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Simple many-body based screening mixing ansatz for improvement of GW/Bethe-Salpeter equation excitation energies of molecular systems

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We propose a simple many-body based screening mixing strategy to considerably enhance the performance of the Bethe-Salpeter equation (BSE) approach for prediction of excitation energies of molecular systems. This strategy enables us to closely reproduce results of highly correlated equation of motion coupled cluster singles and doubles (EOM-CCSD) through optimal use of cancellation effects. We start from the Hartree-Fock (HF) reference state and take advantage of local density approximation (LDA) based random phase approximation (RPA) screening, denoted as W_0-RPA@LDA with W_0 as the dynamically screened interaction built upon LDA wave functions and energies. We further use this W_0-RPA@LDA screening as an initial screening guess for calculation of quasiparticle energies in the framework of G_0W_0@HF. The W_0-RPA@LDA screening is further injected into the BSE. By applying such an approach on a set of 22 molecules for which the traditional GW/BSE approaches fail, we observe good agreement with respect to EOM-CCSD references. The reason for the observed good accuracy of this mixing ansatz (scheme A) lies in an optimal damping of HF exchange effect through the W_0-RPA@LDA strong screening, leading to substantial decrease of typically overestimated HF electronic gap, and hence to better excitation energies. Further, we present a second multiscreening ansatz (scheme B), which is similar to scheme A with the exception that now the W_0-RPA@HF screening is used in the BSE in order to further improve the overestimated excitation energies of carbonyl sulfide (COS) and disilane (Si_2H_6). The reason for improvement of the excitation energies in scheme B lies in the fact that W_0-RPA@HF screening is less effective (and weaker than W_0-RPA@LDA), which gives rise to stronger electron-hole effects in the BSE.

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I. INTRODUCTION

Nowadays, the many-body perturbation approach is an established state-of-the-art method for *ab initio* computation of finite system properties [1–18], representing a reliable alternative to the widely employed time-dependent density functional theory (TD-DFT) [19,20]. This many-body scheme based on Green's function G, dynamically screened interaction W, and the Bethe-Salpeter equation accounting for electron-hole effects, known as the GW/BSE approach, represents a methodology that (i) avoids dependency on the starting orbitals by means of updating of orbital energies through self-consistent iteration of a closed set of one-particle integrodifferential equations (in practice approximated equations), known as Hedin-Pentagon [21]; (ii) avoids asymptotic correction of the exchange potential in the long-range regime [22]; and (iii) avoids tuning of any parameter such as the range-separation parameter in the range-separated hybrid functionals for quantitative predication of charge-transfer excited states as in TD-DFT [23–25].

However, application of GW/BSE on top of HF initial orbitals demonstrated its consistent failure to predict the correct excitation energies regardless of the diverse strategies applied so far, being partial or eigenvalue or eigenfunction self-consistency in G and W [24]. Now in order to enhance the accuracy power of the HF based GW/BSE approach, we propose a simple straightforward screening mixing scheme, which considerably enhances the accuracy of the excitation energies obtained from the traditional GW/BSE strategies in a fully *ab initio* manner with no parameter involved. To show the improved accuracy of the proposed schemes, we present results concerning the first five singlet vertical excitation energies (S_1–S_5) of 20 small molecules. The choice of this particular set of molecules was motivated by the fact that the traditional GW/BSE approaches fails to predict the excitation energies accurately [24]. We further check the consistency and robustness of the proposed screening procedures on the excited states of two large biological systems for which recent EOM-CCSD calculations became possible due to algorithmic improvements [26].

II. SCREENING MIXING

In order to enhance the performance of GW/BSE, it is of utmost importance to adequately enhance the screening quality, as the entire theoretical building block of many-body perturbation theory is based upon screening. To this end, we propose two mixing schemes, which involve the following steps.

Scheme A. (i) We first generate a W_0-RPA screening based on LDA wave functions and energies (denoted as W_0-RPA@LDA).

(ii) We further use the W_0-RPA@LDA screening as an initial screening guess for W_0 in G_0W_0@HF to obtain Hartree-Fock based G_0W_0 quasiparticle (QP) energies being now affected by W_0-RPA@LDA screening.

