Effects of self-consistency and plasmon-pole models on GW calculations for closed-shell molecules

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We present theoretical calculations of quasiparticle energies in closed-shell molecules using the GW method. We compare three different approaches: a full-frequency G_0W_0 (FF-G_0W_0) method with density functional theory (DFT-PBE) used as a starting mean field; a full-frequency GW_0 (FF-GW_0) method where the interacting Green's function is approximated by replacing the DFT energies with self-consistent quasiparticle energies or Hartree-Fock energies; and a G_0W_0 method with a Hybertsen-Louie generalized plasmon-pole model (HL GPP-G_0W_0). While the latter two methods lead to good agreement with experimental ionization potentials and electron affinities for methane, ozone, and beryllium oxide molecules, FF-G_0W_0 results can differ by more than one electron volt from experiment. We trace this failure of the FF-G_0W_0 method to the occurrence of incorrect self-energy poles describing shake-up processes in the vicinity of the quasiparticle energies.

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I. INTRODUCTION

Accurate knowledge of the energy of quasiparticle excitations is necessary to interpret photoemission [1,2], inverse photoemission, tunneling [3], transport [4], and other single-particle excitation experiments. The determination of quasiparticle energies is also an important step in the calculation of optical absorption and reflectivity spectra [5].

The GW method [6,7], in which the electron self-energy is evaluated to first order in the screened Coulomb interaction W and the one-electron Green's function G, is the current state-of-the-art approach for calculating accurate quasiparticle energies in crystalline bulk solids, surfaces, and nanostructures from first principles. To simplify such calculations, additional approximations are often invoked. Most studies employ a one-shot procedure, where the self-energy is evaluated using the Green's function and screened Coulomb interaction from a density functional theory (DFT) mean-field calculation. In addition, many studies employed generalized plasmon-pole models [7–9] to avoid the explicit calculation of the screened interaction at nonzero frequencies.

In recent years, many studies have applied the GW method to molecular systems [10–18]. Despite these efforts, it is not yet clear to what degree the approximations which are commonly used in GW calculations on extended systems are valid or effective in molecular systems. Previous studies explored the dependence of the results of one-shot GW calculations on the mean-field starting point [19–21]. Other studies investigated the effect of self-consistency by iterating Hedin's equations, but neglected vertex corrections [20,22,23]. Also, several works on molecules employed a generalized plasmon-pole model [12,13]. Plasmon-pole models were originally introduced for calculations on the homogeneous electron gas [6], where the inverse dielectric function exhibits a single sharp plasmon peak, and later extended to crystals using additional sum rules [7].

In this paper, we explore the importance of self-consistency and the validity of generalized plasmon-pole models in GW calculations for molecular systems. Instead of focusing on quasiparticle energies, we investigate the frequency-dependent self-energies. We observe that the self-energies exhibit many poles whose positions depend sensitively on the degree of self-consistency used in the GW calculation. These poles describe shake-up processes, where in addition to the quasiparticle an electron-hole pair is created [24]. In non-self-consistent calculations with a DFT starting mean field, we find that self-energy poles can occur erroneously close to the quasiparticle energies leading to *significant disagreement with experiment* for such excitations. Including effects of self-consistency by replacing the DFT-PBE orbital energies by self-consistent quasiparticle energies—or equivalently for molecules by Hartree-Fock energies—moves the self-energy poles away from the quasiparticle energies and gives good agreement with experiment. Remarkably, we find that non-self-consistent calculations employing a generalized plasmon-pole model [7] that conserves sum rules also yield accurate results.

