

Solving multipole challenges in the GW100 benchmark enables precise low-scaling GW calculations

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The GW approximation is a widely used method for computing electron addition and removal energies of molecules and solids. The computational effort of conventional GW algorithms increases as $O(N^4)$ with the system size N , hindering the application of GW to large and complex systems. Low-scaling GW algorithms are currently very actively developed. Benchmark studies at the single-shot G_0W_0 level indicate excellent numerical precision for frontier quasiparticle energies, with mean absolute deviations <10 meV between low-scaling and standard implementations for the widely used GW100 test set. A notable challenge for low-scaling GW algorithms remains in achieving high precision for five molecules within the GW100 test set, namely O_3 , BeO, MgO, BN, and CuCN, for which the deviations are in the range of several hundred meV at the G_0W_0 level. This is because of a spurious transfer of spectral weight from the quasiparticle to the satellite spectrum in G_0W_0 calculations, resulting in multipole features in the self-energy and spectral function, which low-scaling algorithms fail to describe. We show in this paper that including eigenvalue self-consistency in the Green's function (evGW₀) achieves a proper separation between satellite and quasiparticle peak, leading to a single solution of the quasiparticle equation with spectral weight close to one. evGW₀ quasiparticle energies from low-scaling GW closely align with reference calculations; the mean absolute error is only 12 meV for the five molecules. We thus demonstrate that low-scaling GW with self-consistency in G is well suited for computing frontier quasiparticle energies.

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I. INTRODUCTION

GW calculations [1–3] have become a standard tool for calculating electron addition and removal energies of molecules [4–6], two-dimensional materials [7–19], and solids [20–26]. Recent advancements of the GW method span a broad spectrum, including the application to deep core excitations [27–35], relativistic GW schemes [36–42], exploring excited-state potential energy surfaces from GW + Bethe-Salpeter [43–46], electron dynamics from Green's functions [47–58], and applying the GW methodology in magnetic fields [59–62]. There has also been a concerted effort towards benchmarking the accuracy of the GW method [63–66] and the numerical precision of GW implementations [5,67–72]. An increasing number of machine learning models have emerged for predicting quasiparticle (QP) energies without performing a costly GW calculation [73–79]. Concerning method development beyond the GW approximation, vertex corrections [80–93] and connections with coupled-cluster methods [94–96] have been explored. Promising developments for the study of electronic excitations in the solid state have also been reported using coupled-cluster methods [97–103] and low-scaling Bethe-Salpeter approaches [104–106].

Despite that GW method development is blooming, several algorithmic bottlenecks render GW calculations challenging,

particularly in dealing with complex or disordered systems with large simulation cells. In conventional GW implementations, the computational cost increases as $O(N^4)$ with the system size N , restricting conventional GW calculations often to systems with a few hundred atoms [2,73]. Various strategies have been devised to tackle this limitation, ranging from massively parallel implementations [107–113], to physically motivated approximations like embedding [114–119] and low-scaling techniques [120–136]. In this paper, we focus on deterministic, low-scaling GW algorithms based on the GW space-time method by Rojas, Godby, and Needs published in 1995 [120]. The GW space-time method relies on space-local representations and imaginary time-frequency transforms and achieves cubic scaling of the computational cost in the system size $O(N^3)$ instead of quartic scaling $O(N^4)$ of conventional GW algorithms. Many different techniques have been used to increase the computational efficiency of the GW space-time method, including pair-atomic resolution of the identity [130,137–140], separable density fitting [129,135,141–145], and global resolution of the identity with a local metric [14,128,134,146,147].

All of the space-time GW algorithms include three Fourier transforms between imaginary time and imaginary frequency, and vice versa, which are performed numerically. This poses a significant challenge in terms of numerical precision, a challenge that has been addressed by the development of tailored imaginary-time and imaginary-frequency grids [124,148–150]. The precision of these numerical grids has

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undergone rigorous benchmarking against highly accurate GW calculations across various systems, including solids [124,149], two-dimensional materials [149], and molecules [71,134,149]. Overall, the findings indicate excellent numerical precision, typically better than 10 meV for QP energies of the highest valence states and the lowest empty states [134,149].

