Rapid Communications

$GW(\Gamma)$ method without the Bethe-Salpeter equation for photoabsorption energies of spin-polarized systems

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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 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 $GW(\Gamma)$ method not to the neutral ground state but to the cationic state to calculate PAEs without solving the BSE, which allows a rigorous one-to-one correspondence between the photoabsorption peak and the "extended" quasiparticle level. We applied the self-consistent linearized $GW\Gamma$ method including the vertex correction Γ to our method, and found that this method gives the PAEs of B, Na_3, and Li_3 to within 0.1 eV accuracy.

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I. INTRODUCTION

Photoabsorption (PA) plays a decisive role in many photorelated phenomena such as photosynthesis, photovoltaic cells, photocatalysts, photochemical reactions, photoinduced phase transitions, and so on. Photoabsorption energies (PAEs) have important information on these phenomena. The physics behind PAEs for all wavelength regions, if one ignores 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 self-consistent field (ΔSCF) method, which calculates the difference between the two total energies E_ν^N and E_G^N, has been commonly used in 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 peak positions of the PA spectrum [8,9] and n represents the computational cost required in the GS calculation; for example, $n = 6$ for multireference single and double CI (MRDCI) [8]. (This is because E_ν^N is calculated after $E_{\nu-1}^N, E_{\nu-2}^N, \ldots, E_G^N$ in the orthogonality constrained method [9].) Due to their heavy computational cost and low parallel efficiency, 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 a coarse estimation of large molecules.

The GW+BSE approach is still heavy, but, owing 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, $\varepsilon_{\mathrm{LUMO}}^N - \varepsilon_{\mathrm{HOMO}}^N$, 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, which doubly induces 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 many-body perturbation theory (MBPT) unless one uses a more sophisticated approach, such as the self-consistent $LGW\Gamma$+BSE approach [16]. In any approach solving the BSE, the resulting two-particle (electron-hole) wave functions are 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 to an N-particle EES) and the QP energy level (corresponding to an $N \pm 1$-particle EES).

In the present Rapid Communication, we propose a completely different and very tractable approach, which allows a

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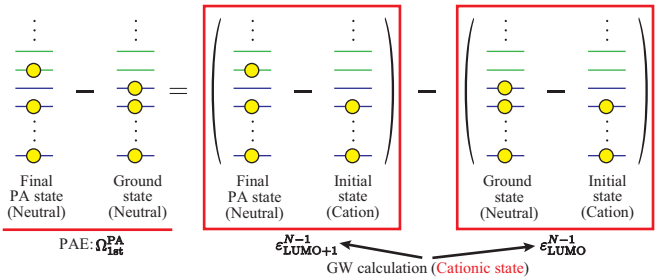

FIG. 1. The first peak PAE $\Omega_{1\mathrm{st}}^{\mathrm{PA}}$ is equal to the extended QP energy difference $\varepsilon_{\mathrm{LUMO}}^{N-1} - \varepsilon_{\mathrm{HOMO}}^{N-1}$ obtained by the GW calculation for the $(N-1)$-electron cationic GS. Here, $\varepsilon_{\mathrm{LUMO}}^{N-1}$ and $\varepsilon_{\mathrm{HOMO}}^{N-1}$ 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.

rigorous one-to-one correspondence between the PA peaks and the ("extended") QP levels [18], although each peak height (intensity or oscillator 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.

A significant point of this method is that the two energy gains, i.e., the minus of the two "extended" QP energies, in processes (1) and (2) can be obtained simultaneously by applying the standard GW method to the cationic system instead of the neutral system, and 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 highest occupied molecular orbital (HOMO) level to the lowest unoccupied molecular orbital (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 a 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. 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 method requires the GW calculation only and does not require the BSE, we named this the "$GW(\Gamma)$ method without BSE." This method is, without doubt, faster and simpler than the $GW(\Gamma)$+BSE method because the complicated BSE is no longer necessary. This method is named "$GW(\Gamma)$" but our framework allows one to replace the $GW(\Gamma)$ calculation with 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 does not need to 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 $GW(\Gamma)$ 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 observable in such a single photoexcitation process is the vertical PAE. The corresponding physical quantity is the PAE defined as

$$\Omega_{\nu}^{\mathrm{PA}} = E_{\nu}^{N} - E_{G}^{N}, \tag{1}$$

where E_{ν}^{N} and E_{G}^{N} represent, respectively, the total energies of the νth EES and the GS of the N-electron neutral system.