II. METHODS

The energies E_n of quasiparticle excitations are the poles of the interacting one-electron Green's function and can be calculated by solving the quasiparticle or Dyson's equation:

$$h(\boldsymbol{r})\Psi_n(\boldsymbol{r}) + \int d\boldsymbol{r}'\,\Sigma(\boldsymbol{r},\boldsymbol{r}',E_n)\Psi_n(\boldsymbol{r}') = E_n\Psi_n(\boldsymbol{r}), \qquad (1)$$

where $h(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 + V_{\text{ion}}(\boldsymbol{r}) + V_H(\boldsymbol{r})$. Here, V_{ion} and V_H denote the ionic potential and the Hartree potential, respectively, and Ψ_n is the quasiparticle wave function. Σ is the electron self-energy, which we calculate in the GW

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approximation as

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

with $\eta = 0^+$. As mentioned, G denotes the interacting Green's function and W denotes the screened Coulomb interaction.

Expressing Eq. (1) in the basis of mean-field orbitals ψ_n and neglecting off-diagonal matrix elements of the self-energy, the quasiparticle equation becomes

$$E_n = \epsilon_n + \Sigma_n(E_n) - V_n^{\mathrm{xc}}, \quad (3)$$

where ϵ_n and V_n^{xc} denote the orbital energies and exchange-correlation potential matrix elements from a mean-field theory calculation and $\Sigma_n(E_n) = \langle\psi_n|\Sigma(E_n)|\psi_n\rangle$.

In practice, G and W, which are needed to construct Σ, must be evaluated within certain approximations. In the G_0W_0 approximation, one uses G and W from a mean-field calculation.

Going beyond the G_0W_0 approximation is challenging. In principle, one could iterate Eqs. (3) and (2) and recalculate G and W using the quasiparticle energies. However, because of the neglect of the vertex corrections, this procedure is not guaranteed to converge accurately to the physical result [25]. Another possibility is to update only the Green's function in Eq. (2), while keeping the screened interaction W_0 from a DFT mean-field theory. This method is motivated by the observation that, for many molecular and other large band-gap systems, the mean-field energies from DFT-PBE differ significantly from the experimental quasiparticle energies. DFT-PBE *energy differences*, however, are often serendipitously close to neutral excitation energies (see below), which are the poles of the screened interaction. This method, the GW_0 approximation, can yield excellent results for both molecular and extended systems [23,25].

Even with the G_0W_0 approximation, the calculation of the self-energy for molecules is computationally challenging. To evaluate the frequency integral in Eq. (2), it is necessary to compute G and W on a sufficiently fine frequency grid. Each evaluation of W requires a sum over all empty states to calculate the polarizability and then a matrix inversion to obtain its inverse. To reduce the computational effort, a generalized plasmon-pole model is often used to extend the zero-frequency inverse dielectric matrix to finite frequencies [7,12,14].

The generalized plasmon-pole model of Hybertsen and Louie [7] assumes the inverse dielectric matrix ($\omega > 0$) can be expressed as

$$\mathrm{Im}\epsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}'}(\omega) = A_{\boldsymbol{G}\boldsymbol{G}'}\delta(\omega - \tilde{\omega}_{\boldsymbol{G}\boldsymbol{G}'}), \quad (4)$$

where $\boldsymbol{G}$ and $\boldsymbol{G}'$ are reciprocal lattice vectors (we assume a periodic supercell approach) and $\tilde{\omega}_{\boldsymbol{G}\boldsymbol{G}'}$ denotes an effective excitation energy. Both $A_{\boldsymbol{G}\boldsymbol{G}'}$ and $\tilde{\omega}_{\boldsymbol{G}\boldsymbol{G}'}$ are determined by imposing the f-sum rule and the Kramers-Kronig relation [7].