(iii) We inject the W_0-RPA@LDA screening from step 1 into the BSE and read at the same time the G_0W_0@HF QP energies from step 2 to proceed further with computation of excitation energies by solving the BS equation.

Because excitation energies strongly depend on accurate relative QP energies [27,28], this screening mixed scheme

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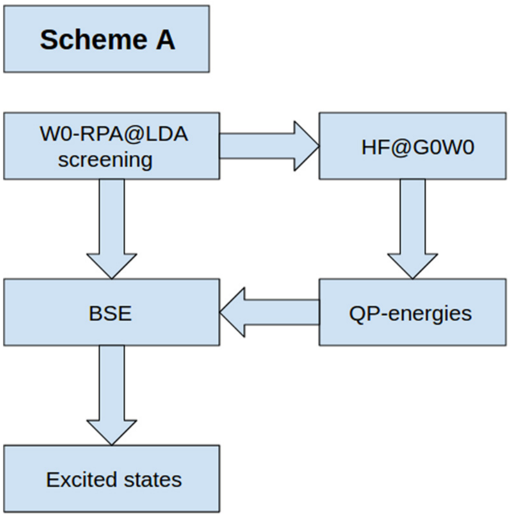

FIG. 1. The flowchart of scheme A is presented. The G_0W_0@HF QP energies and BSE are both affected by W_0-RPA@LDA screening.

gives rise to a reduced HOMO-LUMO QP gap serving as an important intermediate step enabling prediction of excitation energies with considerably better accuracy. The flowchart of scheme A is shown in Fig. 1.

Scheme B. We exactly proceed as in steps (i) and (ii) of scheme A, except in step (iii) we run a new calculation to obtain the W_0-RPA@HF screening, which we then inject into the BSE and read at the same time the G_0W_0@HF QP energies of step (ii) of scheme A. In other words, in the BSE part of scheme B, we use the W_0-RPA@HF screening instead of the W_0-RPA@LDA screening. The flowchart of scheme B is shown in Fig. 2.

III. IMPORTANT NOTES

(i) In this paper we do not compare our results with DFT hybrid orbital based approaches, since we would like to assess the true performance of the GW/BSE method starting from self-interaction free exact orbitals, i.e., we consistently consider Hartree-Fock orbitals as our starting reference point.

(ii) We further compare our GW/BSE results with EOM-CCSD. There are of course other even more accurate and highly correlated approaches such as CASPT2 or MRCI; however, those approaches strongly depend on the size of active space and the choice of correct orbitals, connected with an extremely high computational cost if a larger active space and more flexible basis sets are used.

(iii) In a recent work by Jacquemin *et al.* [29], it has been demonstrated that GW/BSE outperforms EOM-CCSD when eigenvalue self-consistent GW is used with frozen wave functions (i.e., BSE@G_nW_n@Hybrid-DFT with n giving the number of energy updates in G and W); however, the accuracy assessment of GW/BSE was based on DFT hybrid orbitals, leading to good results due to error compensations. In our opinion, for a fair and reliable comparison, the traditional GW/BSE should be performed on top of HF orbitals as EOM-CCSD and CASPT2 calculations are performed on top of HF orbitals. Therefore, since BSE@G_nW_n@HF consistently and considerably overshoots the excitation energies, a comparison of screening mixed approaches (scheme A and B) to EOM-CCSD is justified.