A notable challenge remains in achieving high precision for five molecules within the $GW100$ test set [5], namely O_3 , BeO , MgO , BN , and $CuCN$ [134], at the single-shot G_0W_0 level of theory [2] using the Perdew-Burke-Ernzerhof (PBE) functional [151] for the underlying Kohn-Sham density functional theory [152] (KS-DFT) calculation. We refer to this procedure as $G_0W_0@PBE$. For these molecules, the $G_0W_0@PBE$ energies computed from low-scaling algorithms can differ by several hundred meV from reference calculations [134]. In this paper, we revisit these five molecules and we aim to demonstrate that the multiple $G_0W_0@PBE$ solutions of the QP equation are unphysical and that a physically sound, single solution can be obtained using partial eigenvalue self-consistency in the Green's function or using a hybrid functional as starting point for G_0W_0 . We also aim to show that the low-scaling GW algorithms are numerically precise for the GW flavors, which yield a single solution.

The article is organized as follows: We discuss the G_0W_0 scheme and multipole artifacts in the $GW100$ benchmark in Sec. II and how these multipole artifacts are resolved with eigenvalue-selfconsistency in G (ev GW_0) in Sec. III. We describe the low-scaling space-time GW algorithm in Sec. IV and the reference GW algorithm based on contour deformation in Sec. V. Computational details of our GW calculations are given in Sec. VI. We present and discuss $G_0W_0@PBE$, ev GW_0 and $G_0W_0@PBE0$ calculations in Sec. VII, VIII and IX, respectively.

II. MULTISOLUTION ARTIFACTS AT THE G_0W_0 LEVEL

In this section, we briefly introduce the G_0W_0 approach and different methods to obtain the QP solution, including the evaluation of the spectral function. We showcase the issue of multisolution artifacts for the MgO gas phase molecule, which is part of the $GW100$ benchmark set [5].

The $GW100$ set is the standard molecular test set for assessing the accuracy of GW approaches and GW implementations [31,67,69–71,89,128,134,143,153–157]. $GW100$ contains one hundred small molecules with covalent and ionic bonds covering a wide range of the periodic table. The original $GW100$ study [5] reports the $G_0W_0@PBE$ QP energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for all one hundred molecules. Those $G_0W_0@PBE$ data are the ones against which new low-scaling algorithms are typically benchmarked [71,134,149].

A G_0W_0 calculation starts from a self-consistent KS-DFT calculation [152],

$$[h_0(\mathbf{r}) + v_{xc}(\mathbf{r})]\psi_n(\mathbf{r}) = \varepsilon_n^{\text{DFT}} \psi_n(\mathbf{r}). \quad (1)$$

h_0 contains the kinetic energy, the Hartree potential, and the external potential, while the exchange-correlation potential v_{xc} contains all electron-electron interactions beyond Hartree.

$\psi_n(\mathbf{r})$ is the KS orbital n and $\varepsilon_n^{\text{DFT}}$ the associated KS eigenvalue. The terms G_0 and W_0 indicate that the Green's function G and the screened Coulomb interaction W are both computed using KS orbitals and KS eigenvalues, i.e., self-consistent updates of G and W from Green's function theory are omitted in G_0W_0 .

A central object in a G_0W_0 calculation is the G_0W_0 correlation self-energy, which can be expressed as [2,158]

$$\Sigma_n^c(\omega) = \sum_m \sum_s \frac{\langle \psi_n \psi_m | P_s | \psi_m \psi_n \rangle}{\omega - \varepsilon_m^{\text{DFT}} + (\Omega_s^{\text{RPA}} - i\eta) \text{sgn}(\varepsilon_F - \varepsilon_m^{\text{DFT})}}. \quad (2)$$

Here, ω denotes a frequency, ε_F the Fermi level of KS-DFT and $\eta > 0$ a broadening. Ω_s^{RPA} with $\Omega_1^{\text{RPA}} \leq \Omega_2^{\text{RPA}} \leq \dots$ are the charge-neutral singlet excitation energies computed using the random phase approximation (RPA), i.e., a vanishing exchange-correlation kernel [159] (see also discussion in Appendix B); P_s represents the product of transition densities of the excitation s [2,158].