III. COMPUTATIONAL DETAILS

We calculate self-energies and quasiparticle properties for the beryllium oxide (BeO) molecule, methane (CH_4), and ozone (O_3). We first carry out DFT calculations with the PBE exchange-correlation functional, a plane-wave basis, and norm-conserving pseudopotentials. For this, we employ the QUANTUM ESPRESSO program package [26]. We then calculate the quasiparticle energies in the full-frequency G_0W_0 (FF-G_0W_0) approximation using a basis of Kohn-Sham orbitals [11,21,27]. Because of the large computational expense, carrying out self-consistent FF-GW_0 calculations is challenging. To approximate the result of a FF-GW_0 calculation, we update the DFT-PBE energies by solving Eq. (3) with the Hartree-Fock approximation for the self-energy and use the resulting Green's function, which still has a simple quasiparticle form, in Eq. (2). Because screening is weak in a molecule, the Hartree-Fock energies are often much closer to the final quasiparticle values than DFT-PBE energies, and the Hartree-Fock Green's function is a good approximation to the self-consistent interacting Green's function. Finally, we compute the G_0W_0 self-energy using the generalized plasmon-pole approximation of Hybertsen and Louie (denoted HL GPP-G_0W_0). For all GW calculations, we employ the BERKELEYGW program package [28].

To obtain converged results, we use 950 empty states in the calculation of the screened interaction and the self-energy. In addition, we employ a static remainder correction to approximately include the effects of missing unoccupied states in the self-energy [29]. In the calculation of the screened interaction, we use supercell reciprocal-lattice vectors of kinetic energy up to 12 Ry (CH_4), 24 Ry (BeO), and 30 Ry (O_3). Finally, we employ a truncated Coulomb interaction to avoid interactions between periodic replicas [30].

IV. RESULTS

Figure 1(a) shows the graphical solution of the quasiparticle equation for the highest occupied molecular orbital (HOMO) of the CH_4 molecule from the FF-G_0W_0, FF-GW_0 and HL GPP-G_0W_0 approaches. All self-energies are smooth functions of frequency in the vicinity of the quasiparticle solution. At more negative energies, the self-energies exhibit many poles. The onset of these singularities occurs at *less negative* energies in the FF-G_0W_0 method with the first pole occurring at $\sim$−21 eV. The slower decay of the corresponding tail leads to a $\sim$0.55 eV difference of the HOMO energy compared to FF-GW_0 and HL GPP-G_0W_0, which agree very well with each other and with experiment (see Table I).

Figure 1(b) shows the self-energies associated with the lowest unoccupied orbital (LUMO) of CH_4. Here, no poles of the self-energy are located in the vicinity of the quasiparticle solution and all three approaches are in good agreement.

Figure 2(a) shows the graphical solution of the quasiparticle equation for the HOMO of BeO. The FF-G_0W_0 solution nearly coincides with a pole of the self-energy, while for the other methods the self-energy poles are located at more negative energies and the quasiparticle solution occurs in a region where the self-energy is smooth. The FF-GW_0 result differs from experiment by 0.36 eV and agrees well with the HL GPP-G_0W_0 result. In contrast, the FF-G_0W_0 quasiparticle energy differs from experiment by 1.34 eV. A similar situation occurs for the LUMO [see Fig. 2(b)]. Again, the FF-G_0W_0 quasiparticle solution nearly coincides with a self-energy pole. Such large deviations of FF-G_0W_0 from measured ionization

