties of materials. However, the DFT does not give any information about excited states in principle because the DFT guarantees only ground state properties. As is well known, for example, the LDA band gap of semiconductors and insulators are much smaller than those of experimental values by about 30-50%. In order to calculate the excitation energy correctly, for example, one must employ the theory going beyond the DFT. One of the theories is the *GW* approximation [1], introduced from the viewpoint of the quantum many-body theory.

Firstly *ab-initio GW* calculations were successfully performed by Hybertsen and Louie [2] for typical bulk semiconductors such as silicon and germanium, using pseudopotentials. *GW* calculations were mainly applied to crystals. However, the number of papers about clusters and molecules using the *GW* approximation is small. Some of the present authors successfully applied the *GW* approximation to small alkali-metal clusters [3] and silicon clusters [4]. Grosman *et al.*, performed the *GW* calculation for a silane and methane. Their method uses pseudopotential approach [5].

In the present study, we perform *ab-initio GW* calculations for a methane molecule using an all-electron mixed-basis approach. In such small systems, the effect of atomic relaxation plays an important role to reproduce the experimental quasiparticle energies such as the ionization potential (IP) and the electron affinity (EA) as is proposed by Grosman *et al.*[5]. In the present study, we compare our results with their results and experimental value.

2. METHODOLOGY

We employ an all-electron mixed-basis approach [6]. The mixed-basis approach is firstly introduced by Louie, Ho, and Cohen [7] in order to treat localized *d* orbitals within the pseudopotential approach. The present approach is a natural extension of this approach. A wave function is expanded using plane waves and atomic orbitals. Delocalized components such as a valence wave function are mainly represented by plane waves. Localized components such as a core wave function are mainly represented by atomic orbitals. We employ Herman-Skillman's code [8] to make atomic orbitals.

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 $\epsilon_{GG}(\mathbf{q}, \omega)$, which is usually evaluated within the random phase approximation (RPA) [$\epsilon_{GG}(\mathbf{q}, \omega)$ is usually evaluated in Fourier space]. Note that the self-energy operator is non-local and energy dependent. Final *GW* quasiparticle energies are given by

$$E_n^{\text{GWA}} = E_n^{\text{LDA}} + z \langle n | \Sigma - \mu_{xc}^{\text{LDA}} | n \rangle, \quad (2)$$

$$z = \left[1 - (\partial \Sigma(E) / \partial E)_{E=E_n^{\text{LDA}}} \right]^{-1}$$

as a first iterative solution of Dyson equation, where E_n^{LDA} and μ_{xc}^{LDA} denote a LDA eigenvalue of energy level, n , and LDA exchange correlation potential, respectively.

In the calculations of frequency dependence of dielectric response function and self-energy operator, we employ the generalized plasmon-pole model, which gives reliable quasiparticle energies.

3. RESULTS

The geometry of ground state of a methane molecule, referred to experimental data [9], is well known. This structure has T_d symmetry.

The self-energy operator breaks into two parts:

$$\Sigma = \Sigma_x + \Sigma_c \quad (3)$$

Here the first term of the right hand side of eq.(3) is Fock-exchange energy evaluated using the LDA wave functions and the second corresponds to the correlation energy within the *GW* approximation.

The absolute value of the HOMO (LUMO) energy is the ionization potential (electron affinity) via Koopmans theorem. In the table I, we show the HOMO and LUMO energy of the present *GW* calculation for an isolated methane compared with experimental values and the LDA results. The separate contributions to the *GW* quasiparticle energies from the exchange and correlation part are also shown.

The absolute value of the LDA eigenvalue of the HOMO energy is smaller than experimental IP [9] by about 4 eV and the present *GW* quasiparticle energy seems to be larger than experimental IP but in good agreement with previous result [5]. It is well known that the *GW* approximation is a promising method to reproduce one-particle excitation energy [see, for

example, ref. [2-5]]. As reported by Grossman *et al.* [5], in the case of methane, the geometry of the cation is different from the neutral one and has a C_{2v} structure. Because of that, we performed the same *GW* calculation employing C_{2v} structure. The results are shown in table I. The results of the present study and previous calculation [5] are in good agreement with the experimental value.

As for the LUMO energy, the absolute value of the LDA eigenvalue is larger than that of the *GW* quasiparticle energy by about 1 eV. To our knowledge, there is no experimental result of electron affinity. The present *GW* quasiparticle energy is very near the continuum level ($E = 0$). In this case, one needs to take into account the off-diagonal elements of the self-energy [see eq.(2)]. However, it is a very difficult task to perform this calculation [3,5].

To reproduce the experimental IP, exchange part plays an important role, although correlation part cannot be ignored. These are reasonable results. In the *GW* approximation, self-energy is defined as a first term of the perturbation expansion with respect to the dynamically screened Coulomb interaction. On the other hand, the exchange part is also a first term with respect to bare Coulomb interaction and the correlation part is a second term. From the viewpoint of the perturbation theory, the first term becomes predominant.

Table I. The contributions to the quasiparticle energies (in eV) for the HOMO (H) and LUMO (L) are shown compared with the experimental ionization potential. μ_{xc}^{LDA} , Σ_x , and Σ_c are the Kohn-Sham exchange correlation of the LDA and the exchange part and correlation part of the self-energy, respectively. To our knowledge, there is no experimental result of electron affinity.

Level	E_n^{LDA}	μ_n^{LDA}	Σ_x	Σ_c	E_n^{GWA}	$E_n^{\text{expt.}}$
H(T_d)	-9.6	-13.8	-18.9	0.4	-14.1 (-14.3)*	
L(T_d)	-1.3	-2.6	-0.8	-0.7	-0.1	-----
H(C_{2v})	-8.8	-13.7	-18.6	0.2	-13.0 (-12.5)*	-12.99

* ref.[5]

4. SUMMARY

We performed *ab-initio* quasiparticle energy calculations for a methane molecule within the *GW* approximation using the all-electron mixed-basis approach where a wave function is expanded using both plane waves and atomic orbitals. In the *GW* energy corrections to the Kohn-Sham eigenvalues, the exchange part of the self-energy plays an important role, although correlation part is not negligible. The quasiparticle energies of the HOMO level in the present calculations are in good agreement with available experimental ionization potentials and previous results. The electron affinity obtained by the present *GW* calculation is much larger than those obtained by the Kohn-Sham eigenvalue.

To evaluate the accurate value of the electron affinity, one may need the calculations of off-diagonal elements of the self-energy.

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