

Renormalized Singles Green's Function for Quasi-particle Calculations beyond the *GW* approximation

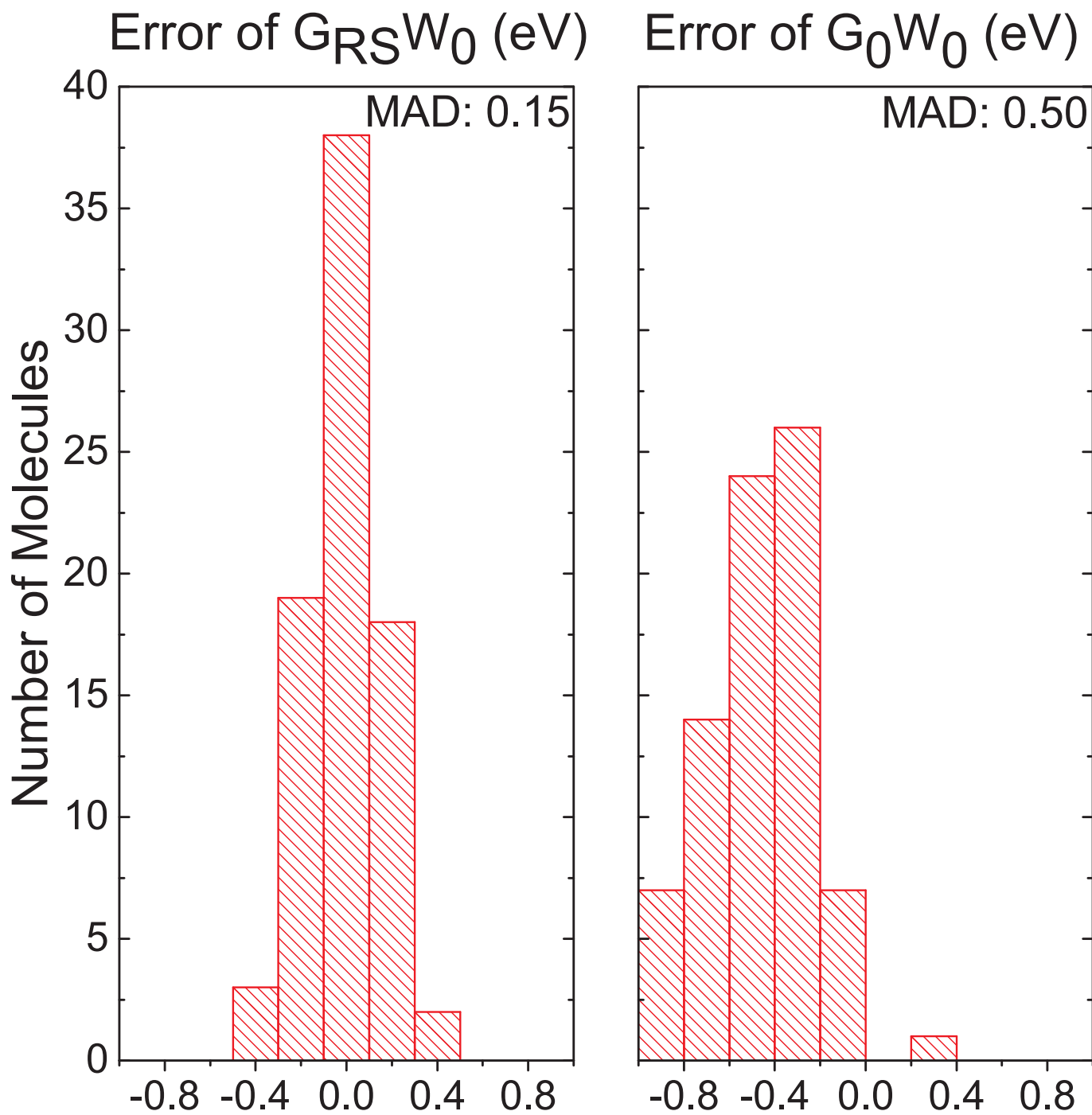
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$$G_{RS}^{-1} = G_0^{-1} - \Sigma_{singles}$$