The simplest and most 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 ν. 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_{ν}^{N}) and the GS (E_{G}^{N}). This γth 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 ν is retrieved if one electron is added to the νth empty level. In other words, the "extended" QP energies, ε_0 and ε_ν, defined as the total energy differences between these states,

$$\varepsilon_0 = E_{G}^{N} - E_{\gamma}^{N-1}, \tag{2a}$$

$$\varepsilon_\nu = E_{\nu}^{N} - E_{\gamma}^{N-1}, \tag{2b}$$

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_ν corresponds to the νth EA of the cationic state γ. Equation (2b) becomes identical to Eq. (2a) when $\nu = 0$ is the neutral GS. By using those energies, the PAEs can be simply obtained as

$$\Omega_{\nu}^{\mathrm{PA}} = \varepsilon_\nu - \varepsilon_0, \tag{3}$$

without introducing any further relaxation.

The electron attachment energies ε_ν (including ε_0) can be calculated by solving the "extended" quasiparticle equation

(EQPE) [18],

$$h_s^{(1)}\phi_\nu(\boldsymbol{r},s) + \int \Sigma_s(\boldsymbol{r},\boldsymbol{r}';\varepsilon_\nu)\phi_\nu(\boldsymbol{r}',s)d\boldsymbol{r}' = \varepsilon_\nu\phi_\nu(\boldsymbol{r},s), \quad (4)$$

where $h_s^{(1)}$ and Σ_s represent the one-body part of the Hamiltonian and the self-energy, respectively. The symbol ν 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 ν for empty states in what follows. In the 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

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

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

and

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

$$\phi_\nu^*(\boldsymbol{r},s) = \left\langle \Psi_\nu^{N} \,\middle|\, \psi_s^\dagger(\boldsymbol{r}) \,\middle|\, \Psi_\gamma^{N-1} \right\rangle, \quad (6b)$$

where $\psi_s(\boldsymbol{r})$ and $\psi_s^\dagger(\boldsymbol{r})$ 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 none 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 PAEs associated with a particular orbital γ. As a matter of fact, the total energy E_ν^N and total electron density n_ν^N of the final N-electron state ν can be calculated via the simple relations

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

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

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 spin-polarized systems can be calculated using spin-unpolarized cations. Consider a spin-polarized system, in particular, a system whose spin multiplicity is a doublet. The 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 ($n = 0, 1, 2, \ldots$). 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 of how to approximate the self-energy Σ_s. One popular approximation is the one-shot GWA (G_0W_0), but this method depends on the exchange-correlation functional of density functional theory (DFT) [19]. The 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 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 random phase approximation (RPA)+SOSEX and about 0.15 eV for the renormalized second-order perturbation theory (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 ($GW\Gamma_{\mathrm{LDA}}$). The first $GW\Gamma$ calculation [the $GW\Gamma^1$@HSE method] was performed by Grüneis *et al.* [24], who used the $GW^{\mathrm{TC-TC}}$@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 $GW^{\mathrm{TC-TC}}$@HSE, but there is still at most a 0.7 eV difference from the experimental values. Maggio and Kresse [25] recently applied the one-shot Hedin's scheme with the vertex function ($GW\Gamma$) 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 $GW\Gamma$ calculation. One is the problem the energy dependence in the correlation part of the self-energy $\Sigma_s^{\mathrm{c}} = \Sigma_s - \Sigma_s^{\mathrm{x}}$. Shishkin *et al.* [21] proposed to linearize the energy dependence, but their method does not satisfy the Ward identity and the nonorthogonality 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 nonorthogonality 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 $GW\Gamma$ approach gives the exact "extended" QP energies, but this is of course impossible. Kuwahara *et al.* [16] developed the self-consistent $GW\Gamma$ method by approximating the vertex function Γ to first order in the dynamically screened Coulomb interaction W (the $GW\Gamma_W$ method) or in the bare Coulomb interaction v (the $GW\Gamma_v$ method). They showed that the linearization procedure mentioned above is applicable also to the

