

# Two-photon absorption spectrum of liquid water and the effect of nondiagonal self-energy elements in the self-consistent $GW$ approach on the band gap

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(Received 29 June 2017; published 7 December 2017)

In the first part of the present paper, the two-photon absorption spectrum of liquid water is calculated using an *ab initio* real-time many-body approach. Correlation effects, such as single-particle and excitonic effects, are included, with the latter showing large impact on the shape and peak positions of the two-photon spectrum. A broad peak at 10.0 eV is calculated, in excellent agreement with the experimental reference. In the second part, we show the impact of the on- and off-diagonal elements of the self-energy operator upon  $GW$  self-consistency (depending on the number of quasiparticle-corrected unoccupied bands) on the electronic band gap of liquid water at the  $\Gamma$  point. The off-diagonal self-energy elements increase the electronic gap, correcting previous results reported by W. Chen *et al.* [*Phys. Rev. Lett.* **117**, 186401 (2016)] by 0.52 eV, and putting at the same time the non-self-consistent bootstrap approximation for the vertex function into question. Furthermore, depending on the calculated band gap using different  $GW$  flavors, the absolute position of the absorption band of the nonlinear spectrum is affected.

DOI: [10.1103/PhysRevB.96.245109](https://doi.org/10.1103/PhysRevB.96.245109)

## I. INTRODUCTION

The *ab initio* Green's function theory [1,2] proved to be a powerful and reliable method for calculation of linear response optical properties beyond the independent-particle approximation (IPA), as it accounts for important many-body effects, such as single-particle and excitonic effects through the self-energy and its derivative with respect to the Green's function. However, in contrast to the linear response Green's function theory, the inclusion of many-body effects for nonlinear optical susceptibilities in the frequency domain turns out to be an extremely difficult and challenging task, as the complexity of the corresponding nonlinear expressions grows with increasing perturbation order. Now in order to lower computational difficulties stemming from higher-order nonlinear expressions, a time-domain-based approach is used [3–9], instead of operating in the usual frequency domain like in the standard  $GW/BSE$  (Bethe-Salpeter equation) approach.

Within this time-domain approach the nonlinear susceptibility is obtained from the dynamical polarization  $P$  of the system which is expanded in powers of the external field  $\varepsilon$ :

$$P = \chi(1)\varepsilon^1 + \chi(2)\varepsilon^2 + \chi(3)\varepsilon^3 + \dots \quad (1)$$

This domain transformation enormously simplifies the complexity allowing for an efficient calculation of nonlinear optical spectra because of the following major advantages: (i) Many-body effects can be easily taken into account by adding the corresponding operator to the effective Hamiltonian. (ii) The time-domain approach is not perturbative, meaning that the nonlinear susceptibilities can be calculated at any external field order without increasing the computational cost.

However, one major problem still remains for both frequency-based and real-time-based approaches. That is the correct definition of the position operator (length gauge) within the Born–von Kármán periodic boundary conditions (PBC) for calculation of dipole matrix elements between the periodic part

of the Bloch functions. A correct definition of the position operator within the PBC was introduced by means of the geometric Berry phase in the modern theory of polarization [9]. We exactly use this definition to proceed further.

To better understand this *ab initio* real-time approach, we briefly present in the following the fundamental equations, and further show the nonlinear two-photon absorption spectrum of liquid water, demonstrating the reliability of the real-time approach in predicting the experimental two-photon spectrum, and hence in general the nonlinear phenomena. In the second part of this paper, we accurately quantify the impact of single-particle effects on the electronic band gap of liquid water. This is of particular importance, since the gap extremely affects the peak positions of any optical calculations. Here, we show the impact of on- and off-diagonal elements of the self-energy operator upon  $GW$  self-consistency with the latter leading to considerable increase of the gap.

## II. THEORETICAL BACKGROUND

In the real-time many-body approach a set of coupled one-particle effective time-dependent Schrödinger equations is solved:

$$i\hbar \frac{d}{dt} v_{mk} = (H_k^{sys} + i\varepsilon \partial_k) v_{mk}, \quad (2)$$

where  $v_{mk}$  is the periodic part of the Bloch functions, determining the system polarization,  $H_k^{sys}$  stands for the system Hamiltonian, and  $\varepsilon \partial_k$  describes the coupling with the external field  $\varepsilon$  in the dipole approximation. This coupling is gauge invariant and takes the form of a  $k$  derivative  $\partial_k$ , since we impose Born–von Kármán periodic boundary conditions.

