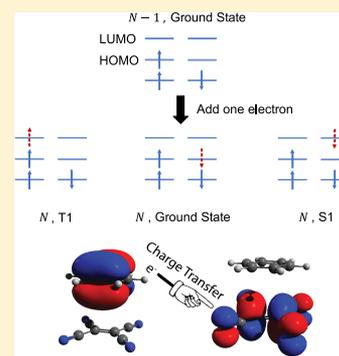


Excitation Energies from the Single-Particle Green's Function with the *GW* Approximation

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Supporting Information

ABSTRACT: Quasi-particle energies are important in predicting molecular ionization energies and bulk band structures. The state-of-the-art method for quasi-particle energy calculations, particularly for bulk systems, is the *GW* approximation. For excited state calculations, one needs to go beyond the *GW* approximation. The Bethe–Salpeter equation (BSE) is the commonly used approach for bulk-system excited state calculations beyond the *GW* approximation, which is accurate but computationally cumbersome. In this Article, we develop a new method to extract excitation energies directly from the quasi-particle energies based on the *GW* approximation. Starting from the ($N - 1$)-electron system, we are able to calculate molecular excitation energies with orbital energies at the *GW* level for HOMO excitations. Our calculations demonstrate that this method can accurately capture low-lying local excitations as well as charge transfer excitations in many molecular systems. Our method is shown to outperform the time-dependent density functional theory (TDDFT) and are comparable with higher level excited state calculations, including the equation-of-motion couple cluster (EOM-CC) theory and the BSE, but with less computational effort. This new approach provides an efficient alternative to the BSE method for accurate excited state calculations.



INTRODUCTION

Accurate description of excited states has been a challenging topic in theoretical chemistry. Especially, the calculation of vertical excitation energies is of great importance to photochemistry, photovoltaics, biochemistry, and many other applications.^{1,2} Although high-level *ab initio* methods, like the couple cluster (CC) theory,^{3–9} can provide reliable results, the expensive computational cost prevents it from describing large systems. Time-dependent density function theory (TDDFT),^{10–12} however, has been widely used in past decades for excited state calculations. Normally, it can offer acceptable accuracy for low-lying excitations with a favorable computational scaling. However, the performance of TDDFT significantly depends on the ground state calculation and commonly used approximate functionals have inherent problems in some challenging cases, including Rydberg excitations, double excitations, and charge transfer (CT) excitations.² In particular, the failure description of CT excitations is attributed to common exchange–correlation kernels, which do not have the correct $1/R$ dependence. Here R represents the separation distance of positive and negative charges.

Another method for excited state calculations is the Bethe–Salpeter equation (BSE), which is based on Green's function many-body perturbation theory. BSE provides a successful description of optical spectrum for bulk systems,¹ and recent work shows that BSE can also be applied to molecular systems for regular and CT excitation calculations.^{13–18} BSE depicts the quasi-particle (QP) excitation process, which depends on

accurate orbital energies calculated from the *GW* approximation^{1,19,20} and the screened Coulomb interaction W . It is usually denoted as *GW*+BSE. The screened Coulomb interaction has accurate nonlocal electron–hole interactions, which leads to the success of BSE in describing CT excitations.²¹ However, *GW*+BSE is in general computationally expensive because it needs the prerequisite *GW* calculation and the construction of the BSE kernel afterward.

Here we propose a new approach from the many-body perturbation theory, where the excitation energy is calculated from the single-particle Green's function at the *GW* level. In the many-body perturbation theory, the single-particle noninteracting Green's function G_0 from the ground state calculation is connected with the interacting Green's function G by the self-energy Σ . If the *vertex correction* is neglected from the self-energy, the self-energy has the expression $\Sigma = iGW$,²² which is known as the *GW* approximation. Through the *GW* approximation, one can achieve accurate QP energies, which is important for predicting accurate band structures in solids and also molecular ionization potentials (IP).^{23–27}

METHOD

For an N -particle system, the Lehmann representation of the interacting Green's function G is