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Renormalized Singles Green's Function for Quasi-particle Calculations beyond the G_0W_0 approximation

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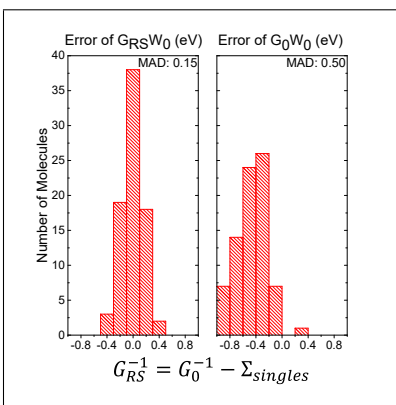
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Abstract

Quasi-particle energies and band gaps in particular are critical for investigating novel materials. Commonly used density functional approximations (DFAs) systematically underestimate band gaps and GW approximation is the established method of choice for good accuracy and reliability. However, G_0W_0 has some undesired dependence on the DFA, while self-consistent GW (sc GW) is expensive and not consistent in accuracy improvement. Here a simple and efficient $G_{RS}W_0$ approach has been developed: a subspace diagonalization of the Hartree-Fock (HF) Hamiltonian with the DFA density matrix provides the new reference Green's function G_{RS} that incorporates the effect of all single excitation contributions to the self-energy, thereby essentially eliminating the starting-point dependence. Calculations for molecules and large band gap solids demonstrate the significant improvement over G_0W_0 and greatly reduced dependence on the initial DFA. $G_{RS}W_0$ approach also improve result for other bulks over G_0W_0 , but to a lesser extent, which could be due to the limitations in current implementation for bulks. The results demonstrate that to achieve good accuracy, it is not necessary to use hybrid DFA, which is expensive for bulks. This work should be greatly significant in making GW a more robust approach.

Graphical TOC Entry



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Accurate description of quasi-particles is important for understanding the properties of novel materials. The commonly used density functional approximations (DFAs) usually fail to predict the spectrum accurately, and particularly underestimate the fundamental gaps.¹ The *GW* approximation,² is currently the state-of-the-art method in describing quasi-particles. It has achieved great success in solid states,³⁻⁵ and is now gaining more attention for molecules.⁶⁻¹¹ *GW* approximation is usually performed perturbatively, known as the G_0W_0 approach. The G_0W_0 approach is based on the orbitals and orbital energies obtained from (generalized) Kohn-Sham ((G)KS) density functional theory (DFT)^{12,13} within a DFA, which introduces the well-known starting-point dependence in G_0W_0 .^{10,14,15} Practically, the reliability of the G_0W_0 predictions can be significantly influenced by the dependence on the initial DFAs. Functionals as PBE0¹⁶⁻¹⁸ and CAM-B3LYP^{19,20} are shown to provide more accurate G_0W_0 results for small molecules as compared with (semi-)local functionals such as local density approximations (LDAs) or generalized gradient approximations (GGAs).¹⁰ But they are not consistently accurate for all systems.

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Self-consistent calculations of *GW* methods provide one way to eliminate this starting-point dependence. Even though full self-consistent *GW*^{6,21-24} (usually denoted as *scGW*) shows no starting-point dependence, but it is exceedingly demanding in computation cost. To reduce the cost, partial-self-consistency methods, including GW_0 ,²⁵ quasi-particle self-consistent *GW* (QSGW)²⁶⁻²⁹ and eigenvalue self-consistent *GW* (ev*GW*) have been widely studied in the past decades. However, the accuracy of such methods, as well as *scGW*, cannot be guaranteed, and the computation effort is still expensive for large systems. Because of the importance of second-order screened exchange (SOSEX) in improving the random phase approximation (RPA) correlation energy,³⁰⁻³² Ren and coworkers³³ further considered SOSEX in the self-energy expression, so as to reduce the starting-point dependence in G_0W_0 approach. However, the scaling of evaluating SOSEX is also not favorable and it can fail for systems with small or zero gap. Therefore, it is essential to find a universal scheme to achieve accurate DFA+*GW* results with reasonable computation cost, with robust accuracy

