GW(Γ) method without the Bethe–Salpeter equation for photoabsorption energies of spin-polarized systems

Tomoharu Isobe,¹ Riichi Kuwahara,² and Kaoru Ohno^{1,*}

¹ *Department of Physics, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*

² *Dassault Systèmes BIOVIA K.K., ThinkPark Tower, 2-1-1 Osaki, Shinagawa-ku,
Tokyo 141-6020, Japan*

(Dated: May 14, 2018)

The one-shot GW method beginning with the local density approximation (LDA) enables one to calculate photoemission and inverse photoemission spectra. In order to calculate photoabsorption spectra, one had to additionally solve the Bethe–Salpeter equation (BSE) for the two-particle (electron-hole) Green’s function, which doubly induces the evaluation errors. It has been recently reported that the GW + BSE method significantly underestimates the experimental photoabsorption energies (PAEs) of small molecules. In order to avoid these problems, we propose to apply the GW(Γ) method not to the neutral ground state but to the cationic state to calculate PAEs without solving the BSE, which allows the rigorous one-to-one correspondence between the photoabsorption peak and the “extended” quasiparticle level. We applied the self-consistent LGWT method including the vertex correction to our method, and found that this method gives the PAEs of B, Na₃, and Li₃ within the 0.1 eV accuracy.

I. INTRODUCTION

Photoabsorption (PA) plays a decisive role in plenty of photo-related phenomena such as photosynthesis, photovoltaic cells, photocatalysts, photochemical reactions, photo-induced phase transitions, and so on. Photoabsorption energies (PAEs) have an important information on these phenomena. Physics behind PAEs for all wave length regions, if one ignores the vibronic effects, is that each PAE is quantum mechanically identified to the total energy difference between the ground state (GS) and an excited eigenstate (EES) with one electron excited from the GS of the Hamiltonian.

So far, we have three different first-principles approaches to calculate PAEs: (i) the quantum chemistry (QC) approaches such as the configuration interaction (CI) and coupled cluster (CC) methods,[1] (ii) time-dependent density functional theory (TDDFT),[2] and (iii) the GW + Bethe–Salpeter equation (BSE) approach.[3–7] The Δ SCF method, which calculates the difference between the two total energies E_v^N and E_G^N , has been commonly used in the QC approaches. They are very accurate but the computational cost required in the QC approaches scales as $O(\nu N^n)$, where ν represents the number of the peak positions of the PA spectrum[8, 9] and n represents the computational cost required in the GS calculation; for example, $n = 6$ for multi-reference single and double CI (MRDCI).[8] (This is because E_v^N is calculated after $E_{v-1}^N, E_{v-2}^N, \dots, E_G^N$ in the orthogonality constrained method.[9]) Due to their heavy computational cost and low parallel efficiency, the QC approaches are not applicable to large molecules. TDDFT is probably the most economic option among the three, but the results strongly depend on a choice of the exchange-correlation functional. TDDFT is suitable for coarse estimation of large molecules.

The GW + BSE approach is still heavy, but, thanks to the high parallel efficiency, its computational cost can be well dispersed. Recently, this approach has been applied to various materials.[10, 11] The approach is composed of two procedures; one is the GW approximation (GWA)[12, 13] to determine the quasiparticle (QP) energies, which represent the difference between the total energies of the N -electron GS and the $(N \pm 1)$ -electron EES. They correspond to photoemission and inverse photoemission spectra (PES/IPES), where one electron is removed from or added to the N -electron GS. The energy gap ϵ_g^N can be obtained by the difference between two QP energies, $\epsilon_{\text{LUMO}}^N - \epsilon_{\text{HOMO}}^N$, but this ϵ_g^N is different from the PAE, Ω^N . To calculate PAEs, one has to additionally treat the electron-hole, two-body problem by solving the BSE.[3–7] In this way, the method has to deal with not only the one-particle Green’s function in the GW part but also the two-particle (electron-hole) Green’s function in the BSE part, and doubly induces the evaluation errors. Indeed, it has been recently reported by several authors that the GW + BSE method significantly underestimates the experimental PAEs of atoms and small molecules.[14–16] The use of the Heyd–Scuseria–Ernzerhof (HSE) functional or the self-consistent GW calculation improves the results, but they are not perfect.[15, 17] This problem is difficult to solve in MBPT unless one uses a more sophisticated approach such as the self-consistent LGWT + BSE approach.[16] In any approach solving the BSE, the resulting two-particle (electron-hole) wave functions are the complicated linear combinations of the products of the electron and hole QP wave functions. Therefore, there is no one-to-one correspondence between each peak of the PA spectrum (corresponding a N -particle EES) and the QP energy level (corresponding to a $N \pm 1$ -particle EES).