Published: March 28, 2019

$$G(p,q;\omega) = \sum_m \frac{\langle \Psi_0^N | \hat{a}_p | \Psi_m^{N+1} \rangle \langle \Psi_m^{N+1} | \hat{a}_q^\dagger | \Psi_0^N \rangle}{\omega - (E_m(N+1) - E_0(N)) + i\eta} + \sum_n \frac{\langle \Psi_0^N | \hat{a}_q^\dagger | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{a}_p | \Psi_0^N \rangle}{\omega - (E_0(N) - E_n(N-1)) - i\eta} \quad (1)$$

where Ψ is the interacting wave function and $\hat{a}_p/\hat{a}_q^\dagger$ represents the annihilation/creation operator. The poles of this Green's function represent the QP energies of the N -electron system in the electron addition/removal domain, $\varepsilon_m^+(N)/\varepsilon_n^-(N)$, where

$$\varepsilon_m^+(N) = E_m(N+1) - E_0(N) \quad \varepsilon_n^-(N) = E_0(N) - E_n(N-1) \quad (2)$$

Now if we shift the reference to an $(N-1)$ -electron system, then the QP energy in the electron addition domain becomes

$$\varepsilon_m^+(N-1) = E_m(N) - E_0(N-1) \quad (3)$$

In particular, the lowest QP energy in this domain is the QP LUMO energy, which is the ground state energy difference of N -electron and $(N-1)$ -electron systems. The energy difference of higher QP energies and the LUMO QP energy is then the corresponding excitation energy of the N -electron system,

$$\begin{aligned} & \varepsilon_m^+(N-1) - \varepsilon_{\text{LUMO}}^+(N-1) \\ &= (E_m(N) - E_0(N-1)) - (E_0(N) - E_0(N-1)) \\ &= E_m(N) - E_0(N) \end{aligned} \quad (4)$$

Under the GW approximation, eq 4 represents the energy difference between two GW-corrected orbital energies of the $(N-1)$ -electron system. The nature of this excitation is a single QP excitation from the HOMO of the N -electron system to a specific virtual orbital.

We illustrate our idea with first triplet (T1) and singlet (S1) states in details, as shown in Figure 1 (in most cases, the first

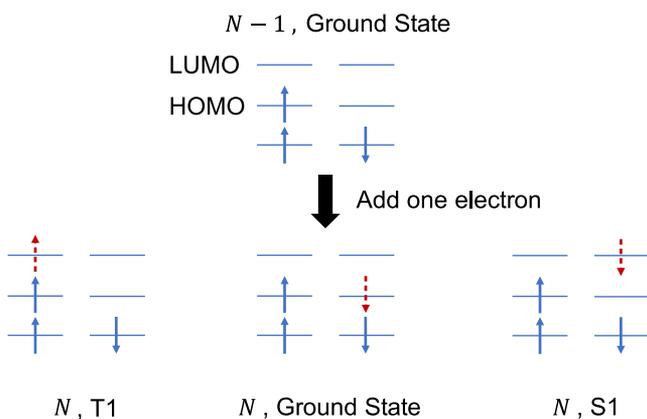


Figure 1. Illustration of obtaining an N -electron system from an $(N-1)$ -electron system. Note that the singlet state obtained is not the eigenstate of \hat{S}^2 . This is a broken symmetry state.

excitation is from HOMO to LUMO). By adding one electron to an $(N-1)$ -electron system, we can obtain the N -electron system ground state or excited states. The excitation energy of the first triplet state is then the energy difference between α -LUMO and β -LUMO of the $(N-1)$ -electron system,

$$E_{T1}^N - E_0^N = \varepsilon_{\text{LUMO},\alpha}^+(N-1) - \varepsilon_{\text{LUMO},\beta}^+(N-1) \quad (5)$$