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3 and without the starting-point dependence.
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5 To understand the origin of starting-point dependence, here the G_0W_0 method is briefly
6 reviewed. In the G_0W_0 approximation, the self-energy Σ_{xc} is approximated as $\Sigma_{xc} = iG_0W_0$,
7 where G_0 is the Green's function constructed by the initial DFA calculation, and W_0 is
8 the screened Coulomb interaction evaluated at the level of RPA by inserting G_0 . The only
9 variable is hence G_0 which is kept unchanged in the G_0W_0 calculation. Therefore, the
10 starting-point dependence originates from this Green's function G_0 . In contrast, *scGW*
11 calculations are carried out in a different way: the Green's function of the system, G , is
12 obtained by the iteration of the Dyson's equation.^{2,21} Different from G_0W_0 , where G is
13 obtained perturbatively, the Green's function of the system is *renormalized* while solving
14 the Dyson's equation self-consistently. The starting-point dependence in G is eliminated
15 during this self-consistency because of the renormalization process, so the resulting self-
16 energy does not contain the starting-point information.
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19 From the viewpoint of correlation energy under the RPA, this renormalization process
20 brings the contribution of higher order terms, including the single contribution, into the total
21 energy iteratively. Singles are the contributions to the perturbation Hamiltonian within
22 the one-particle space and are the main sources of the starting-point dependence in the
23 RPA correlation energy calculation.^{32,34} In the self-consistent RPA approach,³⁴ singles are
24 absorbed into the total energy through the iteration, which is quite similar to the *scGW*
25 process. In the non-self-consistent approach, singles are derived in two ways: from the
26 Rayleigh-Schödinger perturbation theory (RSPT) by Ren and coworkers,³² and from the
27 adiabatic-connection fluctuation-dissipation theorem (ACFDT) by Klimeš and coworkers.³⁵
28 Both methods agree to the second order. By considering higher order contributions from
29 singles, which are also known as the renormalized singles (RS), they are not identical, but
30 practically they give the same performance. However, all three methods only focus on the
31 correlation energy. In this work, we further extend the concept of RS for describing quasi-
32 particles in *GW* approximation so as to eliminate the DFA dependence and achieve robust
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accuracy for GW calculations.

We begin with the Dyson equation for the one-body Green's function G ,

$$G^{-1} = (G_0)^{-1} - (\Sigma_{Hxc} - v_{Hxc}), \quad (1)$$

where G_0 is the Green's function describing a noninteracting (G)KS system within a DFA, with v_{Hxc} and Σ_{Hxc} being the Hartree-exchange-correlation potential and self-energy respectively. The Hartree and exchange self-energy Σ_{Hx} and v_{Hxc} are all within the space of effective non-interacting systems. Our key idea is that this effective non-interacting part of the self-energy can and should be addressed easily beyond the perturbation approach used in G_0W_0 .

Note that the Hartree-Fock (HF) Green's function is defined as the self-consistent solution of the following Dyson equation:

$$G_{\text{HF}}^{-1} = (G_0)^{-1} - (\Sigma_{Hx}(G_{\text{HF}}) - v_{Hxc}). \quad (2)$$

Its self-consistent solution eliminates the dependence on DFA and there is no single contribution in the perturbation theory according to the Brillouin's theorem.³⁶ However, G_{HF} is not a good starting point for GW calculations in general, as is well known and can also be seen in numerical results reported in this work. Instead, we pursue a different strategy: we want to eliminate the dependence on the orbital energies of DFA but use the density and orbitals of DFA because of their good accuracy. We define the renormalized single Green's function G_{RS} as the solution of the following two projected equations

$$PG_{\text{RS}}^{-1}P = P(G_0)^{-1}P - P(\Sigma_{Hx}(G_0) - v_{Hxc})P, \quad (3)$$