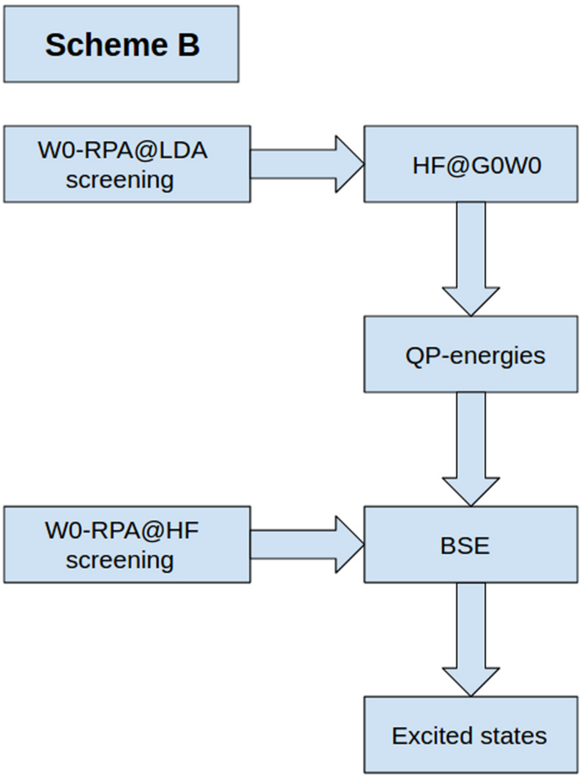

FIG. 2. The flowchart of scheme B is presented. The W_0-RPA@LDA screening is injected into G_0W_0@HF to obtain the QP energies affected by the W_0-RPA@LDA screening, whereas W_0-RPA@HF screening is injected into the BSE to enhance the electron-hole effect (excitonic red-shift).

(iv) The advantage of the presented schemes (A and B) is that even if our results are based on error compensations, we can, however, start from self-interaction free exact HF orbitals, and most importantly circumvent eigenvalue self-consistency through screening mixing, and thus reducing considerably the computational cost, in particular for larger systems with 100–1000 atoms on which self-consistency, EOM-CCSD, or the related wave function based methods can be hardly applied.

(v) The GW/BSE approach for molecules often suffers from remaining deviations from precise quantum-chemical methods. There are several possible reasons for this problem: maybe it is due to the neglect of higher-order vertex terms; maybe it is due to non-self-consistency (being far from the final solution); maybe it is due to self-consistency (double counting of terms that should be compensated by the vertex function, but are not compensated because the vertex function is approximate). For the time being, the pragmatic approach is to use what we have and slightly modify the ingredients, e.g., readjust the screening. One has to keep in mind that this does not conform with the general attitude of the GW/BSE field of systematic improvement, but instead adds some heuristic elements to the method. However, this heuristic approach applies to many systems of single reference character since G_0W_0@HF always overestimates and W_0-RPA@LDA screening always lowers the gap. Therefore, the main aim of the presented schemes is to simulate (in a pragmatic manner) the effect of vertex corrections, if they were explicitly taken into account, which is not the case in this paper.

IV. TECHNICAL DETAILS

The many-body calculations are performed using MOLGW [30,31] with frozen core approximation and the resolution-of-the-identity [32,33]. Depending on computational feasibility whenever possible a more flexible basis set [34] is used for the EOM-CCSD and GW/BSE, as indicated individually in the supporting information (SI). Furthermore, as the Green's function G and dynamically screened interaction W strongly depend on the virtual orbitals, hence all unoccupied orbitals are taken into account to fully ensure convergence of HOMO-LUMO QP gaps. Further, the self-energy is calculated analytically through spectral representation of W and residuum theorem, avoiding errors arising from numerical frequency integration, and hence accurate capture of the important dynamical correlation is guaranteed. Throughout this paper the wave functions are never updated and kept frozen either at LDA or HF level of theory.

BSE calculations are performed in the limit of adiabatic static kernel with mixing of resonant and antiresonant contributions, avoiding the frequently employed Tamm-Dancoff approximation (TDA), which neglects important coupling of electron-hole pairs. Further, all coupled cluster calculations (EOM-CCSD) are performed using the PSI4 package [35].

V. RESULTS AND DISCUSSION

In the Supplemental Material [36] detailed results of the eigenvalue self-consistent scheme starting from HF orbitals are presented along with the screening mixed ansatz (scheme A) and EOM-CCSD for a reliable comparison. As can be seen, the standard method (BSE@G_nW_n@HF) overestimates the singlet transition energies over the entire set of molecular systems by up to 0.64 eV, which is large given the fact that the molecules are small and simple; however, scheme A considerably improves the excitation energies over a large range of energies for each molecule, giving a good and satisfactory coupled-cluster-like accuracy as presented in Fig 3. This shows that W_0-RPA@LDA screening used as initial screening in G_0W_0@HF optimally damps and regulates the HF exchange effect on the QP energies. By contrast, the G_nW_n@HF approach, as expected, overestimates the HOMO-LUMO gaps (and hence the transition energies) due to underscreening of W.