In the present paper, we propose a completely different and very tractable approach, which allows the rigorous one-to-one correspondence between the PA peaks and the (“extended”) QP levels,[18] although each peak height (intensity or oscil-

*Electronic address: ohno@ynu.ac.jp

lator strength) is not obtained. Our idea is to treat a cationic system instead of a neutral system and to consider the following three processes:

1. Consider a cationic state having one hole in the neutral GS and calculate the largest energy gain when one adds one electron to this cationic hole level to retrieve the neutral GS.
2. Calculate the second (or third, ...) largest energy gain when one adds one electron to the higher empty levels of this cationic state to construct the final PA state.
3. The first (or second, third, ...) PA peak energy is directly obtained as the difference between these two energy gains without any relaxation as shown in Fig. 1.

FIG. 1: The first peak PAE Ω_{1st}^{PA} is equal to the extended QP energy difference $\epsilon_{LUMO+1}^{N-1} - \epsilon_{LUMO}^{N-1}$ obtained by the GW calculation for the $(N-1)$ -electron cationic GS. Here, ϵ_{LUMO}^{N-1} and ϵ_{HOMO}^{N-1} correspond, respectively, to the total energy differences between the final PA state and the initial cationic GS and between the neutral GS and the initial cationic GS.

A significant point of this method is that the two energy gains, *i.e.* the minus of the two “extended” QP energies, in the processes 1 and 2 can be obtained simultaneously by applying the standard GW method to the cationic system instead of the neutral system, and the last process 3 is just a simple subtraction of these two energies and does not require any relaxation procedure such as to solve the BSE. Therefore, it offers a very simple and elegant method which enables one to calculate the electron excitations from the HOMO level to the LUMO, LUMO+1, LUMO+2, ... levels just by a single GW calculation. (Note that some other PA peaks may correspond to the energy difference between the HOMO-1 level or, in general, the HOMO- n level and the LUMO+1, LUMO+2, ... levels. To obtain such PA peaks, it is necessary to repeat the similar GW calculation by starting from the cationic EES with one hole at the HOMO-1 level or, in general, at the HOMO- n level. But anyway this is a simple and transparent task on the basis of the “extended QP theory.”[18]) It allows one to identify the rigorous one-to-one correspondence between the PA peaks and the (“extended”) QP levels. Since our new method requires the GW calculation only and does not require the BSE, we named this as the “GW(Γ) method without BSE.” This method is, without doubt, faster and simpler than the GW(Γ) + BSE method because the complicated BSE is no longer necessary. This method is named as “GW(Γ)”

but our framework allows to replace the GW(Γ) calculation to any other method which can calculate the (“extended”) QP energies.

Although the present method is very powerful, some comments should be given here. It delivers excited state energies, but no oscillator strengths. This is crucial in the majority of applications, since experimental absorption spectra need to be understood and/or predicted. The BSE method needs not consider the fact that the excited state can be characterized by a single configuration (for example, a HOMO to LUMO transition), although it cannot specify the characterization of each transition. In addition, the vast majority of systems is spin-unpolarized. For such systems the present approach requires a spin-polarized GW calculation (see below), while the standard GW+BSE approach can be done on closed-shell systems.

II. BASIC THEORY

In this section, we derive the GW(Γ) method without BSE to calculate PAEs and compare the method with the previous formalism. We apply the “extended” QP theory [18] to the $(N-1)$ -electron system to obtain PAEs of the N -electron system.

Our purpose is to calculate the one-electron EES of the N -electron neutral system. One of the observable in such a single photo-excitation process is the vertical PAE. The corresponding physical quantity is the PAE defined as

$$\Omega_v^{PA} = E_v^N - E_G^N, \quad (1)$$

where E_v^N and E_G^N represent, respectively, the total energies of the v th EES and the GS of the N -electron neutral system.