The idea is the same for the first singlet state. Notice that the singlet state obtained in our method is not the eigenstate of the spin Hamiltonian \hat{S}^2 . Therefore, a spin purification process is needed. We adopt the simple spin purification formula,²⁸

$$E_S = 2E_{\uparrow\downarrow} - E_{\uparrow\uparrow} \quad (6)$$

This expression is further expanded in our case by

$$\begin{aligned} E_{S1}^N - E_0^N &= 2\varepsilon_{\text{LUMO}+1,\beta}^+(N-1) - \varepsilon_{\text{LUMO},\alpha}^+(N-1) \\ &\quad - \varepsilon_{\text{LUMO},\beta}^+(N-1) \end{aligned} \quad (7)$$

For higher excited states, the procedure is the same. In practice, we can further simplify the self-energy at the G_0W_0 level.^{19,29} And to achieve better accuracy, we are using eigenvalue-self-consistent GW (evGW) to eliminate the starting-point dependence in G_0W_0 calculations.^{30,31}

One can also calculate the excitation energies in the electron removal domain, where the excitation energy is extracted from an $(N+1)$ -electron system. However, the excitation energy calculated from the $(N+1)$ -electron system does not perform well, as shown in Table 1 in the Supporting Information. The

Table 1. MSDs and MADs of Computed Vertical Excitation Energies (eV)^a

		evGW@ PBE	G_0W_0 @ PBE0+BSE	evGW@ PBE0+BSE	TDDFT/ B3LYP
singlet	MAD	0.26	0.68	0.29	0.20
	MSD	-0.11	-0.68	-0.25	-0.16
triplet	MAD	0.17			0.43
	MSD	0.04			-0.43
total	MAD	0.22			0.30
	MSD	-0.04			-0.27

^aevGW@PBE represents the eigenvalue self-consistent GW calculation started from PBE orbitals and orbital energies. BSE singlet excitation results are from.³⁷ TDDFT results are from Thiel's benchmark test.³⁶

reason is that the ground state calculation of the $(N+1)$ -electron system is not accurate. In fact, most of the HOMO orbital energies in the α -channel are positive, even with the evGW calculation, which indicates that the HOMO orbitals are not bounded with the current approximations in DFA and in the GW method. Therefore, the results from the $(N+1)$ -electron system lead to a poor approximation. One should calculate the excitation energy from the $(N-1)$ -electron system instead. We note that recent work used generalized Kohn–Sham orbital energies to approximate quasi-particle energies and excitation energies within the framework of density functional theory from two groups,^{32–34} using the $N-1$ or $N+1$ electron system as the reference system. In our current approach, we similarly use the $N-1$ or $N+1$ electron system as the reference but obtain excitation energies calculation using quasi-particle energies from the single-particle Green's function, currently at the GW approximation.

RESULTS AND DISCUSSION

Local Excitations. We first tested 23 molecules in Thiel's test set, including 48 low-lying local excitation energies (29 singlet states and 19 triplet states).³⁵ The original data are in the

Supporting Information. TDDFT/B3LYP results are from ref 36, BSE results are from ref 37, and the reference results are from ref 38 (denoted as TBE-2). While other versions of the GW approximation can be used, we aim to reduce the dependence on the starting DFAs and used evGW@PBE in our present work, where the PBE functional was chosen for $(N - 1)$ ground state calculations and the evGW calculations were done in the QM^4D package.³⁹ The convergence test in the Supporting Information shows that the Def2-TZVPD basis⁴⁰ should be used in all calculations. Here we show the mean absolute deviation (MAD) and mean signed deviation (MSD) (Table 1). The MAD of all vertical excitation energies calculated in our method is 0.22 eV, which is lower than TDDFT/B3LYP results of 0.30 eV. Singlets in our method have a negative MSD of -0.11 eV. The reason for this underestimation might be the simple spin purification formula. But at the current stage, we do not have a better correction formula for singlet states. Nevertheless, this is still a good approximation, as the MAD of singlets from evGW@PBE (0.26 eV) is similar to that from the TDDFT/B3LYP (0.20 eV) as well as evGW@PBE0+BSE (0.29 eV). And our method has a better MSD. All methods outperform $G_0W_0@PBE0+BSE$ in singlet excitation energies. However, triplet excitation energies are significantly improved compared with TDDFT/B3LYP because triplets do not have strong multiconfigurational effects as singlets. The MAD is improved from 0.43 to 0.17 eV, and the MSD is only 0.04 eV. Triplet excitation energies with evGW+BSE are not reported in the reference. However, from ref 41, even the best functional for G_0W_0+BSE (tCAM-B3LYP) still yields similar results with TDDFT. We believe that evGW+BSE will have the same problem and will be worse than our method. Considering all singlet and triplet states, evGW@PBE is overall more accurate than TDDFT/B3LYP as well as BSE.