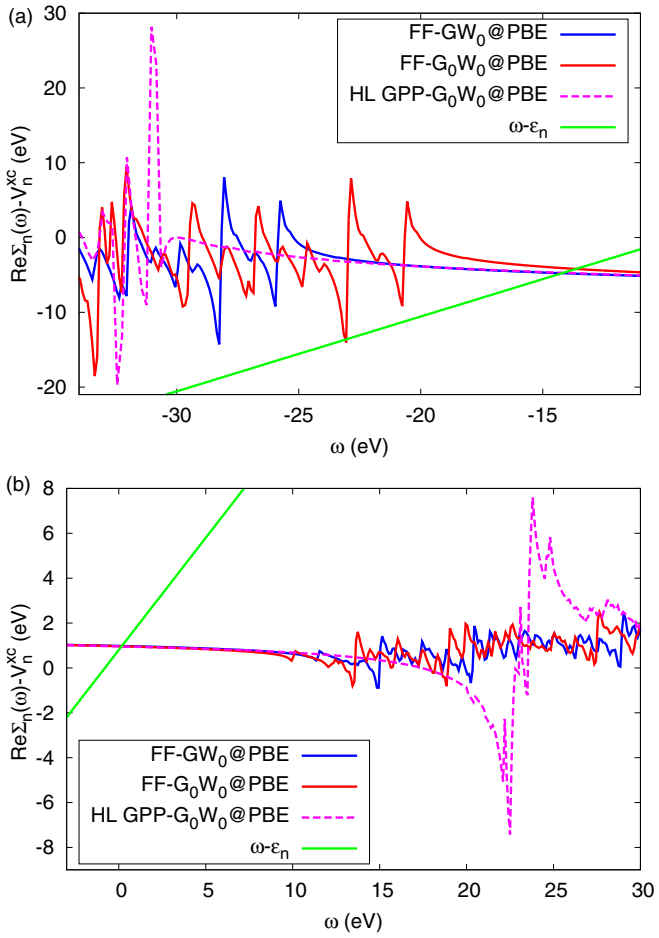

FIG. 1. (Color online) Graphical solution of the quasiparticle equation for the HOMO (a) and the LUMO (b) of methane. The quasiparticle energies E_n are given by the values of ω at the intersections of $\omega - \epsilon_n$ and $\mathrm{Re}\Sigma_n(\omega) - V_n^{\mathrm{xc}}$. Shown are self-energies from full-frequency G_0W_0 theory, full-frequency GW_0 theory, and G_0W_0 theory with the generalized Hybertsen-Louie plasmon-pole approximation. All calculations employed a DFT-PBE starting point.

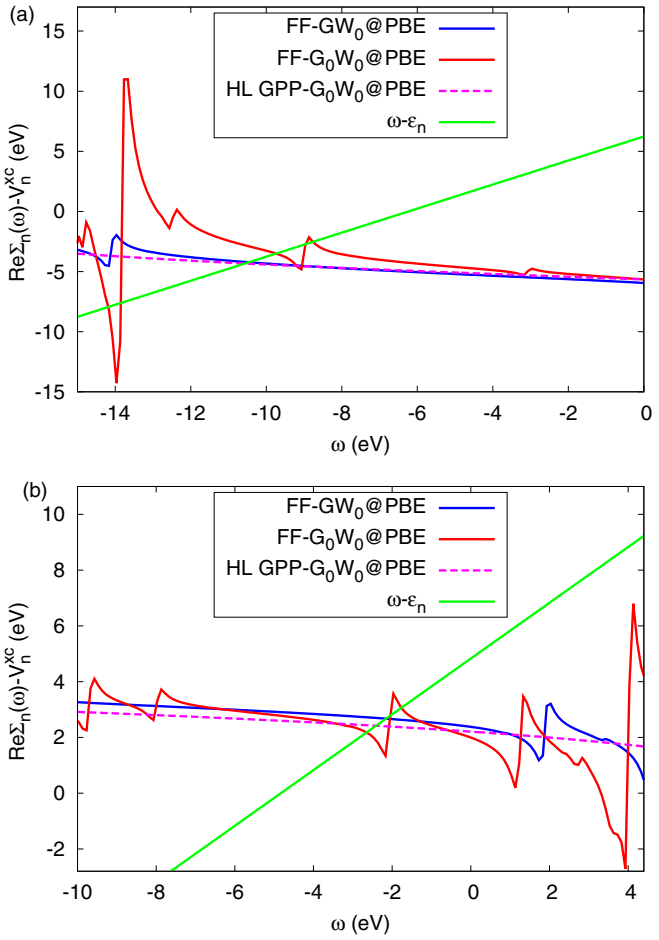

FIG. 2. (Color online) Graphical solution of the quasiparticle equation for the HOMO (a) and the LUMO (b) of the beryllium oxide molecule. The quasiparticle energies E_n are given by the values of ω at the intersections of $\omega - \epsilon_n$ and $\mathrm{Re}\Sigma_n(\omega) - V_n^{\mathrm{xc}}$. Shown are self-energies from full-frequency G_0W_0 theory, full-frequency GW_0 theory, and G_0W_0 theory with the generalized Hybertsen-Louie plasmon-pole approximation. All calculations employed a DFT-PBE starting point.

potentials have been pointed out before by Blase *et al.* [15] for a number of gas-phase molecules.