By integrating Eq. (2), and from  $v_{mk}$ , the time-dependent polarization of the system  $P_{||}$  along the lattice vector  $\mathbf{a}$  is calculated as

$$P_{||} = -\frac{ef|\mathbf{a}|}{2\pi\Omega_c} \text{Im} \log \prod_{i=k}^{N_k-1} \det S(k, k+q), \quad (3)$$

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where  $S(k, k+q)$  is the overlap matrix between the valence states  $v_{nk}$  and  $v_{mk+q}$ ,  $\Omega_c$  is the unit cell volume,  $f$  is the spin degeneracy,  $N_k$  is the number of  $k$  points along the polarization direction, and  $q = 2\pi/(N_k a)$ . In Eq. (2) the system Hamiltonian incorporates different levels of approximation such as the following:

(1) The independent-particle approximation:

$$H_k^{\text{IP}} \equiv H_k^{\text{KS}}, \quad (4)$$

where  $H_k^{\text{KS}}$  is the unperturbed Kohn-Sham Hamiltonian.

(2) The quasiparticle (QP) approximation:

$$H_k^{\text{QP}} \equiv H_k^{\text{KS}} + \Delta H_k, \quad (5)$$

where a scissor operator shift  $\Delta H_k$  is added to the KS Hamiltonian, estimated from many-body perturbation theory in order to account for QP effects.

(3) The full  $GW+BSE$  approximation:

$$H_k^{GW+BSE} \equiv H_k^{\text{KS}} + \Delta H_k + V_h(\mathbf{r})[\Delta\rho] + \Sigma_{\text{SEX}}[\Delta\gamma], \quad (6)$$

where  $V_h(\mathbf{r})$  is the time-dependent Hartree term as a functional of density variation:

$$\Delta\rho \equiv \rho(\mathbf{r}; t) - \rho(\mathbf{r}; t = 0). \quad (7)$$

The Hartree term describes local-field effects arising from inhomogeneities in crystal densities, while  $\Sigma_{\text{SEX}}$  is the screened exchange self-energy term and accounts for the electron-hole effects (as known from BSE).  $\Sigma_{\text{SEX}}$  is a functional of the variation of the nonlocal density matrix induced by the external field  $\varepsilon$ .  $\Delta\gamma$  is written as

$$\Delta\gamma \equiv \gamma(\mathbf{r}, \mathbf{r}'; t) - \gamma(\mathbf{r}, \mathbf{r}'; t = 0). \quad (8)$$

The terms beyond the KS Hamiltonian describe correlation effects, impacting the nonlinear spectra. It should be noted that in the limit of small perturbation Eq. (6) reproduces the standard  $GW+BSE$  optical absorption spectra.

### III. TECHNICAL DETAILS

In the following, we calculate the two-photon absorption spectrum of liquid water (snapshots obtained from Ref. [10]) at different approximation levels, and verify the effect of correlation approximations on the nonlinear spectrum. We perform a ground-state calculation with a density cutoff of 400 Ry using QUANTUM ESPRESSO [11] with the PBE [12] exchange-correlation functional and norm-conserving Troullier-Martins [13] pseudopotential to mimic core effects. We further calculate the QP energies within the frequency-dependent Green's function formalism using YAMBO [14]. In order to integrate Eq. (2), we run a polarization simulation for a time interval of 60 fs using the numerical approach described in Refs. [15,16], with a time step of  $\Delta t = 0.01$  fs which guarantees numerically stable and sufficiently accurate simulations. A dephasing of 0.4 eV is used to simulate the experimental finite broadening. Simulation of time-dependent polarization is performed using LUMEN [9] which is a subprogram of YAMBO. In both  $GW$  and nonlinear optical calculations nonlocal parts of the pseudopotential are explicitly taken into account.

Further, for the computation of the self-consistent self-energy effects the Wiener *ab initio* simulation package

(VASP) [17,18] is used with the PBE functional and the projector augmented wave method [19,20]. The self-energy effects are computed for a 32-water snapshot obtained from Ref. [21]. We use a kinetic energy cutoff of 100 Ry for the wave function, up to 4032 bands for the Green's and polarization functions, and 10 Ry and 20 frequencies for the dielectric function cutoff and its frequency sampling for accurate capturing of dynamic correlation.