Note that TDDFT usually underestimates the excitation energy due to the fundamental delocalization error of commonly used DFAs for the ground state calculation.^{42,43} In this test set, TDDFT underestimates excitation energies for both singlets and triplets, with a total MSD of -0.27 eV. But since the GW approximation does not inherit the same problem from the DFT, our method does not suffer from this underestimation. The total MSD is only -0.04 eV, which demonstrates that the result is not biased. From Figure 2, it is obvious that almost all TDDFT data are underestimated, while evGW results are evenly distributed.

Other Forms of Self-Energy. We have also used the self-energy Σ at a lower-level approximations, up to the first order, known as Hartree–Fock (HF), and second order MP2 approximation. The formula of MP2-corrected orbital energies can be found in refs 44 and 45 from the perspective of DFT generalized Kohn–Sham orbital energy corrections. Both sets of results can be found in the Supporting Information. HF orbital energies cannot give physical results because of the lack of electron correlation. For MP2, S1, and T1 are usually reasonable except some challenging cases like ethene or cyclopropene. However, for second singlets and triplets, the results are far from the reference. The failure of molecules like ethene is due to the poor $(N - 1)$ HF SCF result. This could be properly treated by applying the self-consistent MP2 scheme.^{46,47}

Multiconfiguration and Non-HOMO Excitations. Although our method can accurately predict low-lying local excitation energies, limitations still remain. There are two main difficulties in our current method: degenerate systems with multiconfigurational excitations and non-HOMO contribution to excited states. Since our method is in fact a one-electron

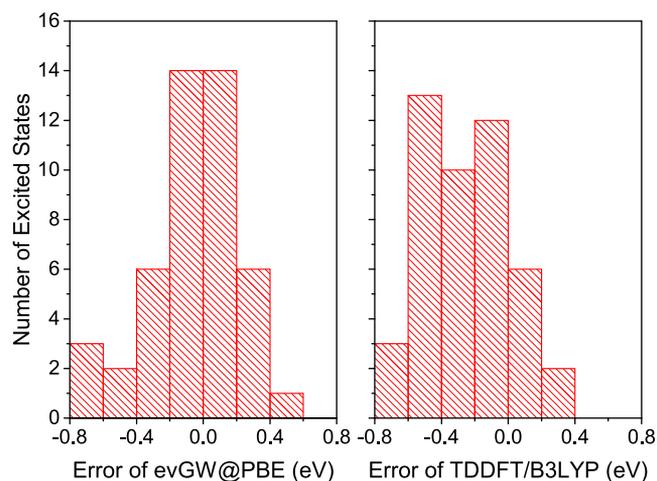


Figure 2. Error histogram of vertical excitation energies for (left) evGW@PBE and (right) TDDFT/B3LYP. The Pearson correlation coefficient of evGW@PBE with the reference is 0.9762. The TDDFT data are from ref 36.

process, degenerate systems like benzene, where the 1E_u excitation has equal probability from $\text{HOMO} \rightarrow \text{LUMO}+1$ and $\text{HOMO}-1 \rightarrow \text{LUMO}$, cannot be calculated accurately. The reference excitation energy of 1E_u state is 7.13 eV,³⁵ while our calculation gives 6 eV. And for non-HOMO contribution, the $(N - 1)$ -electron system should be a nonaufbau state, but the GW approximation based on a nonaufbau state has not been developed. This limitation prevents us to calculate excited states like S_3 or higher, which usually has the contribution from non-HOMO orbitals. But it is still a powerful tool for low-lying local excitations, especially S_1 and T_1 .