One observable computed in a G_0W_0 calculation is the molecular spectral function, which takes the form of a many-body density of states [2,160],

$$A(\omega) = \frac{1}{\pi} \text{Im} G(\omega) \text{sgn}(\varepsilon_F - \omega), \quad (3)$$

where $G(\omega)$ is the trace over spatial arguments of the single-particle Green's function. We express the spectral function as

$$A(\omega) = \sum_n A_n(\omega), \quad (4)$$

where n runs over all KS orbitals with a contribution $A_n(\omega)$ to the spectral function [2,28,124,161]

$$\begin{aligned} A_n(\omega) &= \frac{1}{\pi} \text{Im} \frac{\text{sgn}(\omega - \varepsilon_F)}{\omega - (\varepsilon_n^{\text{DFT}} + \Sigma_n^c(\omega) + i\eta + \Sigma_n^x - v_n^{\text{xc}})} \\ &= \frac{1}{\pi} \frac{|\gamma|}{(\omega - (\varepsilon_n^{\text{DFT}} + \text{Re} \Sigma_n^c(\omega) + \Sigma_n^x - v_n^{\text{xc}}))^2 + \gamma^2}. \end{aligned} \quad (5)$$

Here, $\gamma = \text{Im} \Sigma_n^c(\omega) + \eta$, $\Sigma^x(\mathbf{r}, \mathbf{r}')$ is the exchange self-energy [2] and Σ_n^x and v_n^{xc} are the (n, n) -diagonal elements of the respective quantities.

The peak positions $\varepsilon_n^{G_0W_0}$ of $A(\omega)$, known as QP energies, correspond to the negative of the ionization energies and to electron affinities of the molecule. QP energies are the frequencies where the real part of the denominator in Eq. (5) equals zero, i.e., the QP energies $\varepsilon_n^{G_0W_0}$ satisfy the QP equation

$$\varepsilon_n^{G_0W_0} = \varepsilon_n^{\text{DFT}} + \text{Re} \Sigma_n^c(\varepsilon_n^{G_0W_0}) + \Sigma_n^x - v_n^{\text{xc}}. \quad (7)$$

The nonlinearity of $\Sigma_n^c(\omega)$ with respect to ω , allows for multiple solutions $\varepsilon_n^{G_0W_0}$ for a given level n . Such multiple solutions have been observed for five molecules in the $GW100$ test, namely O_3 , BeO , MgO , BN , and $CuCN$ at the $G_0W_0@PBE$ level [5].

We illustrate multiple solutions of Eq. (7) for state $n = \text{HOMO}$ of the MgO molecule, see Fig. 1(a). The black-dashed traces visualize the linear function

$$f(\omega) = \omega - (\varepsilon_{\text{HOMO}}^{\text{DFT}} + \Sigma_{\text{HOMO}}^x - v_{\text{HOMO}}^{\text{xc}}) \quad (8)$$