and

$$QG_{\text{RS}}^{-1}Q = Q(G_0)^{-1}Q - Q(\Sigma_{Hx}(G_0) - v_{Hxc})Q, \quad (4)$$

where $P = \sum_i^{\text{occ}} |\psi_i\rangle \langle \psi_i|$ is the projection into the occupied orbital space obtained from the starting DFA calculations, and $Q = I - P$ is the projection into the virtual orbital space. Our G_{RS} is defined as the sum of the two projections

$$(G_{\text{RS}})^{-1} = PG_{\text{RS}}^{-1}P + QG_{\text{RS}}^{-1}Q = (G_0)^{-1} - P(\Sigma_{Hx}(G_0) - v_{Hxc})P - Q(\Sigma_{Hx}(G_0) - v_{Hxc})Q, \quad (5)$$

where we use the fact that $(G_0)^{-1} = P(G_0)^{-1}P + Q(G_0)^{-1}Q$. Solution of Eq. (3)/(4) is straightforward: it is the one-shot occupied/virtual subspace diagonalization of the HF Hamiltonian evaluated at the density matrix given by the DFA; namely

$$PH_{\text{HF}}(G_0)P|\psi_i^{\text{RS}}\rangle = \epsilon_i^{\text{RS}}P|\psi_i^{\text{RS}}\rangle, \quad (6)$$

and

$$QH_{\text{HF}}(G_0)Q|\psi_a^{\text{RS}}\rangle = \epsilon_a^{\text{RS}}Q|\psi_a^{\text{RS}}\rangle, \quad (7)$$

where ϵ_n^{RS} and $|\psi_n^{\text{RS}}\rangle$ are the eigenvalues and eigenfunctions from the subspace diagonalization. The diagonalizations rotate the orbitals within each subspace and G_{RS} is diagonal in the space of $|\psi_i^{\text{RS}}\rangle$ and $|\psi_a^{\text{RS}}\rangle$,

$$(G_{\text{RS}})_{nm}(\omega) = \frac{1}{\omega - \epsilon_n^{\text{RS}} + i\eta \text{sgn}(\epsilon_n^{\text{RS}} - \mu)}. \quad (8)$$

The resulting Green's function G_{RS} describes an effective non-interacting reference system and includes most of the effects of the single contributions by having the self-energy

$$\Sigma_{\text{RS}} = P(\Sigma_{Hx}(G_0) - v_{Hxc})P + Q(\Sigma_{Hx}(G_0) - v_{Hxc})Q, \quad (9)$$

which is the essential part of $\Sigma_{Hx} - v_{Hxc}$. The single contribution, originated from $\Sigma_{Hx} - v_{Hxc}$, is thus included fully in the two subspaces of P and Q, far beyond perturbation - that is the meaning of the name renormalized singles. We thus expect the starting-point DFA

dependence will be greatly reduced if G_{RS} is used as the starting Green's function.

Combine Eq. (5) and Eq. (1), we have

$$G^{-1} = (G_{\text{RS}})^{-1} - \Sigma_c - \Delta\Sigma, \quad (10)$$

where we define

$$\Delta\Sigma = (\Sigma_{Hx} - v_{Hxc}) - P(\Sigma_{Hx}(G_0) - v_{Hxc})P - Q(\Sigma_{Hx}(G_0) - v_{Hxc})Q. \quad (11)$$

We expect $\Delta\Sigma$ to be small. Eq. (10) is exact and also allows perturbative solution, using G_{RS} as the starting point. We now define our key contribution, the $G_{\text{RS}}W_0$ approximation, by combining the GW approximation and the first-order perturbation based on the RS reference Green's function G_{RS} for quasi-particle energy, in the same spirit as the commonly used G_0W_0 approximation. Note that within this first-order approximation, $\Delta\Sigma$ makes no contribution to the quasi-particle energy because $\langle \psi_n^{\text{RS}} | \Delta\Sigma | \psi_n^{\text{RS}} \rangle = 0$. The quasi-particle energy is then given by the equation