The simplest and clever way to calculate the PAEs is to consider the $(N-1)$ -electron cationic system γ , in which the photoexcited electron is removed from the final PA state v . In this idea, the PAEs are obtained by comparing the total energy of this system (E_γ^{N-1}) with those of the final state (E_v^N) and the GS (E_G^N). This γ th eigenstate of the $(N-1)$ -electron system plays a central role as the initial state. The N -electron neutral GS is retrieved if one electron is added to the one-electron-missing hole level in the initial cationic state γ , while the final photoabsorbed state v is retrieved if one electron is added to the v th empty level. In other words, the “extended” QP energies, ϵ_0 and ϵ_v , defined as the total energy differences between these states,

$$\epsilon_0 = E_G^N - E_\gamma^{N-1}, \quad (2a)$$

$$\epsilon_v = E_v^N - E_\gamma^{N-1}, \quad (2b)$$

represent the energy gains when one electron is added to this initial $(N-1)$ -electron cationic state γ . Such electron attachment energies of cations can be observed by the PES/IPES. Note that the former energy ϵ_0 is identical to the electron affinity (EA) of the cationic state γ (or to the ionization potential (IP) of the neutral GS if γ is the cationic GS), while the latter energy ϵ_v corresponds to the v th EA of the cationic state γ . Eq. (2b) becomes identical to Eq. (2a) when $v = 0$ is the

neutral GS. By using those energies, the PAEs can be simply obtained as

$$\Omega_v^{\text{PA}} = \varepsilon_v - \varepsilon_0 \quad (3)$$

without introducing any further relaxation.

The electron attachment energies ε_v (including ε_0) can be calculated by solving the “extended” quasiparticle equation (EQPE):[18]

$$h_s^{(1)} \phi_v(\mathbf{r}, s) + \int \Sigma_s(\mathbf{r}, \mathbf{r}'; \varepsilon_v) \phi_v(\mathbf{r}', s) d\mathbf{r}' = \varepsilon_v \phi_v(\mathbf{r}, s), \quad (4)$$

where $h_s^{(1)}$ and Σ_s represent the one-body part of the Hamiltonian and the self-energy, respectively. The symbol v may be either an occupied state or an empty state, but, in order to distinguish occupied and empty states, we will use μ for occupied states and v for empty states in what follows. In usual cases, the equation is solved for the neutral GS of the N -electron neutral system, but, in the present case, it must be solved for the initial $(N - 1)$ -electron cationic state γ . Although the form of this equation is the same as the usual QP equation, we call it the EQPE to clarify that the initial system is not the N -particle neutral GS $|\Psi_G^N\rangle$ but the $(N - 1)$ -electron cationic state $|\Psi_\gamma^{N-1}\rangle$. For atoms and small molecules, we have confirmed that the EQPE can yield reasonable values of the extended QP energies[18] by using the GWA.

Eigenvalues and eigenfunctions of Eq. (4) are identical to

$$\varepsilon_\mu = E_\gamma^{N-1} - E_\mu^{N-2}, \quad (5a)$$

$$\varepsilon_v = E_\gamma^N - E_v^{N-1}, \quad (5b)$$

and

$$\phi_\mu(\mathbf{r}, s) = \langle \Psi_\mu^{N-2} | \psi_s(\mathbf{r}) | \Psi_\gamma^{N-1} \rangle, \quad (6a)$$

$$\phi_v^*(\mathbf{r}, s) = \langle \Psi_v^N | \psi_s^\dagger(\mathbf{r}) | \Psi_\gamma^{N-1} \rangle, \quad (6b)$$

where $\psi_s(\mathbf{r})$ and $\psi_s^\dagger(\mathbf{r})$ represent for annihilation and creation operators, respectively. Here, the level from which one electron is excited by the PA process of the neutral GS is labeled by the index γ , and the initial cationic state $|\Psi_\gamma^{N-1}\rangle$ is no other than the state with one electron missing at this γ level in the neutral GS. If $\gamma = 0$, then the PA energies correspond to the HOMO-electron excitations. In principle, there is no difficulty to consider the $\gamma > 0$ cases (corresponding to the (HOMO-1)-electron, (HOMO-2)-electron, ... excitations) as well. This enables us to know only the special sort of the PAEs associated with a particular orbital γ . As a matter of fact, the total energy, E_γ^N , and total electron density, n_γ^N , of the final N -electron state v can be calculated via the simple relations