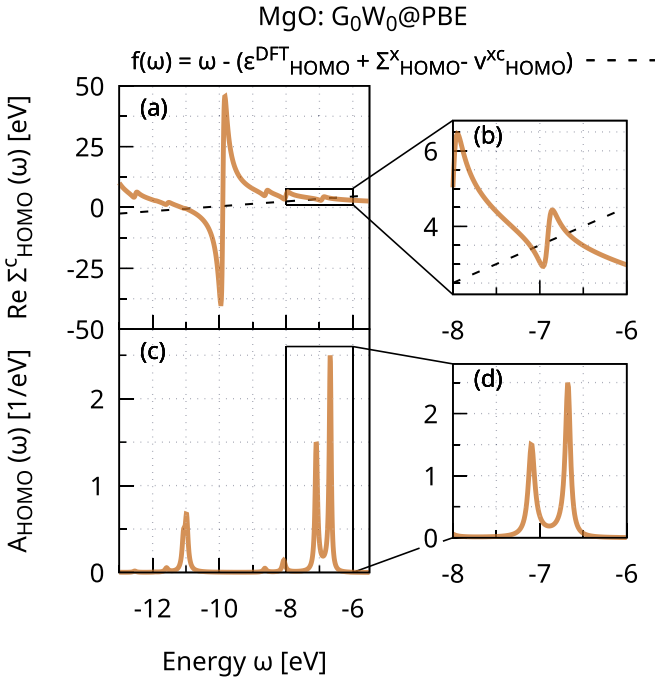


FIG. 1. [(a), (b)] Real part of the G_0W_0 @PBE HOMO self-energy $\Sigma_{\text{HOMO}}^c(\omega)$, Eq. (2), for the MgO molecule from the GW100 set. Intersections of the straight line $f(\omega)$ and $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$ lead to five solutions of the QP equation (7), as already discussed in Ref. [5]. [(c), (d)] G_0W_0 @PBE HOMO contribution $A_{\text{HOMO}}(\omega)$ to the spectral function, Eq. (5). We have computed all quantities using the numerically precise contour deformation as implemented in FHI-aims [27] and a broadening $\eta = 1$ mHa, see further details in Secs. V and VI.

such that the intersections ε of $f(\omega)$ and $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$, $f(\varepsilon) = \text{Re } \Sigma_{\text{HOMO}}^c(\varepsilon)$, are the solutions of the QP equation (7). Five intersections are apparent, $\varepsilon \in \{-11.00 \text{ eV}, -9.90 \text{ eV}, -7.09 \text{ eV}, -6.91 \text{ eV}, -6.68 \text{ eV}\}$, where the highest solution has been picked in the original paper [5] as G_0W_0 @PBE HOMO energy. The large number of intersections is caused by the many poles in the self-energy (2).

Each intersection ε comes with a spectral weight Z_ε that quantifies the number of electrons associated with a given peak in the spectral function. Z_ε is usually approximately computed as

$$Z_\varepsilon \approx \left[1 - \text{Re} \frac{\partial \Sigma_n^c(\omega)}{\partial \omega} \bigg|_{\omega = \varepsilon} \right]^{-1}, \quad (9)$$

see Appendix A for a derivation. Because of the small slope of $\Sigma_{\text{HOMO}}^c(\omega)$ at the intersections $\varepsilon \in \{-7.09 \text{ eV}, -6.68 \text{ eV}\}$, the associated spectral weight is large, whereas the other intersections exhibit a relatively small spectral weight. This is also apparent in the HOMO contribution $A_{\text{HOMO}}(\omega)$ to the G_0W_0 @PBE spectral function (5), see Figs. 1(c) and 1(d). Three major peaks are visible at -11.0 eV , -7.09 eV , and -6.68 eV , precisely located at intersections of $f(\omega)$ and $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$. In particular, the two peaks at $\varepsilon \in \{-7.09 \text{ eV}, -6.68 \text{ eV}\}$ carry both significant spectral weight, i.e., a distinct single QP peak is absent.

TABLE I. PBE and PBE0 eigenvalues and excitation energies $\Omega_{\text{TDDFT/RPA}}^{\text{DFT}}$ from time-dependent DFT (TDDFT) and RPA of the MgO molecule. All values in eV. In Appendix B, we give details on TDDFT and RPA and we discuss the origin of the relationship $\Omega_1^{\text{PBE}} \approx \Omega_1^{\text{PBE0}} \approx \Omega_1^{\text{RPA@PBE}} \ll \Omega_1^{\text{RPA@PBE0}}$. TDDFT and RPA excitation energies have been computed using pyscf [162].