### IV. TWO-PHOTON ABSORPTION SPECTRUM OF LIQUID H<sub>2</sub>O

The two-photon absorption (TPA) was first predicted by Göppert-Mayer in 1931 in her doctoral dissertation [22]. TPA is a nonlinear phenomenon which is related to the imaginary part of the third-order nonlinear susceptibility. Further, TPA in contrast to one-photon absorption follows different selection rules. This stems from the fact that photons have spin of  $\pm 1$ ; therefore, one-photon absorption involves an electron changing its molecular orbital by an angular momentum of  $\pm 1$ , while two-photon absorption requires a change of  $+2$ ,  $0$ , or  $-2$ , because of the involvement of two simultaneous incoming photons each of which with spin  $\pm 1$ .

Since TPA is a third-order optical process and hence quite weak, a very high laser field intensity is required in order to realize a much faster increase of the strength of the interaction with the electric field of the light than in the linear process. Here for liquid water, we set the field intensity to  $10^6$  and  $10^7$  kWL/m<sup>2</sup>, and chose a monochromatic light with an energy of 6.2 eV to calculate the nonlinear response. This initial photon energy is chosen in accordance with the two-photon experimental setup. The QP energies are obtained from the single-shot ( $G_0 W_0$ ) and eigenvalue  $GW$  approach (i.e.,  $G_n W_n$  with  $n$  being the number of iterations in the self-consistent loop) in the diagonal approximation using a real-axis integration method and are accordingly included in the two-photon absorption spectra. The single-particle self-energy corrections to the KS energy bands induce a rigid shift towards higher energy regimes as a consequence of the band gap opening upon decrease of screening effects through the energy update in  $G$  and  $W$ .

#### Correlation effects on the nonlinear spectrum

In the following, we show the effect of the correlation approximations on the TPA spectrum of liquid water, namely, (i) the independent-particle approximation with QP energies obtained from both single-shot and eigenvalue self-consistent  $GW$  approaches, denoted as IPA+QP; (ii) IPA and QP energies with excitonic effects described with the Bethe-Salpeter equation (BSE), denoted as IPA+QP+BSE.

The TPA spectra of the 27-water system averaged over five configurations are shown in Fig. 1 within the independent-particle approximation with QP energies and excitonic effects (BSE). As can be seen, the IP+ $G_0 W_0$  and IP+ $G_n W_n$  methods overestimate the experimental broad band at 10.0 eV by 0.5 and 1.5 eV, respectively. Inclusion of excitonic effects gives rise to a redshift of the maximum of the absorption band by about 1.5 eV relative to the non-self-consistent  $GW$  approach. Only if the excitonic effects in combination with

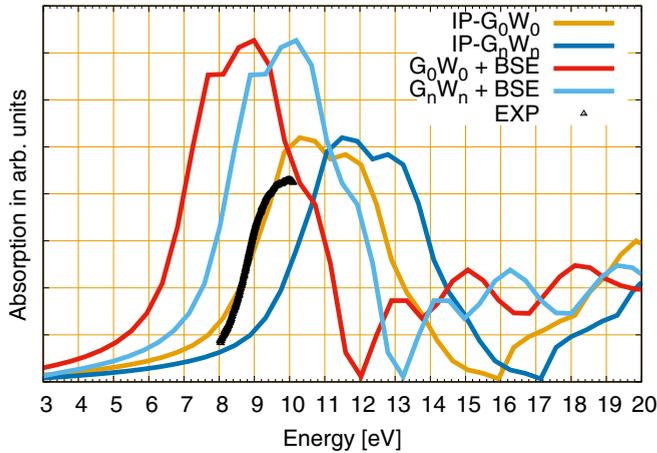


FIG. 1. The calculated two-photon absorption spectra of liquid water (27-water box) based on the IP+ $G_0W_0$ , IP+ $G_nW_n$ ,  $G_0W_0$ +BSE, and  $G_nW_n$ +BSE methods are shown. A broad main peak at about 10 eV fully consistent with the experimental reference (black tile), followed by a shoulder at about 12 eV, is observed based on the  $G_nW_n$ +BSE method. 64 (un)occupied bands are used as transition bands to achieve convergence for spectral weights.

update of QP energies both in  $G$  and  $W$  are explicitly taken into account, a quantitative agreement is obtained with the experimental reference measured by Elles *et al.* [23] at 10.0 eV (the experimental spectrum was measured only between 8 and 10 eV). This is an interesting aspect since in the linear spectrum, depending on the dispersion correction schemes used for water structures, a  $G_0W_0$  or a partially eigenvalue self-consistent  $G_nW_0$  for electronic structure calculations is enough to be able to reproduce the experimental first absorption band at 8.1 eV [10] (assuming one uses here classical water structures), whereas for the nonlinear case energy update in both  $G$  and  $W$  (i.e.,  $G_nW_n$ ) is required.