$$E_\gamma^N = E_\gamma^{N-1} + \varepsilon_v, \quad (7)$$

$$n_\gamma^N(\mathbf{r}) = n_\gamma^{N-1}(\mathbf{r}) + \phi_v^*(\mathbf{r}, s) \phi_v(\mathbf{r}, s), \quad (8)$$

where E_γ^{N-1} and n_γ^{N-1} stand for the total energy and the total electron density of the $(N - 1)$ -electron cationic state γ .

Another merit of this method is that PAEs of spin-polarized systems can be calculated more easily than those of spin-unpolarized systems, because PAEs of the spin-polarized systems can be calculated using the spin-unpolarized cations. Consider a spin-polarized system, in particular, a system whose spin multiplicity is doublet. Hamiltonian of the system is, of course, spin-polarized. However, by removing one electron from the HOMO level, the cationic system becomes spin-unpolarized, which makes the calculation easier. This simplification occurs in the case of $\gamma = 0$, *i.e.*, the excitation from the HOMO level to the LUMO+ n levels ($n = 0, 1, 2 \dots$). In what follows, we restrict ourselves to the $\gamma = 0$ case only, although this is not a necessary constraint in our framework.

The most important issue here is how to solve the EQPE (4). This issue is identical to the problem how to approximate the self-energy Σ_s . One of the popular approximation is one-shot GWA (G_0W_0) but this method depends on exchange-correlation functional of density functional theory (DFT) [19]. Self-consistent GWA has no functional dependence but usually overestimates the energy gap.[20, 21]

Ren *et al.*[22] treated the second-order screened exchange (SOSEX) and the renormalized single excitation (rSE). Their results for the binding energies of rare gas and copper clusters are in fairly good agreement with the experimental data; the mean absolute error is about 0.25 eV for RPA + SOSEX and about 0.15 eV for rPT2. Hung *et al.* [23] calculated IPs, EAs, and PAEs of aromatic molecules within the GW + BSE method. They included in their GW calculation a local density approximation (LDA)-derived vertex function ($\text{GW}\Gamma_{\text{LDA}}$). The first $\text{GW}\Gamma$ calculation (the $\text{GW}\Gamma^1$ @HSE method) was performed by Grüneis *et al.*,[24] who used $\text{GW}^{\text{TC-TC}}$ @HSE + single-shot vertex correction for the self-energy with the static approximation. The results for the QP energies of various semiconductors and insulators are slightly better than those of $\text{GW}^{\text{TC-TC}}$ @HSE, but there is still at most 0.7 eV difference from the experimental values. Maggio and Kresse [25] recently applied one-shot Hedin’s scheme with the vertex function ($\text{GW}\Gamma$) for a set of small molecules. The agreement with the experimental IP is fairly good although not excellent.

There are two important steps toward the self-consistent $\text{GW}\Gamma$ calculation. One is the problem of the energy dependence in the correlation part of the self-energy $\Sigma_s^c = \Sigma_s - \Sigma_s^x$. Shishkin *et al.* [21] proposed to linearize the energy dependence, but their method does not satisfy the Ward identity and the non-orthogonality problem remains in the resulting QP wave functions. Kuwahara *et al.*[26] proposed to linearize the energy dependence so as to satisfy the Ward identity and remove the non-orthogonality problem of the QP wave functions. The Green’s function G_s and the polarization function P are renormalized in the LGW approach as follows: G_s is renormalized using the lower triangular matrix L as $\tilde{G}_s(\omega) = L^\dagger G_s(\omega) L$. This L is defined by the Cholesky decomposition of Λ as

$$\Lambda = 1 - \left. \frac{\partial \Sigma_s(\omega)}{\partial \omega} \right|_{\omega=\omega_0} = LL^\dagger, \quad (9)$$