	PBE	PBE0
$\varepsilon_{\text{HOMO}-3}^{\text{DFT}}$	-19.52	-22.13
$\varepsilon_{\text{HOMO}-2}^{\text{DFT}}$	-6.09	-6.87
$\varepsilon_{\text{HOMO}}^{\text{DFT}} = \varepsilon_{\text{HOMO}-1}^{\text{DFT}}$	-4.79	-6.07
$\varepsilon_{\text{LUMO}}^{\text{DFT}}$	-4.29	-3.60
$\Omega_{s=1}^{\text{TDDFT}} = \Omega_{s=2}^{\text{TDDFT}}$	0.67	0.62
$\Omega_{s=1}^{\text{RPA}} = \Omega_{s=2}^{\text{RPA}}$	0.82	2.83
$\Omega_{s=3}^{\text{TDDFT}}$	2.87	2.86
$\Omega_{s=3}^{\text{RPA}}$	3.21	4.91

A closer inspection of $\Sigma_{\text{HOMO}}^c(\omega)$ at the two intersections $\varepsilon \in \{-7.09 \text{ eV}, -6.68 \text{ eV}\}$ in Fig. 1(b) reveals a shallow pole of $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$ at $\omega_{\text{pole}}^{\text{MgO}} = -6.91 \text{ eV}$. As evident from Eq. (2), poles in the real part of the self-energy occur at

$$\omega_{\text{pole}} = \varepsilon_i^{\text{DFT}} - \Omega_s^{\text{RPA}} \quad \text{or} \quad \omega_{\text{pole}} = \varepsilon_a^{\text{DFT}} + \Omega_s^{\text{RPA}}, \quad (10)$$

where i denotes an occupied and a an empty KS orbital index. For a calculation with $2N_{\text{el}}$ electrons and N_{basis} basis functions, this makes in total $N_s = N_{\text{el}}(N_{\text{basis}} - N_{\text{el}})$ excitation energies Ω_s^{RPA} , $s = 1, \dots, N_s$ and thus $N_{\text{basis}}N_s$ poles in $\Sigma_{\text{HOMO}}^c(\omega)$ [163]. We list KS eigenvalues and RPA charge-neutral excitation energies Ω_s^{RPA} of MgO in Table I and we identify the self-energy pole at -6.91 eV based on Table I as

$$\omega_{\text{pole}}^{\text{MgO}} = \varepsilon_{\text{HOMO}-2}^{\text{PBE}} - \Omega_{s=1}^{\text{RPA@PBE}} = -6.91 \text{ eV}. \quad (11)$$

Poles in the real-part of the self-energy have corresponding peaks in the imaginary part of Σ^c [2]. A distinct QP peak in $A_n(\omega)$ at $\omega = \varepsilon^*$ emerges when $\text{Im } \Sigma^c$ is small, as obvious from Eq. (6). This is the case when the QP peak is far away from any pole of $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$. The spectral weight Z_{ε^*} of the QP peak is then close to one because of a small slope of the self-energy, $|\text{Re } \partial_\omega \Sigma_n^c(\omega = \varepsilon^*)| \ll 1$ [2]. Further intersections of $f(\omega)$ and $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$ exist at energies lower than $\omega = \varepsilon^*$. All these solutions are close to a pole in $\text{Re } \Sigma_{\text{HOMO}}^c(\omega)$. $\text{Im } \Sigma^c$ is consequently large, resulting in low spectral weights. In other words, we obtain further solutions with satellite character. In the molecular case, satellites are the result of multielectron excitations, i.e., the charged electron or hole excitation couples to charge-neutral electronic excitations.

The PBE eigenvalues $\varepsilon_i^{\text{PBE}}$ of occupied KS states are overestimated and usually a few electron volts higher in energy compared to the GW energies. The poles at $\varepsilon_i^{\text{PBE}} - \Omega_s^{\text{RPA}}$ are therefore at too high frequencies. Or in other words, the satellites occur erroneously at too high energy and are too close to the QP peak. For HOMO excitations computed at the G_0W_0 @PBE level, satellites and QP peak are still well separated for most molecules and solids. Exceptions are, for example, the five molecules we discuss in this paper. As we

demonstrated for MgO, $\omega_{\text{pole}}^{\text{MgO}} = \varepsilon_{\text{HOMO}-2}^{\text{PBE}} - \Omega_{s=1}^{\text{RPA}}$ is located close to the QP solution. This results in an erroneous redistribution of spectral weight from the QP to the satellite solution, ultimately causing the observed multisolution behavior. The location of the satellites becomes increasingly incorrect for deeper excitations. While $\varepsilon_i^{\text{PBE}}$ is overestimated by a few electron volts for HOMO excitations, this overestimation is significantly larger, around 20–30 eV for 1s excitations of second-row elements [27]. In these cases, the poles are drastically too high in energy and the satellites always overlap with the QP solution, leading to a pronounced multisolution scenario with no identifiable QP peak at the G_0W_0 @PBE level [28,33]. This stands in stark contrast to experimental observations, where one sharp 1s main peak with very small satellites is observed in x-ray photoemission spectra of closed shell molecules [164–166].