Further, as for the linear spectrum of liquid water where excitonic correlations (coupled motion of electron-hole pairs) are of extreme importance for a quantitative description of the spectrum, such a two-particle correlation is important for TPA as well, altering weight distributions and peak positions considerably.

It should be noted that the average band gap calculated for this set of five water snapshots is 8.5 eV, and update of the QP energies in  $G$  and  $W$  results in a gap of 9.69 eV. This gap increase of almost 1.2 eV is reflected in the nonlinear spectrum as a rigid blueshift of the spectrum, improving considerably the agreement with the experimental reference in combination with excitonic effects.

## V. NONDIAGONAL SELF-CONSISTENT $GW$ EFFECTS

In order to be able to reliably predict peak positions of optical absorption spectra, it is generally of extreme importance to calculate the electronic band gaps accurately, as we have seen in Sec. IV. Such a calculation was carried out for liquid water by Chen *et al.* [21] inspecting several important aspects affecting the gap. They studied the impact of self-consistency effects both in the Green's function  $G$  and the dynamically screened interaction  $W$  by updating both

TABLE I. The effect of band corrections, depending on the number of corrected bands (indicated by the corresponding number in the parentheses), in the diagonal approximation ( $GW$ ) and in the full self-energy matrix (sc $GW$ ) is shown for one classical water snapshot (32-box). The result of Chen using QSGW is also given. Furthermore, all calculations are performed at the  $\Gamma$  point. A finer  $k$  mesh ( $2 \times 2 \times 2$ ) increases the gap by about 0.1 eV. 14 iterations are run and all gaps are given in eV.

Approach (bands) (corrected bands)	$\Gamma \rightarrow \Gamma$ (direct gap)
$GW$ (2016) (256)	9.687
$GW$ (2016) (1216)	9.752
$GW$ (2016) (2016)	9.743
sc $GW$ (2016) (256)	9.854
sc $GW$ (2016) (350)	10.032
sc $GW$ (2016) (1216)	10.426
sc $GW$ (2016) (2016)	10.426
sc $GW$ (3008) (3008)	10.528
sc $GW$ (4032) (4032)	10.556
QSGW (2016) (350)	10.327 [21]
NQE	-0.7 [21]
Vertex (non-sc bootstrap)	-0.9 [21]
Expt.	8.7 [26]

quasiparticle (QP) energies and wave functions. They also included vertex corrections in  $W$  and nuclear quantum effects (proton delocalization) with a 0.9 and 0.7 eV decrease in the gap, respectively. In a previous study by us [24], we analyzed in water the effect of electron-phonon coupling, and energy-only  $GW$  self-consistency (ev $GW$ ) in the diagonal approximation (diagonal self-energy) on the band gap. We pointed out that the diagonal ev $GW$  simulates implicitly vertex corrections due to fortunate error compensation between the off-diagonal elements of the self-energy of the self-consistent  $GW$  (keyword in VASP "ALGO=sc $GW$ ") and the vertex corrections in  $W$ . The impact of the higher-correlation diagrams (vertex effects) was calculated by Chen based on the head element of the non-self-consistent bootstrap kernel [25] and reported to be a 0.9 eV decrease in gap.

Now in this study we go a step further, and calculate explicitly the impact of off-diagonal elements of the self-energy operator on the band gap depending on the number of QP-corrected unoccupied bands. As shown in Table I in the diagonal eigenvalue  $GW$  scheme (keyword in VASP "ALGO=GW"), the effect of QP band corrections of higher-lying unoccupied bands (2016 bands) on the band gap is negligible and of about 0.05 eV increase. By contrast, the sc $GW$  band corrections of the higher-lying unoccupied bands in the nondiagonal approximation is sizable and of 0.68 eV increase (relative to 256 band corrections) for the direct gap. It should be noted (as shown in Table I) that the convergence of the nondiagonal self-energy elements is extremely slow and therefore sc $GW$  QP band corrections are required for a large number of bands, which in turn decrease the screening, giving rise to an increased band gap.

We observe that the convergence is almost reached with 3008 bands and band corrections with an error of less than 0.03 eV relative to 4032 bands. This is an important aspect when using the nondiagonal self-consistent  $GW$  approaches

in combination with different approximations for the vertex function, since the induced gap increase upon the off-diagonal elements puts the reliability of the non-self-consistent bootstrap kernel  $f_{xc}$  in the description of the vertex corrections into question, as applied by Chen *et al.* [21].