where ω_0 means the energy around which the self-energy is

expanded. It can be set, for example, at the mean value of the HOMO and LUMO eigenenergies. Renormalization of the polarization function $\tilde{P}$ is achieved by replacing the Green's function with the renormalized one: $\tilde{P} = -i \sum_s \tilde{G}_s \tilde{G}_s$. If the exact vertex function Γ is known, then the GW method gives the exact “extended” QP energies, but this is of course impossible. Kuwahara *et al.*[16] developed the self-consistent GW method by approximating the vertex function Γ to first order in the dynamically screened Coulomb interaction W (the GW_W method) or in the bare Coulomb interaction v (the GW_v method). They showed that the linearization procedure mentioned above is applicable also to the self-consistent GW approach just by replacing the Green's function G_s with its renormalized version $\tilde{G}_s$ (the LGWT_W and LGWT_v methods).[16] Their LGWT_W + BSE calculations produced excellent PAEs of Na, Na₃, B₂, and C₂H₂ within 0.1 eV difference from the experimental values. In this paper, we use the (L)GW $_W$ methods without BSE for cationic systems.

III. CALCULATION RESULTS AND DISCUSSION

A. Computational detail

We calculate the PAEs and IP of some spin-polarized isolated atoms and molecules by solving the extended QP equation (4) for the $(N - 1)$ -electron cationic GS, where one electron is removed from the HOMO level of the neutral GS. All calculations are performed using the all-electron mixed basis code, TOMBO,[16, 26, 27] which uses (numerical) atomic orbital (AO) and plane wave (PW) basis sets together. The minimal number of AOs including all occupied orbitals is used, although valence AOs are truncated within the non-overlapping atomic spheres. The cutoff energies of 11.06 (44.20) Ry, 14.44 (57.76) Ry, 2.18 (30.7) Ry, and 2.76 (38.9) Ry are used for PW, P , and Σ_s^c (for the cutoff energy for Σ_s^x), respectively, for Al, B, Na₃, and Li₃. The edge lengths of the face-centered-cubic unit cell are chosen as 18 Å, 14 Å, 18 Å, and 16 Å, respectively, for Al, B, Na₃, and Li₃. Moreover, the Coulomb spherical cutoff[3] is adopted to avoid the unphysical electrostatic interaction between periodic images. To apply this technique, a large enough unit cell is used. The bond lengths are 3.23, 3.23, and 5.01 Å for Na₃, and 2.76, 2.76, and 3.38 Å for Li₃. We use the plasmon-pole models [12, 28] and 800, 1400, 600, 600 levels, respectively, for Al, B, Na₃, and Li₃. For the LGWT calculations for B, Na₃, and Li₃, we set ω_0 at the value of HOMO + 3 eV.

B. Comparison of the results for IP/EA and 1st PAE

Theoretically, the IP of the neutral systems must be identical to the EA of the cationic systems if the same atomic geometry is assumed for neutral and cationic systems.[29] Here, the one-shot GW results for the IP of the neutral systems (GW(IP)) are listed in Table I together with the one-shot GW and self-consistent LGWT results for the EA of the cationic systems (GW(EA) and LGWT(EA)), all of which

should be compared with the experimental data,[30–33] for Al, B, Na₃, and Li₃. If we compare GW(EA) with GW(IP), the former is in better agreement with the experimental value for Al (the difference between GW(EA) and the experiment is 0.1 eV), while GW(EA) is in worse agreement with the experiment for Na₃ and Li₃. Therefore, we performed the self-consistent LGWT calculations for B, Na₃, and Li₃. The resulting LGWT(EA) is in excellent agreement with the experimental value for these systems; the difference between LGWT(EA) and the experiment is about 0.1 eV.

TABLE I: GW results for the ionization potential (IP) of neutral systems (GW(IP)), GW and LGWT results for the electron affinity (EA) of cationic systems (GW(EA) and LGWT(EA)), and the corresponding experimental data[30–33] in units of eV

atom/molecule	GW(IP)	GW(EA)	LGWT(EA)	Experiment
Al	5.81	5.88	-	5.98 ^a
B	8.45	8.45	8.20	8.30 ^b
Na ₃	4.24	4.35	4.21	4.08±0.05 ^c
Li ₃	4.24	4.44	4.12	3.97±0.05 ^d