We observe similar multisolution behavior as described for MgO for the HOMO of BeO, BN, O₃ and CuCN from the GW_{100} set, see Figs. 5 and 6 in the Appendix. These multiple solutions at the G_0W_0 @PBE level are not only unphysical as discussed above, but they also pose a numerical challenge to low-scaling GW algorithms [128,134]. In this paper, we address this issue.

III. CORRECTION OF MULTIPOLE ARTIFACTS WITH EIGENVALUE-SELFCONSISTENCY IN G

The crucial role of eigenvalue self-consistency in the Green's function (evG) has long been recognized in the literature [33,75,163,167–170] as essential for preventing an artificial transfer of spectral weight from the QP peak to the satellites and suppressing multisolution behavior. We denote this procedure as $\text{ev}GW_0$ where W is fixed at the G_0W_0 level, while G in Eq. (23) is recomputed from Eq. (16) using the QP energies (7). This procedure is repeated until self-consistency in the QP energies $\varepsilon_m^{\text{QP}}$ is reached [2]. In $\text{ev}GW_0$, the energies $\varepsilon_m^{\text{DFT}}$ in Eq. (2) are replaced by $\varepsilon_m^{\text{QP}} = \varepsilon_m^{\text{DFT}} + \Delta_m^{\text{QP}}$, where Δ_m^{QP} is the QP correction for state m . The poles of $\text{Re } \Sigma_n^c$ (Eq. (2)) in $\text{ev}GW_0$ are consequently at

$$\omega_{\text{pole}} = \varepsilon_i^{\text{DFT}} + \Delta_i^{\text{QP}} - \Omega_s^{\text{RPA}} \quad \text{for occupied orbital } i, \quad (12)$$

$$\omega_{\text{pole}} = \varepsilon_a^{\text{DFT}} + \Delta_a^{\text{QP}} + \Omega_s^{\text{RPA}} \quad \text{for empty orbital } a. \quad (13)$$

When using the PBE functional in KS-DFT, Δ_m^{QP} is usually negative for occupied states and positive for the empty states. Compared to G_0W_0 @PBE, poles at frequency below the Fermi level thus often shift to more negative frequencies and poles at frequencies above the Fermi level to more positive frequencies. We will demonstrate this for the MgO case in Sec. VIII.

We want to assess now in which frequency ranges poles in $\text{Re } \Sigma_n^c(\omega)$ occur at the $\text{ev}GW_0$ level, following the discussion of V  ril *et al.* [163]. In addition to requiring $\text{ev}G$, we also assume positive, nonzero singlet RPA excitation energies $\Omega_s^{\text{RPA}} > 0$, which should be the case for weakly correlated systems. For every level n close to HOMO and LUMO with

$$\varepsilon_n^{\text{QP}} \in [\varepsilon_{\text{HOMO}}^{\text{QP}} - \Omega_1^{\text{RPA}}, \varepsilon_{\text{LUMO}}^{\text{QP}} + \Omega_1^{\text{RPA}}], \quad (14)$$

the denominator of $\Sigma_n^c(\omega)$ in Eq. (2) is strictly nonzero (even for $\eta \rightarrow 0$) because Eq. (14) implies

$$\begin{aligned} \omega - \varepsilon_i^{\text{QP}} + \Omega_s^{\text{RPA}} &> 0 \quad \text{for } \omega = \varepsilon_n^{\text{QP}}, \text{ occupied orbital } i, \text{ all } s, \\ \omega - \varepsilon_a^{\text{QP}} - \Omega_s^{\text{RPA}} &< 0 \quad \text{for } \omega = \varepsilon_n^{\text{QP}}, \text{ empty orbital } a, \text{ all } s. \end{aligned}$$