$$\epsilon_n = \epsilon_n^{\text{RS}} + \langle \psi_n^{\text{RS}} | \Sigma_c^{G_{\text{RS}}W_0}(\omega) | \psi_n^{\text{RS}} \rangle, \quad (12)$$

which can be linearized to

$$\epsilon_n = \epsilon_n^{\text{RS}} + Z_n \langle \psi_n^{\text{RS}} | \Sigma_c^{G_{\text{RS}}W_0}(\epsilon_n^{\text{RS}}) | \psi_n^{\text{RS}} \rangle, \quad (13)$$

where Z_n is the normalization factor

$$Z_n = \left(1 - \left\langle \psi_n^{\text{RS}} \left| \frac{\partial \Sigma_c^{G_{\text{RS}}W_0}(\omega)}{\partial \omega} \Big|_{\epsilon_n^{\text{RS}}} \right| \psi_n^{\text{RS}} \right\rangle \right)^{-1} \quad (14)$$

Eq. (12) for quasi-particle energies can be easily implemented, in same way as in G_0W_0 except with the use of the renormalized reference ϵ_n^{RS} and $|\psi_n^{\text{RS}}\rangle$. Other than Eq. (6) and

(7), a full-space diagonalization can also be implemented:

$$H_{\text{HF}}(G_0)|\psi_i^{\text{RS2}}\rangle = \epsilon_i^{\text{RS2}}|\psi_i^{\text{RS2}}\rangle. \quad (15)$$

And the corresponding Green's function $(G_{\text{RS2}})_{nn}(\omega) = (\omega - \epsilon_n^{\text{RS2}} + i\eta\text{sgn}(\epsilon_n^{\text{RS2}} - \mu))^{-1}$ is diagonal in the $|\psi_i^{\text{RS2}}\rangle$ space. Notice that in Eq. (15), the HF Hamiltonian is evaluated with the fixed DFA density matrix, otherwise it will give the HF solution. They yield similar results (shown in SI, Table I), however the sub-space diagonalization associated with G_{RS} is computationally much more favorable. Furthermore, in practice, the orbitals directly from DFA calculations are used for greater simplicity, as we have shown that the IP differences between two choices are within 0.02 eV (shown in SI, Table II).

We first examine our $G_{\text{RS}}W_0$ approximation on the ionization potentials (IPs) of 100 molecules from the $GW27^9$ and $GW100$ test set.¹¹ Molecules with Ag, Cu and Au are not considered because of the DFA convergence problem in our program. The details of computations and results can be found in the SI. Here we only show the mean signed deviation (MSD) and mean absolute deviation (MAD) compared to the CCSD(T) references, listed in Table 1. Our G_0W_0 results are consistent with literature.^{9,11} G_0W_0 shows large errors when combined with LDA and PBE, the MSD/MAD are -0.44/0.44 and -0.50/0.50 eV, respectively, with the IPs being systematically underestimated based on the MSDs. Whilst with hybrid functional B3LYP, the MAD becomes smaller (0.26 eV), however, it still systematically underestimates IPs. In contrast, $G_{\text{RS}}W_0$ significantly improves the results. The systematic underestimation errors in G_0W_0 are not observed with $G_{\text{RS}}W_0$. Most importantly, the starting-point dependence is largely eliminated, the MADs are 0.19, 0.15, and 0.14 eV for $G_{\text{RS}}W_0$ with LDA, PBE, and B3LYP respectively, which are much more accurate than G_0W_0 . The correction of $G_{\text{RS}}W_0$ can be clearly visualized in Fig. 1.

While G_0W_0 with hybrid DFA is usually better than with (semi)local DFA, our results demonstrate that to achieve good accuracy, it is not necessary to use hybrid DFA, which

is expensive for bulks. $G_{\text{RS}}W_0$ calculations show similar excellent accuracy for (semi)local and hybrid DFAs, with significant improvement over G_0W_0 with either (semi)local or hybrid DFA as the starting point.