^a Ref. 30, ^b Ref. 31, ^c Ref. 32, ^d Ref. 33,

Next, we show the GW + BSE (neutral) results and the GW (cation) results without BSE of the 1st PAE corresponding to the HOMO-LUMO transition for Al, B, Li₃, and Na₃ together with the experimental data [31, 34–36] (the peak corresponding to the A band observed by experiments for Na₃[35] and Li₃[36]) in Table II. The GW + BSE (neutral) results significantly underestimate the experimental PAEs as anticipated (the mechanism of the underestimation is reported in the previous research[16]), while the GW (cation) results without BSE are in fair agreement with the experimental PAEs; the difference between the GW method without BSE and the experiment is about 0.2 eV. This means that the GW method without BSE for spin-unpolarized cation systems is simpler and more accurate than the GW + BSE method for spin-polarized neutral systems.

TABLE II: GW + BSE (neutral) and GW (cation) results without BSE (present work) for the 1st PAE compared with the experimental data[31, 34–36] in eV

atom/molecule	GW + BSE	GW present work	Experiment
Al	2.94	3.23	3.14 ^a
B	4.53	5.24	4.96 ^b
Na ₃	0.76	1.71	1.85 ^c
Li ₃	0.50	1.64	1.81 ^d

^a Ref. 34, ^b Ref. 31, ^c Ref. 35, ^d Ref. 36,

C. Comparison between the GW, GWT and LGWT methods without BSE and the QC methods for PAEs

Here, we show the PAEs of B, Na₃, and Li₃ calculated by the GW, GWT and LGWT methods without BSE and compare them with the previous results of highly accurate QC calculations such as multi-configuration HF (MCHF),[37] MRDCI,[38, 39] full CI,[40] and estimated full CI[39] as well as the corresponding experimental data.[31, 35, 36, 41] We employed the self-consistent GWT approach and its linearized version (LGWT) as the beyond GW methods without BSE. All these data are listed in Tables III-V, which show the PAEs for the transitions designated in the left column.

Our self-consistent LGWT results show excellent agreement with the experiments within 0.06 eV in average and 0.10 eV at maximum. This accuracy is enough to compare with other highly accurate QC calculations such as MRDCI and full CI.

TABLE III: B: GW, GWT and LGWT results (without BSE) for the PAEs compared with the previous MCHF results[37] and experimental data[31] in units of eV

Transition	GW	GWT	LGWT	MCHF ^a	Experiment ^b
$2s^2 2p - 2s^2 3s$	5.24	4.39	4.92	4.93	4.96
$2s^2 2p - 2s^2 3p$	6.37	5.57	6.09	5.99	6.02
$2s^2 2p - 2s^2 3d$	7.00	6.15	6.71	6.76	6.79
$2s^2 2p - 2s^2 4s$	7.02	6.34	6.89	6.78	6.82

^a Ref. 37, ^b Ref. 31.

TABLE IV: Na₃: GW, GWT and LGWT results (without BSE) for the PAEs compared with the previous MRDCI[38] and full CI[40] results and experimental data[35] in units of eV

Transition	GW	GWT	LGWT	MRDCI ^a	FCI ^b	Expt. ^c
$^2B_2 - ^1A_1$	0.75	0.77	0.80	0.52	0.48	
$^2B_2 - ^2B_1$	1.14	1.14	1.10	-	-	
$^2B_2 - ^2A_1$	1.21	1.34	1.34	1.07	1.09	
$^2B_2 - ^2B_2$	1.43	1.69	1.67	1.33	-	
$^2B_2 - ^1A_2$	1.71	1.92	1.94	1.77	-	1.85
$^2B_2 - ^4A_1$	1.96	1.99	2.12	1.97	1.96	2.02
$^2B_2 - ^3B_1$	2.34	2.36	2.50	-	-	
$^2B_2 - ^2A_2$	2.55	2.38	2.56	2.61	2.51	2.58
$^2B_2 - ^6B_2$	3.04	2.56	2.60	2.85	-	

^a Ref. 38, ^b Ref. 40, ^c Ref. 35.