Finally, Fig. 3(a) shows the self-energy for the DFT-PBE HOMO of ozone. Again, FF-GW_0 and HL GPP-G_0W_0 lead to excellent agreement with experiment; however, FF-G_0W_0 yields a significant discrepancy of 1.3 eV because the quasiparticle energy is located in the vicinity of a self-energy pole.

We thus find a strong correlation between the accuracy of the self-energies poles and the accuracy of the resulting quasiparticle energies. For all three molecules, FF-GW_0 and

TABLE I. Comparison of quasiparticle energies from various theoretical approaches with experiment [31]: DFT-PBE, Hartree-Fock (HF), full-frequency G_0W_0 (FF-G_0W_0), full-frequency GW_0 (FF-GW_0), and G_0W_0 with the Hybertsen-Louie generalized plasmon-pole approximation (HL GPP-G_0W_0). In all calculations, a DFT-PBE starting mean field was employed. All energies are given in eV.

		DFT-PBE	HF	FF-G_0W_0@PBE	FF-GW_0@PBE	HL GPP-G_0W_0@PBE	Exp.
CH_4	HOMO	−9.44	−14.63	−13.64	−14.21	−14.16	−14.35
CH_4	LUMO	−0.80	0.60	0.16	0.18	0.16	
BeO	HOMO	−6.24	−11.35	−8.76	−10.46	−10.56	−10.1
BeO	LUMO	−4.83	−0.88	−2.65	−2.16	−2.41	
O_3	HOMO	−7.96	−14.31	−11.43	−12.97	−12.72	−12.73
O_3	LUMO	−6.16	−1.07	−2.53	−2.55	−1.86	−2.10