Table 1: The MSD and MAD of IPs from G_0W_0 and $G_{\text{RS}}W_0$ calculations with different starting points (in eV). All calculations were done with def2-QZVP basis set in QM⁴D.³⁷

	$G_0W_0@LDA$	$G_{\text{RS}}W_0@LDA$	$G_0W_0@PBE$	$G_{\text{RS}}W_0@PBE$	$G_0W_0@B3LYP$	$G_{\text{RS}}W_0@B3LYP$	$G_0W_0@HF$
MSD	-0.44	0.04	-0.50	0.00	-0.23	0.03	0.34
MAD	0.44	0.19	0.50	0.15	0.26	0.14	0.35

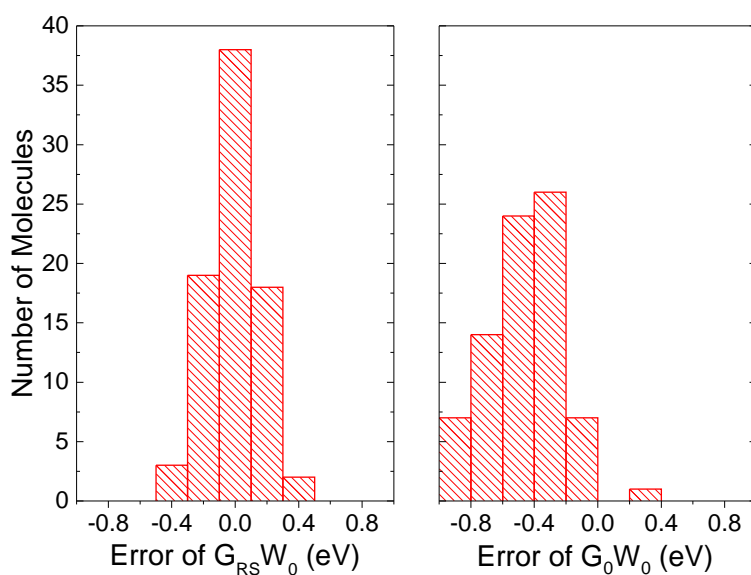


Figure 1: Error distributions of $G_{\text{RS}}W_0@PBE$ (left) and $G_0W_0@PBE$ (right). The pattern of $G_{\text{RS}}W_0@PBE$ shows a correction to the underestimation of $G_0W_0@PBE$.

It is very interesting to compare $G_{\text{RS}}W_0$ with $G_0W_0@HF$. When HF is the DFA, $G_{\text{RS}}W_0@HF$ is equivalent with $G_0W_0@HF$, which does not have good performances, as shown in Table 1. It overestimates the IPs with a MSD of 0.34 eV. Since singles do not contribute in the HF because of the Brillouin’s theorem, the comparison between $G_0W_0@HF$ and $G_{\text{RS}}W_0@DFA$ shows that the density matrix from the HF reference are not as good as those from a commonly used DFA references, such as LDA or PBE. $G_0W_0@LDA/PBE$ does not perform well because the Green’s function is not renormalized to include the single contributions beyond

the first-order approximation, but the subspaces described by the LDA or PBE orbitals are fine. The subspace diagonalization of Eqs. (6,7) are the key to capitalize the quality in the two subspaces of orbitals from DFA calculations. We thus conclude that a good many-body perturbation theory starting from the DFA reference should consider the single contributions beyond the perturbative approach within the fixed DFA orbital subspaces, as captured in the renormalized singles reference G_{RS} .

Electron affinities (EAs) were also calculated. Table 2 contains a subset including 45 molecules because not all CCSD(T) calculations for $(N + 1)$ -electron system are converged. We notice that some molecules show unphysical negative EAs. The reason is that the basis set is not converged for molecules with the unbounded LUMO. However, the comparison is still meaningful because both GW and CCSD(T) calculations are with the same basis set. From Table 2, G_0W_0 does not suffer much from the starting-point dependence in EA calculations. However, the EAs are overestimated systematically with all functionals considered. With the $G_{RS}W_0$ method, the overestimation is largely reduced, and the MAD is brought down by about 0.1 eV for all cases. Thus $G_{RS}W_0$ is capable of correcting both HOMO and LUMO, compared with G_0W_0 calculations.