Charge Transfer Excitations. Charge transfer systems were also tested. We calculated CT excitations with common donor–TCNE complexes. For singlet CT excitations, the electron is transferred from the donor to the acceptor. So in our method, for the first singlet CT process, the electron should be transferred from LUMO to LUMO+1 in the β channel (as shown in Figure 1). Then we should expect that for the $(N - 1)$ -electron system, β -LUMO is localized on the donor and β -(LUMO+1) is localized on the acceptor. This is demonstrated with the benzene–TCNE system, as shown in Figure 3. We then calculated CT excitation energies with evGW@B3LYP , because B3LYP has a good convergence

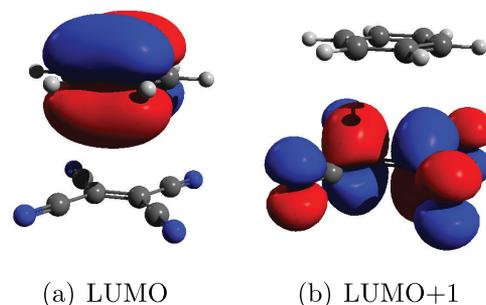


Figure 3. Isosurface contour of LUMO and LUMO+1 in the β channel of the benzene–TCNE complex with a positive charge. The charge transfer character is obvious: LUMO is located on benzene, and LUMO +1 is located on TCNE (see discussions in main text).

Table 2. Experimental and Theoretical CT Excitation Energies of Donor–TCNE Complexes (eV)^a

donor	exp	G_0W_0 +BSE	evGW+BSE	evGW@PBE	evGW@B3LYP	TDDFT/B3LYP	TDDFT/CAM-B3LYP	TDDFT/ ω B97X-D
benzene	3.59	3.03	3.58	3.50	3.43		2.88	2.97
naphthalene	2.60	1.96	2.55	2.51	2.48		1.84	2.00
toluene	3.36	2.52	3.27	3.36	3.14		2.61	2.69
<i>o</i> -xylene	3.15	2.23	2.89	3.03	2.91		2.36	2.44
cyano	2.33	1.89	2.32	2.21	2.16	0.5	1.56	1.79
chloro	2.06			1.99	1.90	1.0	1.62	1.70
carbomethoxy	2.16	1.64	2.05	2.02	1.92	0.9	1.61	1.70
methyl	1.87	1.21	1.99	1.87	1.75	1.1	1.59	1.63
dimethyl	1.76	2.00	2.21	1.98	1.82	1.4	1.77	1.79
formyl	2.22	1.89	2.32	2.17	2.05	1.0	1.70	1.80
formylchloro	2.28			2.20	2.10	0.9	1.72	1.83
MAD		0.57	0.13	0.09	0.17		0.56	0.46
MSD		-0.52	0.02	-0.05	-0.15		-0.56	-0.46

^aResults of evGW@B3LYP are obtained with FHI-aims.⁴⁸ BSE results are from ref 49 with the TZ2P basis. Experimental results below *o*-xylene were obtained in the liquid phase, and a 0.32 eV constant energy has been added, as suggested by Stein and coworkers.⁵⁰ The TDDFT/B3LYP results are from ref 50. TDDFT/CAM-B3LYP and TDDFT/ ω B97X-D are calculated with Gaussian16.⁵¹

behavior of $(N - 1)$ -SCF calculations for these systems. Def2-SVPD basis set is chosen for all calculations. From the previous convergence test, we note that this basis set is enough for the first excited state to converge.

From Table 2, our method, evGW@B3LYP/PBE, gives a MAD of 0.17/0.09 eV, which is comparable with the high-level evGW+BSE calculation (0.13 eV). The result also proves that for this set of molecules, the starting DFA reference has small influence within the evGW approach. However, both functionals slightly underestimate the excitation energies. As we have analyzed in the low-lying vertical excitation energy calculations, the underestimation is possibly caused by the spin purification formula. Despite this small underestimation, the results are on the same level as the evGW+BSE method, and are significantly better than G_0W_0 +BSE results. TDDFT with different functionals was also calculated. Since the B3LYP kernel does not contain the correct $1/R$ behavior, it cannot describe the CT excitations well. For range-separate functionals, including CAM-B3LYP⁵² and ω B97X-D,⁵³ the results are better than TDDFT/B3LYP and on the same level of G_0W_0 +BSE. But they still strongly underestimate the CT excitations. We conclude that CT excitation energies are obtained accurately only at the evGW level, which is computationally more favorable than the evGW+BSE.