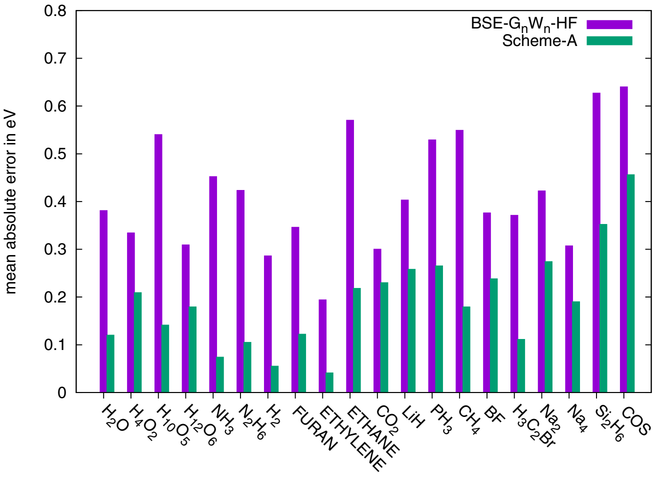

FIG. 3. Average (over the first five singlet states) absolute error relative to EOM-CCSD references is given for each system. Use of W_0-RPA@LDA screening as initial screening for G_0W_0@HF considerably reduces the average absolute error over the entire set of molecules, in some cases such as water pentamer and ammonia monomer errors are massively decreased. In extreme cases such as Si_2H_6 and COS the error of scheme A is still considerable. To further reduce the absolute errors of Si_2H_6 and COS, we switch to multiscreening ansatz (scheme B).

A. Notes on consistency and theoretical base

Since the traditional eigenvalue self-consistent GW based on HF (G_nW_n@HF) overestimates the HOMO-LUMO QP gap and in the end the excitation energies, it is then possible to decrease the gap through W_0-RPA@LDA screening. Therefore, the obtained improvement out of this screening mixing procedure is indeed systematic; however, the effectivity and hence the resulting improvement depends on the individual system. Regarding the screening, the choice of the LDA functional is justified by the fact that its overscreening character is stronger than other functionals; however, other functionals with a good overscreening character can also be used. Further, we point out that this ansatz has no profound theoretical justification and relies purely on cancellation effects; however, for problematic systems it can indeed be regarded as an alternative to the existing strategies, providing transition energies with a good accuracy.

B. Basis set effect

In this section, we investigate the basis effects on the mean absolute error accuracy of BF and COS molecules with respect to EOM-CCSD. As shown in Fig. 4 the errors increase the more flexible the basis set becomes, and a good accuracy is obtained when using the aug-cc-pVQZ basis

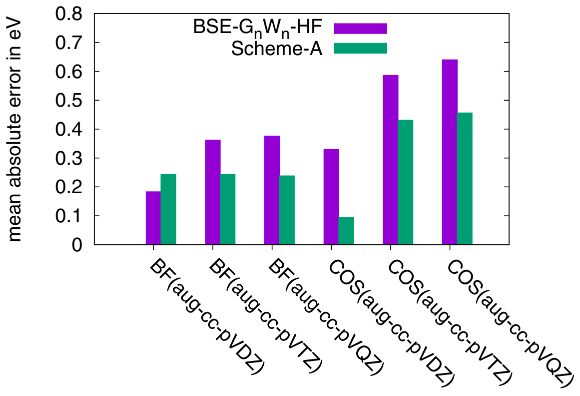

FIG. 4. Basis set effect on the mean absolute errors. The errors increase upon basis set increase; however the relative absolute error nearly converges in aug-cc-pVTZ and aug-cc-pVQZ.

TABLE I. HOMO-LUMO gap of COS and Si_2H_6 at different levels of theory in eV.