self-consistent $GW\Gamma$ approach just by replacing the Green's function G_s with its renormalized version $\tilde{G}_s$ (the $LGW\Gamma_W$ and $LGW\Gamma_v$ methods) [16]. Their $LGW\Gamma_W$+BSE calculations produced excellent PAEs of Na, Na_3, B_2, and C_2H_2 within a 0.1 eV difference from the experimental values. In this Rapid Communication, we use the $(L)GW\Gamma_W$ 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 nonoverlapping atomic spheres. Cutoff energies of 11.06 (44.20), 14.44 (57.76), 2.18 (30.7), 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, Na_3, and Li_3. The edge lengths of the face-entered-cubic unit cell are chosen as 18, 14, 18, and 16 Å, respectively, for Al, B, Na_3, and Li_3. 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 Na_3, and 2.76, 2.76, and 3.38 Å for Li_3. We use the plasmon-pole models [12,28] and 800, 1400, 600, and 600 levels, respectively, for Al, B, Na_3, and Li_3. For the $LGW\Gamma$ calculations for B, Na_3, and Li_3, we set ω_0 at the value of HOMO+3 eV.

B. Comparison of the results for IP/EA and first 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 $LGW\Gamma$ results for the EA of the cationic systems [GW(EA) and $LGW\Gamma$(EA)], all of which should be compared with the experimental data [30–33], for Al, B, Na_3, and Li_3. 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 Na_3 and Li_3. Therefore, we performed the self-consistent $LGW\Gamma$ calculations for B, Na_3, and Li_3. The resulting $LGW\Gamma$(EA) is in excellent agreement with the experimental value for these systems; the difference between $LGW\Gamma$(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 $LGW\Gamma$ results for the electron affinity (EA) of cationic systems [GW(EA) and $LGW\Gamma$(EA)], and the corresponding experimental data [30–33] in units of eV.

Atom/molecule	GW(IP)	GW(EA)	$LGW\Gamma$(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]Reference [30].
[b]Reference [31].
[c]Reference [32].
[d]Reference [33].

TABLE II. GW+BSE (neutral) and GW (cation) results without BSE (present work) for the first 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]Reference [34].
[b]Reference [31].
[c]Reference [35].
[d]Reference [36].

Next, we show the GW+BSE (neutral) results and the GW (cation) results without BSE of the first PAE corresponding to the HOMO-LUMO transition for Al, B, Li_3, and Na_3 together with the experimental data [31,34–36] (the peak corresponding to the A band observed by experiments for Na_3 [35] and Li_3 [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.

C. Comparison between the GW, $GW\Gamma$, and $LGW\Gamma$ methods without BSE and the QC methods for PAEs

Here, we show the PAEs of B, Na_3, and Li_3 calculated by the GW, $GW\Gamma$, and $LGW\Gamma$ methods without BSE and compare them with the previous results of highly accurate QC calculations such as multiconfiguration Hartree-Fock (MCHF)

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

Transition	GW	$GW\Gamma$	$LGW\Gamma$	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]Reference [37].
[b]Reference [31].

TABLE IV. Na_3: GW, $GW\Gamma$, and $LGW\Gamma$ 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	$GW\Gamma$	$LGW\Gamma$	MRDCI[a]	FCI[b]	Expt.[c]
$^2B_2$-1 $^2A_1$	0.75	0.77	0.80	0.52	0.48	
$^2B_2$-2 $^2B_1$	1.14	1.14	1.10			
$^2B_2$-2 $^2A_1$	1.21	1.34	1.34	1.07	1.09	
$^2B_2$-2 $^2B_2$	1.43	1.69	1.67	1.33		
$^2B_2$-1 $^2A_2$	1.71	1.92	1.94	1.77		1.85
$^2B_2$-4 $^2A_1$	1.96	1.99	2.12	1.97	1.96	2.02
$^2B_2$-3 $^2B_1$	2.34	2.36	2.50			
$^2B_2$-2 $^2A_2$	2.55	2.38	2.56	2.61	2.51	2.58
$^2B_2$-6 $^2B_2$	3.04	2.56	2.60	2.85		

[a]Reference [38].
[b]Reference [40].
[c]Reference [35].