Table 2: The MSD and MAD of EAs from G_0W_0 and $G_{RS}W_0$ calculations with different starting points (in eV). All calculations were done with def2-QZVP basis set.

	$G_0W_0@LDA$	$G_{RS}W_0@LDA$	$G_0W_0@PBE$	$G_{RS}W_0@PBE$	$G_0W_0@B3LYP$	$G_{RS}W_0@B3LYP$
MSD	0.33	0.10	0.29	0.09	0.29	0.16
MAD	0.36	0.20	0.33	0.18	0.32	0.23

Other than frontier orbitals, $G_{RS}W_0$ also improves the description of photoelectron spectra. For furan, $G_0W_0@PBE$ spectrum is not in good agreement with the experimental spectrum. Especially the first two peaks are largely shifted, as marked in Fig. 2. In comparison, $G_{RS}W_0@PBE$ nearly reproduces the shape of the experimental spectrum. The first two peaks are very close to the experimental ones, and peaks in inner shells are similar to experimental data within the same energy range. This result shows that $G_{RS}W_0$ can also

correct the IPs of non-HOMO electrons. Photoelectron spectra of benzene and acetylene were also calculated to show good comparison with experiments (see SI).

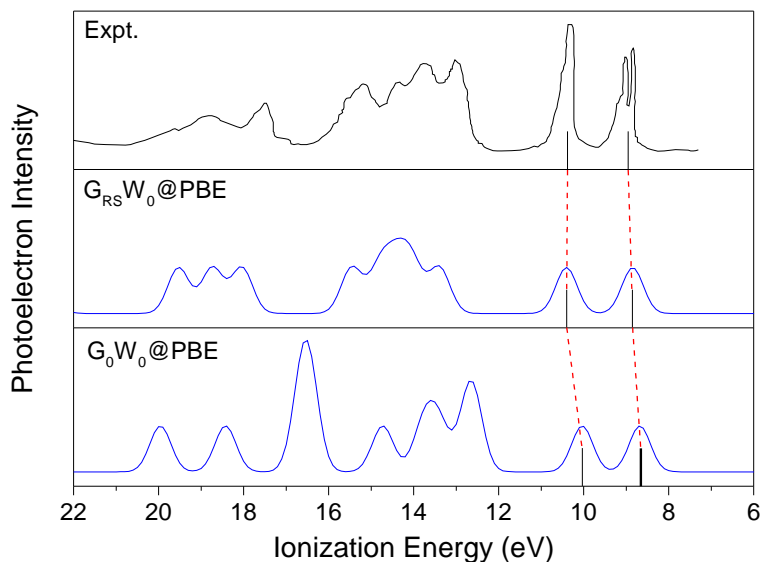


Figure 2: Photoelectron spectrum of furan. The experimental spectrum is from Ref.³⁸ Including the first two peaks, $G_{RS}W_0$ outperforms G_0W_0 for the whole spectrum within the same energy range.

Next we also explore the $G_{RS}W_0$ for one-dimensional polymer systems using polyenes and polyynes. Such π -conjugated systems have been extensively studied in molecular electronics experimentally.³⁹ The IPs are important in understanding the properties of these systems, their derivatives and compounds. The test results can be found in the SI (Table V/VI). In general, $G_0W_0@PBE$ underestimates the IPs for both systems, while $G_{RS}W_0@PBE$ corrects the results and offers an accuracy similar to CASPT2 calculations.