The LGWT results are roughly the same or better accuracy compared with the QC calculations; see also Fig. 2. However, the non-linearized GWT results for B atom and, in particular, higher excitations for Na₃ and Li₃ are not very good. This disagreement is caused by the wide gap between the QP energies at the HOMO and LUMO levels. In the case of narrow gap systems, *i.e.* when the HOMO and LUMO QP energies are not much different, approximating the energy dependence of the self-energy by substituting the HOMO QP energy is a

good approximation. On the other hand, if the LUMO QP energy is much higher than the HOMO QP energy, the approximation is no longer valid and should be improved by using the linearized LGWT method as shown here.

TABLE V: Li₃: GW, GWT and LGWT results (without BSE) for the PAEs compared with the previous MRDCI and estimated full CI (esFCI) results[39] and experimental data[36, 41] in units of eV

Transition	GW	GWT	LGWT	MRDCI ^a	esFCI ^a	Expt.
$^2B_2 - ^1A_1$	0.32	0.34	0.36	0.317	0.216	
$^2B_2 - ^1B_1$	0.71	0.73	0.71	0.787	0.711	
$^2B_2 - ^2A_1$	1.16	1.19	1.25	1.206	1.136	
$^2B_2 - ^2B_2$	1.33	1.63	1.67	1.430	1.346	
$^2B_2 - ^3A_1$	1.64	1.80	1.89	1.612	1.498	1.81 ^b
$^2B_2 - ^1A_2$	1.77	2.08	2.18	1.975	1.937	
$^2B_2 - ^2B_1$	2.22	2.32	2.47	2.320	2.245	
$^2B_2 - ^3B_2$	2.73	2.43	2.63	2.615	2.407	2.61 ^c

^a Ref. 39, ^b Ref. 36, ^c Ref. 41.

FIG. 2: Comparison of PAEs calculated by GW + BSE, GW present work (without BSE), MCHF (for B), FCI (for Na₃), MRDCI (for Li₃), and LGWT present work (without BSE). Green, blue, red bars represent, respectively, the deviations of the calculated PAEs from the experimental values for B, Na₃, and Li₃. The GW present work greatly improves the GW + BSE result but most of the deviation is still more than 0.1 eV. The LGWT present work shows excellent agreement with the experimental value within 0.1 eV, while the MRDCI result for Li₃ shows >0.1 eV deviation. Experimental values as well as MCHF, MRDCI, and FCI values are taken from Refs. 31, 35–40

IV. CONCLUSION

In this paper, we proposed the GW(Γ) method without BSE to calculate photoabsorption energies (PAEs). This method is in particular useful to spin-polarized systems. As a result, this method yields good agreement with the experimentally observed PAEs for Al, B, Na₃, and Li₃. The results are much better than those of the GW + BSE method. The result for Al is already excellent within the 0.1 eV difference from the experimental value. We also applied the beyond GW methods without BSE such as the self-consistent GWT and (linearized) LGWT methods, and found that the LGWT method without BSE yields excellent agreement with the available experimental data within 0.1 eV for B, Na₃, and Li₃. Our non-linearized

GWT results (without BSE) suggest that, in the calculation of the QP energies much higher than the HOMO energy, the energy dependence of the self-energy becomes a very important problem. The linearization of the energy dependence is essential to avoid this problem. The best is to use the self-consistent (linearized) LGWT method including the vertex correction. Its computational cost scales as $O(N^2M^3)$, where N and M are the numbers of basis functions and empty states, respectively, if the plasmon-pole model[28] is used for the Γ -related calculations (full frequency integration can be used for the GW-related calculations)[16]. This is comparable to the MRDCI method, but much less expensive than the full CI calculations. It is left for the future study to apply this method to larger molecules.

Acknowledgments

This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan as a social and scientific priority issue (Creation of new functional devices and high-performance materials to support next-generation industries) to be tackled by using post-K computer for the use of the supercomputer facilities of the Supercomputer Centers at the Institute for Solid State Physics, the University of Tokyo, at Hokkaido University, and at IMR, Tohoku University (Project IDs. hp160072, hp160234, hp170268, and hp170190).