[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 $GW\Gamma$ approach and its linearized version ($LGW\Gamma$) 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 $LGW\Gamma$ results show excellent agreement with the experiments within 0.06 eV on 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.

The $LGW\Gamma$ results are roughly the same or more accurate compared with the QC calculations; see also Fig. 2. However, the nonlinearized $GW\Gamma$ results for the B atom and, in particular, higher excitations for Na_3 and Li_3 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 very 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 $LGW\Gamma$ method as shown here.

TABLE V. Li_3: GW, $GW\Gamma$, and $LGW\Gamma$ 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	$GW(\Gamma)$	$LGW\Gamma$	MRDCI[a]	esFCI[b]	Expt.
$^2B_2$-1 $^2A_1$	0.32	0.34	0.36	0.317	0.216	
$^2B_2$-1 $^2B_1$	0.71	0.73	0.71	0.787	0.711	
$^2B_2$-2 $^2A_1$	1.16	1.19	1.25	1.206	1.136	
$^2B_2$-2 $^2B_2$	1.33	1.63	1.67	1.430	1.346	
$^2B_2$-3 $^2A_1$	1.64	1.80	1.89	1.612	1.498	1.81[b]
$^2B_2$-1 $^2A_2$	1.77	2.08	2.18	1.975	1.937	
$^2B_2$-2 $^2B_1$	2.22	2.32	2.47	2.320	2.245	
$^2B_2$-3 $^2B_2$	2.73	2.43	2.63	2.615	2.407	2.61[c]

[a]Reference [39].
[b]Reference [36].
[c]Reference [41].

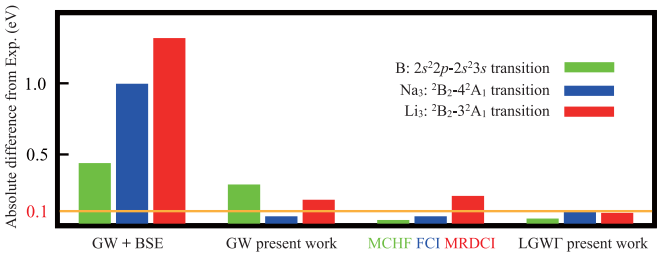

FIG. 2. Comparison of PAEs calculated by GW+BSE, GW present work (without BSE), MCHF (for B), FCI (for Na_3), MRDCI (for Li_3), and $LGW\Gamma$ present work (without BSE). Green, blue, and red bars represent, respectively, the deviations of the calculated PAEs from the experimental values for B, Na_3, and Li_3. The GW present work greatly improves the GW+BSE result but most of the deviation is still more than 0.1 eV. The $LGW\Gamma$ present work shows excellent agreement with the experimental value to within 0.1 eV, while the MRDCI result for Li_3 shows a >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 Rapid Communication, we proposed the $GW(\Gamma)$ method without BSE to calculate photoabsorption energies (PAEs). This method is in particular useful for spin-polarized systems. As a result, this method yields good agreement with the experimentally observed PAEs for Al, B, Na_3, and Li_3. The results are much better than those of the GW+BSE method. The result for Al is already excellent within a 0.1 eV difference from the experimental value. We also applied the beyond GW methods without BSE such as the self-consistent $GW\Gamma$ and (linearized) $LGW\Gamma$ methods, and found that the $LGW\Gamma$ method without BSE yields excellent agreement with the available experimental data to within 0.1 eV for B, Na_3, and Li_3. Our nonlinearized $GW\Gamma$ 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) $LGW\Gamma$ 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 a future study to apply this method to larger molecules.

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