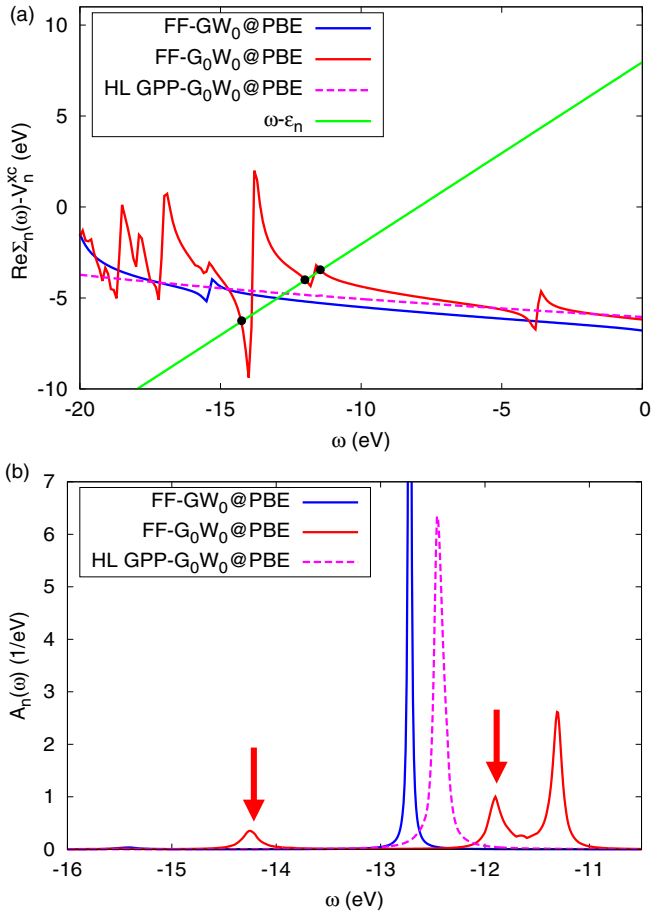

FIG. 3. (Color online) (a) Graphical solution of the quasiparticle equation for the HOMO of ozone. The quasiparticle energies E_n are given by the values of ω at the intersections of $\omega - \epsilon_n$ and $\mathrm{Re}\Sigma_n(\omega) - V_n^{\mathrm{xc}}$. Shown are self-energies from full-frequency G_0W_0 theory, full-frequency GW_0 theory, and G_0W_0 theory with the generalized Hybertsen-Louie plasmon-pole approximation. All calculations employed a DFT-PBE starting point. (b) Resulting spectral functions for the HOMO of ozone. Arrows denote the position of shake-up features. Note that some solutions of the quasiparticle equation do not give rise to peaks in the spectral function because they are suppressed by strong peaks in the imaginary part of the self-energy. The solutions which give rise to peaks in the spectral functions are marked by black dots.

HL GPP-G_0W_0 lead to self-energy poles separated by multiple electron volts from the quasiparticle energy of the DFT-PBE HOMO and LUMO and give good agreement with experiment. In contrast, we find significant disagreement between experiment and FF-G_0W_0 results when the quasiparticle energies are close to the incorrectly computed self-energy poles. To understand the differences in the positions of the self-energy poles, we express the FF-G_0W_0 self-energy as the sum of a bare exchange contribution and a frequency-dependent correlation contribution given by

$$\langle m|\Sigma^c(\omega)|m\rangle = \sum_{nI} \frac{|V_{mnI}|^2}{\omega - \epsilon_n - \Omega_I \mathrm{sgn}(\epsilon_n - \mu) + i\eta}, \quad (5)$$

TABLE II. Comparison of lowest experimental neutral singlet excitation energies of the molecules [34–38] with energy differences from density-functional theory (DFT-PBE) and Hartree-Fock (HF) calculations. The neutral excitation energies are the poles of the screened interaction. All energies are given in eV.

	DFT-PBE	HF	Exp.
CH_4	8.64	14.03	9.87–10.5
BeO	1.41	10.47	1.48
O_3	1.80	13.24	2.0

where μ denotes the chemical potential and V_{jnI} is a fluctuation potential [27,32]. Also, Ω_I is a pole of the screened interaction W and corresponds to a neutral excitation energy of the system [6]. For molecular systems, the poles of the screened interaction within the random-phase approximation are typically quite close to energy differences of the DFT-PBE mean-field theory used to calculate W [33]. Table II shows that DFT-PBE energy differences agree very well with experimental optical excitation energies in the three molecules, indicating that the screened interaction from DFT-PBE is reasonably accurate. In contrast, Hartree-Fock energy differences differ by multiple electron volts from experiment, as expected, as electron-hole attractions in optical excitations are neglected within Hartree-Fock theory.

According to Eq. (5), the FF-G_0W_0 self-energy poles occur at $\omega = \epsilon_n - \Omega_I$ (if n is an occupied state). Even if the values of Ω_I were accurate, the FF-G_0W_0 self-energy poles would be incorrectly positioned if the mean-field energies ϵ_n differ from the quasiparticle energies. In our approximate FF-GW_0 method, the DFT-PBE orbital energies are replaced by Hartree-Fock energies, which are closer to the correct quasiparticle energies and more negative by multiple electron volts (see Table I). This FF-GW_0 approach thus moves the self-energy poles to *more negative* energies. In the HL GPP-G_0W_0 method, DFT-PBE energies are used in Eq. (5), but for each $W_{GG'}$ all poles are replaced by a single effective pole. To conserve sum rules [7], the energy of the effective pole must be larger than the smallest Ω_I (see Fig. 4). In effect, this also results in a shift of the self-energy poles to more negative energies. We thus find that *different reasons* are responsible for the shift of the self-energy poles to more appropriate values in FF-GW_0 and HL GPP-G_0W_0 approaches. We note that while the resulting self-energies agree quite well in the vicinity of the quasiparticle solution they disagree at higher energies where shake-up structures are important. This could result in inaccuracies of the generalized plasmon-pole approximations for the so-called inner valence states [24].