	HF	G_0W_0@HF	G_nW_n@HF	Scheme A
COS (aug-cc-pVQZ)				
HOMO-LUMO gap	12.604	12.635	12.617	12.274
Si_2H_6 (aug-cc-pVTZ)				
HOMO-LUMO gap	11.930	11.784	11.775	11.328

set. However, the relative mean absolute error between the GW/BSE methods is nearly converged for the less flexible aug-cc-pVTZ basis set. Nevertheless, the aug-cc-pVQZ basis set was used wherever the EOM-CCSD calculations were still computationally tractable. The increase of errors upon increase of basis set flexibility is a peculiar property of the GW/BSE approaches, as in other highly correlated approaches basis set errors typically decrease upon basis set increase.

C. Renormalization effect in *GW* and BSE

In this section, the impact of screening in each calculation part (GW and BSE) is outlined. As shown in Table I, the W_0-RPA@LDA screening reduces the QP gaps in scheme A, renormalizing considerably the HOMO-LUMO gap of COS and Si_2H_6 by 0.33 and 0.60 eV relative to HF gaps, respectively. By contrast, the G_nW_n@HF only moderately and hence insufficiently damps the HOMO-LUMO HF gap of Si_2H_6, showing that W_0-RPA@LDA screening used in scheme A is much stronger than W_n-RPA@HF screening used in the G_nW_n@HF approach. Interestingly, both G_0W_0@HF and G_nW_n@HF slightly overestimate the HOMO-LUMO HF gap of COS. Such a peculiar behavior was also observed in transition metals [5]. However, for both molecules the W_0-RPA@LDA screening in scheme A decreases the HF, G_0W_0@HF and G_nW_n@HF gaps.

Furthermore, we can either inject the W_0-RPA@LDA or the W_0-RPA@HF screening into the BSE. For extreme cases, a better agreement with the EOM-CCSD excitation energies can be reached if one uses the W_0-RPA@LDA screening for the W_0 in G_0W_0@HF and the W_0-RPA@HF screening for the BSE. This is the more advanced scheme B.

For carbonyl sulfide (COS) and disilane (Si_2H_6) with the largest mean absolute errors of excitation energies, we show in Table II the effect of injection of W_0-RPA@LDA screening in G_0W_0@HF and W_0-RPA@HF screening in BSE, which leads to a further considerable reduction of the absolute errors, and consequently to much better vertical transition energies. The reason for the better agreement is that the W_0-RPA@HF screening is weaker relative to the W_0-RPA@LDA and hence excitonic effects are more effective, leading to a further red shift of excitation energies. This multiscreening injection scheme is only meaningful if scheme A still overestimates the vertical energies, and hence injection of W_0-RPA@HF screening into the BSE brings a further improvement of excitation energies.

D. Extensivity

One further interesting point is how the quality of excitation energies of the screening mixed GW/BSE (scheme A) behaves upon increase of the size of cluster. As shown in Fig. 5, the singlet state and mean absolute error of scheme A relative to EOM-CCSD remains largely unaffected upon cluster size increase, and hence the quality of the excitation energies based on the screening ansatz does not degrade for larger clusters, which is a good sign for applicability of this ansatz on larger systems for which wave function based methods are out of reach.

E. Screening effect on the BSE absorption spectra of water monomer and dimer

The effect of W_0-RPA@LDA screening in scheme A is presented over large energy regimes in the absorption spectra of water monomer and dimer. As can be seen in Fig. 6 injection of W_0-RPA@LDA screening in G_0W_0@HF results in a consistent red shift of the entire water spectra due to a consistent HOMO-LUMO QP gap reduction. This is further observed for larger water clusters (pentamer and hexamer) and other smaller molecular systems. Furthermore, the intensities of the screening mixed BSE spectra are moderately reduced;

TABLE II. Screening mixing effects in scheme A and scheme B are shown.