Our method captures CT state energies accurately and also has the correct $1/R$ behavior. To see this, let us consider the singlet excitation energy without the spin purification formula, where $\tilde{E}_{S1} = \epsilon_{LUMO+1,\beta}^+(N - 1) - \epsilon_{LUMO,\beta}^+(N - 1)$. In this equation, only LUMO and LUMO+1 in the β -channel contributes to this excitation. Recall that in Figure 3, LUMO is localized on the donor and LUMO+1 is localized on the acceptor. For an $(N - 1)$ -electron system like Figure 3, the positive charge is carried by the donor (benzene). With the increasing distance between the donor and acceptor, LUMO+1 will show an $1/R$ behavior because the positive charge on the donor is moving away from the acceptor, on which LUMO+1 is localized. However, LUMO will not be affected because the donor always carries the positive charge. Therefore, by combining both orbitals together, the singlet excitation energy has the correct $1/R$ behavior.

Connection with BSE. For both low-lying local and CT excitations, our results are very similar to evGW+BSE

calculations. The success of BSE, especially in CT excitations, is because two-particle Green's function can describe the electron–hole interaction correctly, which is also known as the excitonic effect. Since our method is also in the one-particle Green's function picture, the natural question is the following: Does our method contain the electron–hole interaction? The answer is positive. The one-particle Green's function for an N -electron system by definition has its poles at the excited state energies of the corresponding $(N \pm 1)$ -electron systems. Therefore, the one-particle Green's function for an $(N - 1)$ -electron system has its poles at the excited state energies of the corresponding N -electron and $(N - 2)$ -electron systems. That is the solid mathematical foundation of our work. Our starting reference is a $(N - 1)$ -electron system, where a hole is created by removing an electron from the N -electron system. By use of the Green's function of $(N - 1)$ -electron system, this hole will interact with the added electron. Therefore, our method does contain the electron–hole interaction, but the hole is a collective hole that is generated from the ground state calculation of the $(N - 1)$ -electron system. This explains the success of our method in describing both low-lying local and CT excitations.

Recently, we developed a renormalized-single GW method to eliminate the starting-point dependence at the cost of G_0W_0 calculation.⁵⁴ Combining both methods, one can estimate the low-lying local and CT excitations accurately with the G_0W_0 cost (and only a few quasi-particle energies are required, not the full spectrum), which is very appealing for relatively large systems.

CONCLUSIONS

In summary, we develop a simple approach for excitation energy calculation from single-particle Green's function at the evGW level. We have shown that low-lying local excitation energies from HOMO can be obtained accurately with evGW@PBE. The result outperforms TDDFT/B3LYP as well as evGW+BSE, with a total MAD of 0.22 eV for 48 excited states, where the MAD of triplets is 0.17 eV and that of singlets is 0.26 eV. In the CT test set, the MAD of evGW@B3LYP/PBE is 0.17/0.09 eV, which is similar with the high-level evGW+BSE result. Overall, our result is comparable with high-level theories including CC and BSE, but with less computational effort. As a further consideration, we would like to investigate a formalism that can describe non-

HOMO excitations, probably starting from a nonaufbau ($N - 1$) state to perform GW calculations. We believe that our method provides a powerful tool for simple and accurate excitation energy calculations with a low computational cost.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b02379.

Basis set convergence test, excitation energies from ($N + 1$)-electron system and ($N - 1$)-electron system with different self-energy constructions (PDF)

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■ ACKNOWLEDGMENTS

Y.J. acknowledges support from the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575. W.Y. acknowledges the support from the National Science Foundation (Grant No. CHE-1362927). Y.J. also appreciates Mr. Yuncai Mei for helpful discussions.

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