For unoccupied states in the sum in Eq. (5), the self-energy poles are located at $\omega = \epsilon_n + \Omega_I$. The orbital energies in Hartree-Fock are again closer to the true quasiparticle energies than those from DFT-PBE (see Table I), resulting in a shift of the self-energy poles to more positive energies. The increase of the effective Ω_I in the HL GPP-G_0W_0 theory has the same effect. The above discussion shows that use of FF-G_0W_0 is particularly problematic for molecules with a small DFT-PBE HOMO-LUMO gap, resulting in self-energy poles in the vicinity of the quasiparticle energy.

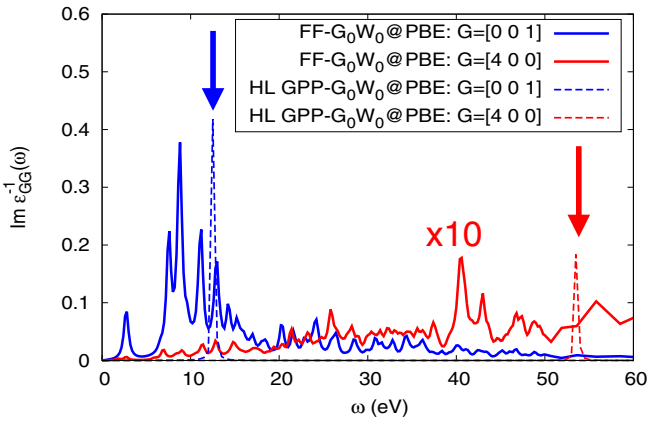

FIG. 4. (Color online) Imaginary part of the inverse dielectric matrix for the BeO molecule in a supercell calculation. Shown are the full-frequency result (FF) and the Hybertsen-Louie generalized plasmon-pole (HL GPP) model for $\boldsymbol{G} = \boldsymbol{G}' = [001]2\pi/a_0$ and $\boldsymbol{G} = \boldsymbol{G}' = [400]2\pi/a_0$ (multiplied by a factor of 10) with a_0 denoting the linear dimension of the supercell. Arrows denote the positions of the effective excitations in the generalized plasmon-pole model. The molecular axis is along the z direction.

Finally, we discuss the physical meaning of the singular structures in the self-energy. These poles give rise to additional peaks in the spectral function [see Fig. 3(b)] describing so-called shake-up processes where an electron-hole pair is excited *in addition* to a quasiparticle [24]. Also, in electronic systems with open shells, the self-energy poles are responsible for the *multiplet structure* arising from the coupling of angular momenta of the outer valence shell and of the hole left behind in the photoemission process [11]. In extended systems, additional features in spectral functions arising from the shake-up of plasmon modes, known as plasmon satellites, have received much attention recently [1,39,40].

V. CONCLUSIONS

We have computed self-energies and quasiparticle properties for three molecules using three approximate GW methods employing a DFT-PBE mean-field starting point. Results of the full-frequency G_0W_0 approximation can differ significantly (by more than 1 eV) from experimental findings. We have traced this failure of the full-frequency G_0W_0 method to the occurrence of inaccurate self-energy poles in the vicinity of the quasiparticle energy. Both a full-frequency GW_0 method and G_0W_0 with the generalized plasmon-pole approximation shift the self-energy poles away from the quasiparticle energies and lead to excellent agreement with experiment. The generalized plasmon-pole model is therefore a valuable approximation for molecular systems, reducing the computational cost significantly compared to full-frequency self-consistent approaches. We expect that the effects of self-consistency are important for a wide range of molecules, particularly those with a mean-field HOMO-LUMO gap of similar or smaller size than the typical quasiparticle shifts.

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