-
- [1] A. Szabo, and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover, New York, 1996).
 - [2] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
 - [3] G. Onida, L. Reining, R. W. Godby, R. Del Sole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
 - [4] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998).
 - [5] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **80**, 3320 (1998).
 - [6] M. Rohlfing and S. G. Louie, Phys. Rev. B **62**, 4927 (2000).
 - [7] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
 - [8] D. B. Krisiloff and E. A. Carter, Phys. Chem. Chem. Phys. **14**, 7710 (2012).
 - [9] V. N. Glushkov and X. Assfeld, Theor. Chem. Acc. **135**, 3 (2015).
 - [10] D. Jacquemin, I. Duchemin, and X. Blase, J. Chem. Theory Comput. **11**, 3290 (2015).
 - [11] L. Hung, F. Bruneval, K. Baishya, and S. Ögt, J. Chem. Theory Comput. **13**, 2135 (2017).
 - [12] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
 - [13] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10159 (1988).
 - [14] D. Hirose, Y. Noguchi, and O. Sugino, Phys. Rev. B **91**, 205111 (2015).
 - [15] D. Jacquemin, I. Duchemin, X. Blase, J. Chem. Theory Comput. **11**, 3290 (2015).
 - [16] R. Kuwahara, Y. Noguchi, and K. Ohno, Phys. Rev. B **94**, 121116(R) (2016).
 - [17] F. Bruneval, S. M. Hamed, and J. B. Neaton, J. Chem. Phys. **142**, 244101 (2015).
 - [18] K. Ohno, S. Ono, and T. Isobe, J. Chem. Phys. **146**, 084108 (2017).
 - [19] J. Bois and T. Körzdörfer, J. Chem. Theory Comput. **13**, 4962 (2017).
 - [20] T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Phys. Rev. B **76**, 165106 (2007).
 - [21] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).
 - [22] X. Ren, P. Rinke, G. E. Scuseria, and M. Scheffler, Phys. Rev. B **88**, 035120 (2013).
 - [23] L. Hung, F. H. da Jornada, J. Souto-Casares, J. R. Chelikowsky, S. G. Louie, and S. Ögt, Phys. Rev. B **94**, 085125 (2016).
 - [24] A. Grüneis, G. Kresse, Y. Hinuma, and F. Oba, Phys. Rev. Lett. **112**, 096401 (2014).
 - [25] E. Maggio and G. Kresse, J. Chem. Theory Comput. **13**, 476574778 (2017).
 - [26] R. Kuwahara and K. Ohno, Phys. Rev. A **90**, 032506 (2014).
 - [27] S. Ono, Y. Noguchi, R. Sahara, Y. Kawazoe, and K. Ohno, Computer Phys. Commun. **189**, 20 (2015).
 - [28] W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988).
 - [29] F. Bruneval, Phys. Rev. Lett. **103**, 176403 (2009).
 - [30] K. Victor and W. C. Martin, J. Phys. Chem. Ref. Data **20**, 775 (1991).
 - [31] A. E. Kramida and A. N. Ryabtsev, Phys. Scr. **76**, 544 (2007).
 - [32] A. Herrmann, S. Leutwyler, E. Schumacher, and L. Wöste, Helv. Chim. Acta **61**, 453 (1978).
 - [33] Ph Dugourd, D. Rayane, P. Labastie, B. Vezin, J. Chevalere, and M. Broyer, Chem. Phys. Lett. **197**, 433 (1992).
 - [34] W. C. Martin and R. Zalubas, J. Phys. Chem. Ref. Data **8**, 817 (1979).
 - [35] C. R. C. Wang, S. Pollack, T. A. Dahlseid, G. M. Koretsky, and M. M. Kappes, J. Chem. Phys. **96**, 7931 (1992).
 - [36] H.-G. Krämer, M. Keil, C. B. Suarez, W. Demtröder, and W. Meyer, Chem. Phys. Lett. **299**, 212 (1999).
 - [37] H. Lundberg, Z. S. Li, and P. Jönsson, Phys. Rev. A **63**, 032505 (2001).
 - [38] V. Bonačickoutecký, P. Fantucci, and J. Koutecký, J. Chem. Phys. **93**, 3802 (1990).
 - [39] H. O. Beckmann, Chem. Phys. Lett. **93**, 240 (1982).
 - [40] P. K. Priya, D. K. Rai, and A. Shukla, Eur. Phys. J. D **71**, 116 (2017).
 - [41] Ph. Dugourd, J. Chevalere, M. Broyer, J. P. Wolf, and L. Wöste, Chem. Phys. Lett. **175**, 555 (1990).