BSE@:	G_nW_n@HF	Scheme A	Scheme B	EOM-CCSD
COS (aug-cc-pVQZ)				
S_1 (1A2)	6.264	6.144	5.839	5.765
S_2 (1A1)	6.519	6.384	6.096	5.831
S_3 (2A2)	6.519	6.384	6.096	5.831
S_4 (1B1)	8.199	7.936	7.844	7.537
S_5 (1B2)	8.199	7.936	7.844	7.537
mean absolute error	0.640	0.456	0.244	
Si_2H_6 (aug-cc-pVTZ)				
S_1 (1Ag)	8.211	7.848	7.744	7.634
S_2 (1Au)	8.244	8.078	7.672	7.618
S_3 (1Bu)	8.244	8.078	7.672	7.618
S_4 (2Bu)	8.635	8.271	8.155	7.984
S_5 (2Ag)	8.885	8.568	8.390	8.231
mean absolute error	0.627	0.352	0.110	

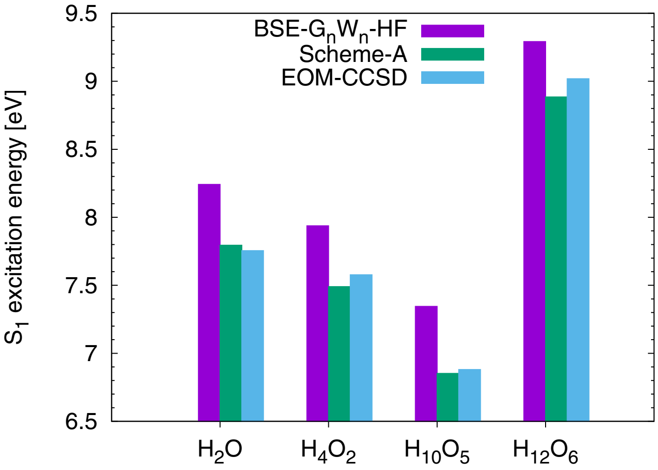

FIG. 5. Size extensivity of the accuracy of the screening mixed *GW*/BSE (scheme A) versus BSE@G_nW_n@HF and EOM-CCSD is shown. Upon cluster size increase, the accuracy of the first most important excitation energy S_1 (optical gap) does not degrade, and shows a EOM-CCSD-like accuracy.

however, the spectral weight distributions remain unaffected at all energy scales.

F. Application to large biological molecules

In this section, we aim at the application of the presented many-body screening ansatz on the large molecular systems for which both experimental and EOM-CCSD calculations are available. The large systems are biological molecular species, namely, 11-cis-retinal protonated Schiff base (with 156 electrons) and chloropyll A (with 340 electrons). The optimized molecular geometries were obtained from Ref. [26]. Here we compare different variants of the *GW*/BSE methodology to demonstrate the screening effects and exhibit the consistency of the screening mixed approach in comparison to the available experimental and theoretical data. For both species the aug-cc-pVDZ basis set is used with 400 virtual orbitals in *G* and *W* to ensure convergence of the excited-state energies within 50 meV accuracy.

As can be seen from Table III, in the case of retinal the S_1 energy of EOM-CCSD and scheme A overlap to a large extent, whereas for the S_2 energy the deviation is larger. As of BSE@G_nW_n@HF, the excitation energies are consistently overestimated, which can be consistently improved using the W_0-RPA@LDA screening within scheme A.