Finally, we consider bulk systems. We implemented our method in the exciting Code.^{40,41} The exciting Code is based on the full-potential linearized augmented plane waves (FLAPW) method, which is considered the benchmark choice of the electronic structure calculations for solids. All parameters for setting up the calculations of solids are the same to Ref.,⁴¹ and the default basis set mentioned in the reference is used. In practice, core electrons are treated separately. Here we only built the HF Hamiltonian for non-core orbitals for subspace

diagonalization, with eigenvalues of core orbitals kept unchanged, which should have little effect on the GW calculations for the valence properties. From Table 3, the $G_0W_0@LDA$ results are consistent with literature.⁴¹ Overall, $G_0W_0@LDA$ underestimates the band gaps by 0.65 eV. With $G_{RS}W_0@LDA$, the MAD/MSD error is reduced to 0.55/0.34 eV from 0.67/-0.65 eV for $G_0W_0@LDA$. In particular, $G_{RS}W_0$ works well for large gap insulators, like Ar or Ne. $G_0W_0@LDA$ can underestimate by 1 eV for large gap systems and $G_{RS}W_0$ improves the result significantly. In general, the improvement of our method for solids is less than that for molecules. This behavior might be caused by the lack of consistent treatment for the core electrons in our current implementation for bulk solids, the approximation of using DFA orbitals instead of RS orbitals, or the first-order approximation to Eq. 11. We will explore these possibilities in the near future.

Table 3: Fundamental gaps of $G_0W_0@LDA$ and $G_{RS}W_0@LDA$ for bulk systems (in eV). All structures and references are from Ref.²² Spin-orbit coupling (SO) is not considered because it is negligible in these systems.²²

	$G_0W_0@LDA$	$G_{RS}W_0@LDA$	Ref.
AlP	2.31	3.00	2.45
Ar	12.51	13.54	14.2
BN	6.26	7.16	6.4
C	5.60	6.32	5.48
CdS	1.93	2.71	2.42
GaAs	1.41	1.95	1.52
GaN	2.79	3.70	3.2
LiF	13.44	14.74	14.2
MgO	7.26	8.22	7.83
Ne	19.99	21.28	21.7
MSD	-0.65	0.34	
MAD	0.67	0.55	

We want to clarify that although our method may appear somewhat similar to HF, it is certainly different and not an approximation to the HF theory. HF is the first-order term of the many-body perturbation theory (MBPT), but it does not mean that it is a proper starting point for the MBPT. Recall that in our test, $G_0W_0@HF$ for IPs has a MSD/MAD of 0.35/0.35 eV (compared to 0.00/0.15 eV in our method with $G_{RS}W_0@PBE$). On the other

hand, DFA provides more accurate density and density matrix and thus it is a better reference as the starting point for perturbation theory. However, G_0W_0 with DFA starting point in common applications only contains single contributions to the first order in a perturbative way, leading to the strong dependence on the starting DFA. In our method, by performing the sub-space diagonalization, we keep the better density from DFA and account for most single contributions with strong renormalization of singles into the reference G_{RS} . Our method based on G_{RS} thus depicts a proper starting theory from DFA to carry out MBPT and is clearly beyond the first-order HF theory.

It is also worth noting that the renormalization of the Green's function provides a correction on top of G_0W_0 , but it cannot overcome the intrinsic problem within the GW theory. For instance, it is known that GW theory does not work well on band gaps for homogeneous electron gas because of the lack of vertex correction.^{21,25} Since $G_{RS}W_0$ is still within the framework of GW theory, it is expected that $G_{RS}W_0$ may not be sufficient to address this challenge.

In summary, the $G_{RS}W_0$ approximation developed in this letter provides a simple and efficient method to improve the accuracy and eliminate the starting-point dependence in G_0W_0 by introducing RS into the starting reference. $G_{RS}W_0$ combines the merits of RS from HF potential and the more accurate density matrix from DFA starting point, which can be realized through a easily calculated subspace diagonalization of the HF Hamiltonian evaluated at the DFA density matrix. The tests on different types of systems, including IPs and EAs of small-sized molecules and polymers, and photoemission spectra demonstrate that $G_{RS}W_0$ can consistently improve the accuracy of G_0W_0 calculations and effectively reduce the undesired starting-point dependence. The results on solids are improved over the G_0W_0 results to a lesser extent than for molecular system. But the improvement is particularly significant for large gap bulk systems. We will explore this in the future to achieve systematic improvement for both finite and bulk systems. This work should be greatly significant in making GW a more robust approach.

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