The diagonal self-consistent energy-only  $GW$  approximation in combination with the nuclear quantum effect (NQE) (leading to a decrease of the band gap by 0.7 eV [21]) gives a much more accurate prediction of the experimental gap. This is due to the fact that the diagonal eigenvalue  $GW$  already contains to some extent vertex effects in an implicit manner, or in other words the off-diagonal elements of the self-energy operator and vertex corrections would have canceled each other if they were both taken into account explicitly. Furthermore, we point out that if a vertex correction is added to an approach, such as energy-only  $GW$ , which already implicitly accounts for the vertex effect, one ends up with the vertex double counting problem [24,27], which should be avoided, since otherwise the gap will be underestimated.

In Table I the result of the quasiparticle self-consistent  $GW$  approach (QSGW) with inclusion of off-diagonal elements from Ref. [21] is given. The implementation details of sc $GW$  in VASP can be found in Ref. [28]. It should be noted that sc $GW$  differs slightly from QSGW due to different renormalization factors  $Z$  [ $Z(\text{sc}GW) < 1$  and  $Z(\text{QSGW}) = 1$ ]. However, the sc $GW$   $Z$  factors are near 1 for liquid water (0.88–0.93). Furthermore, the effect of off-diagonal elements of the self-energy operator on the band gap depending on the number of corrected unoccupied bands is independent of the value of the renormalization factors  $Z$  in sc $GW$  and QSGW, because off-diagonal elements change the Green's function in both approaches.

A further interesting point is that the sc $GW$  approach with 350 corrected bands shows a deviation of  $-0.3$  eV from the QSGW reference result. This indicates that even the sc $GW$  approach implicitly contains to some extent vertex effect but much less than the diagonal energy-only  $GW$  approach.

In Table II it is explicitly shown that in the sc $GW$  approach the increase of the number of corrected unoccupied bands mainly affects the absolute energy position of the valence band maximum (VBM), whereas the conduction band minimum (CBM) is much less sensitive to the QP corrections from higher-lying states. The VB energy position is decreased by about 1 eV, while the CB energy shows a small decrease of 0.07 eV.

In the end, in the QSGW approach with QP corrections for a large number of bands (off-diagonal self-energy effects) and inclusion of nuclear quantum effects, one needs a more accurate vertex approximation to be able to accurately predict

TABLE II. The effect of the number of corrected unoccupied bands in the sc $GW$  approach on the absolute energy position (in eV) of the valence band maximum (VBM) and conduction band minimum (CBM) at the  $\Gamma$  point is shown for one classical water snapshot (32-box).

	(Bands) (Corrected bands)	Absolute position
VBM	(2016) (256)	$-6.81$
CBM	(2016) (256)	$2.87$
VBM	(2016) (1216)	$-7.59$
CBM	(2016) (1216)	$2.83$
VBM	(3008) (3008)	$-7.70$
CBM	(3008) (3008)	$2.82$
VBM	(4032) (4032)	$-7.75$
CBM	(4032) (4032)	$2.80$

the experimental gap of liquid water in the full  $GW$  theory; otherwise the gap will be overestimated, and the agreement with experimental reference is deteriorated.

## VI. CONCLUSIONS

We presented the nonlinear two-photon absorption spectrum of liquid water using an *ab initio* real-time many-body approach which includes the single-particle and excitonic effects through addition of the corresponding Hamiltonians. We showed that correlation effects considerably impact the spectrum. The IP approximation with the single-shot QP corrections is not sufficient to describe the experimental spectrum. Only a combination of eigenvalue  $GW$  and excitonic effects results in an experimentally consistent two-photon spectrum. Further, we highlighted the importance of the effect of QP energy corrections of higher-lying unoccupied bands increasing the strength of the off-diagonal elements of the self-energy matrix. This led to an increase of the band gap by 0.52 eV in comparison to the reported result of Chen *et al.*, clearly challenging the reliability of the non-self-consistent vertex correction in the bootstrap approximation.

## ACKNOWLEDGMENTS

We thank the Deutsche Forschungsgemeinschaft for financial support for this work within the Collaborative Research Center SFB 813: Chemistry at Spin Centers, Project A2, Theoretical methods for studying long-range charge and spin separation in excited states of large molecules, solids, and surfaces. We thank Dr. Wei Chen for providing us with the 32-water snapshots.

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