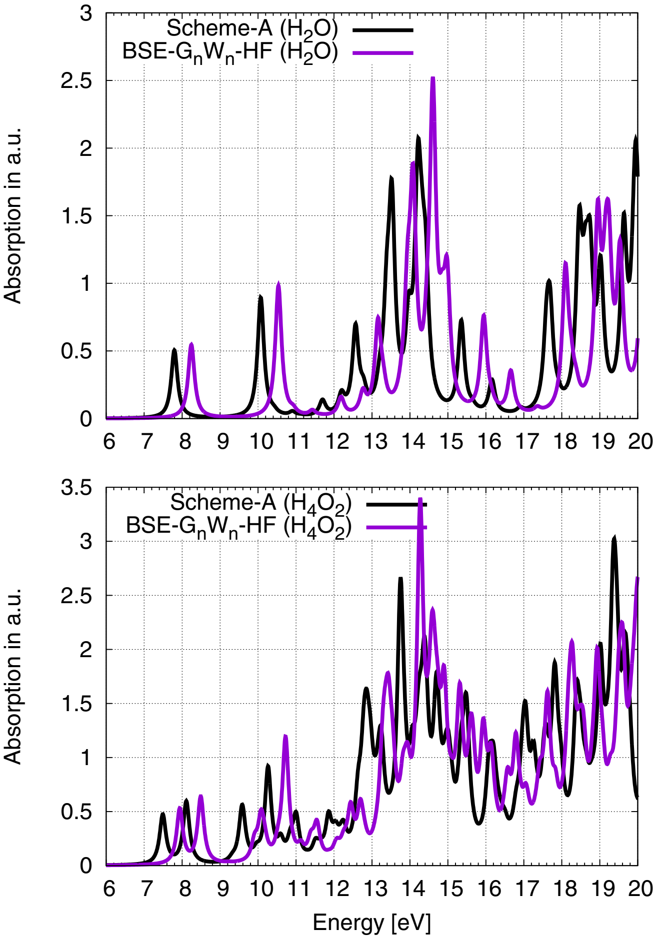

FIG. 6. The effect of injection of W_0-RPA@LDA screening into G_0W_0@HF on optical absorption spectra of water monomer and dimer is shown. The W_0-RPA@LDA screening pushes the standard screening unmodified BSE@G_nW_n@HF spectrum consistently to lower energies over the full energy range. We further point out that in the presented spectra there is no information about vibrational progressions.

In the case of chloropyll A, BSE@G_0W_0@HF overestimates the S_1 experimental energy by about 0.3 eV; however, updating of orbital energies in *G* and *W* (BSE@G_nW_n@HF) improves the agreement. The scheme A slightly reduces the S_1 energy (compared with BSE@G_nW_n@HF) realizing a slightly better agreement with the experimental S_1 energy. With respect to the S_2 energy, scheme A transition energy is in good agreement with EOM-CCSD, whereas BSE@G_0W_0@HF and

TABLE III. Excitation energies of the first two singlet states in eV based on BSE@G_0W_0@HF, BSE@G_nW_n@HF, scheme A, and EOM-CCSD approaches.

BSE@:	G_0W_0@HF	G_nW_n@HF	Scheme A	EOM-CCSD [26]	EXP [37]
11-cis-Retinal (aug-cc-pVDZ)					
S_1 (1A)	2.424	2.237	1.861	1.809	2.03
S_2 (2A)	3.795	3.574	2.802	3.302	3.18
Chloropyll A (aug-cc-pVDZ)					
S_1 (1A)	2.186	2.011	1.987	1.706	1.9
S_2 (2A)	2.764	2.553	2.336	2.371	—

BSE@G_nW_n@HF considerably overestimate. We note that particularly for larger systems EOM-CCSD and iterative GW schemes become computationally intractable; therefore the noniterative screening mixed GW (scheme A) provides a reliable alternative for computing excited-state energies with a good accuracy at much lower cost from a self-interaction free exact reference state (HF).

VI. CONCLUSIONS

We showed that through injection of W_0-RPA@LDA screening into G_0W_0@HF, one can optimally reduce the overestimated HF gaps resulting in a consistent and robust enhancement of the quality of excitation energies. By contrast, both BSE@G_0W_0@HF and BSE@G_nW_n@HF overestimate the excitation energies. In extreme cases such as COS and Si_2H_6, where we had a large mean absolute error, it is possible to enhance the performance by injecting the W_0-RPA@LDA screening into G_0W_0@HF in the GW part to obtain adequate QP energies and using the W_0-RPA@HF screening for the BS equation (scheme B) in order to increase the excitonic red shift.

The accuracy power of screening mixed GW/BSE theory is consistent both in the low- and high-energy regimes. Furthermore, within this screening scheme, introduction of any kind of parameter as usually encountered for instance in the advanced TD-DFT is strictly avoided. Further, the screening mixing schemes A and B are in particular, with respect to large molecules, much more computationally efficient, as they avoid update of orbital energies, and hence explicit calculation of W at each iteration step is avoided.

As a final important remark, the applicability and consistency of the proposed mixing approach strongly relies on cancellation effects between HF exchange and overscreening character of the LDA functional, which is crucial for systematic improvement of excitation energies. This is clearly the limit of the presented screening mixing approach.

For detailed results concerning electronic excitations based on the traditional and screening mixed GW/BSE schemes, see the Supplemental Material [36].

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