Therefore, $\Sigma_n^c(\omega = \varepsilon_n^{\text{QP}})$ is never singular for $\text{ev}G$, $\Omega_s > 0$, and n with (14) [163]. Poles of $\text{Re } \Sigma_n^c(\omega)$ only appear at energies

$$\omega_{\text{pole}}^{\text{ev}GW_0} \in [-\infty, \varepsilon_{\text{HOMO}}^{\text{QP}} - \Omega_1^{\text{RPA}}] \cup [\varepsilon_{\text{LUMO}}^{\text{QP}} + \Omega_1^{\text{RPA}}, \infty]. \quad (15)$$

When considering $n = \text{HOMO}$ or $n = \text{LUMO}$ in $\text{ev}G$ with $\Omega_s^{\text{RPA}} > 0$, all poles $\omega_{\text{pole}}^{\text{ev}GW_0}$ of $\Sigma_{\text{HOMO/LUMO}}^c(\omega)$ are thus separated from $\omega = \varepsilon_{\text{HOMO/LUMO}}^{\text{QP}}$ by the energy Ω_1^{RPA} . By design, multiple solutions will not occur at the $\text{ev}GW_0$ level for HOMO and LUMO, given that the system has a nonzero optical gap. Furthermore, it has also been shown that $\text{ev}GW_0$ suppresses multisolution behavior for deeper states, inhibiting erroneous transfer of spectral weights from QP peak to satellites [28,169]. We note that Eqs. (12)–(15) hold also for the $\text{ev}GW$ scheme, where eigenvalues are also iterated in W .

A computationally less expensive alternative to $\text{ev}G$ is introducing the so-called Hedin shift [1,2,75,167,170,171] in the denominator of Eq. (2). The Hedin shift can be viewed as an approximation to $\text{ev}GW_0$, where the individual shifts Δ_m^{QP} in Eqs. (12) and (13) are approximated with a global shift ΔH . Another alternative is to start the G_0W_0 calculation from a hybrid DFT starting point, such as PBE0. In G_0W_0 @PBE0, the poles will effectively also shift to more negative frequencies below the Fermi level because $\varepsilon_i^{\text{PBE0}} < \varepsilon_i^{\text{PBE}}$ and $\Omega_s^{\text{RPA@PBE0}} > \Omega_s^{\text{RPA@PBE}}$, as shown in Table I. We note that the latter was also discussed in literature before [28,70].

In this paper, we aim to show that low-scaling GW is numerically precise for computing frontier QP energies from GW schemes that are free of multipole artifacts.

IV. LOW-SCALING GW SPACE-TIME ALGORITHM

Many low-scaling GW algorithms [122–124,127–132,134,143] build on the GW space-time method [120]. In this paper, we execute GW calculations using the low-scaling algorithm from Ref. [134], which adapts the space-time method for use with Gaussian basis functions. In order to introduce the basic idea of the GW space-time method, we use a generic formulation in this section for nonperiodic systems projecting all quantities on real-space grids. It is important to note that this formulation differs from the original GW space-time method [120] where some quantities were calculated using a plane-wave basis set.

KS orbitals and eigenvalues are used to calculate the single-particle Green's function in imaginary time,

$$G(\mathbf{r}, \mathbf{r}', i\tau) = \begin{cases} i \sum_i^{\text{occ}} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') e^{-|\varepsilon_i^{\text{DFT}} - \varepsilon_F| \tau}, & \tau < 0, \\ -i \sum_a^{\text{virt}} \psi_a^*(\mathbf{r}) \psi_a(\mathbf{r}') e^{-|\varepsilon_a^{\text{DFT}} - \varepsilon_F| \tau}, & \tau > 0, \end{cases} \quad (16)$$

where the sum over the index i runs over all occupied KS orbitals and the sum over the index a over all virtual, i.e.,

empty KS orbitals. ε_F is the Fermi level. We note that for the nonrelativistic molecular calculations conducted in this study, the KS orbitals are real valued. The irreducible polarizability follows

$$\chi^0(\mathbf{r}, \mathbf{r}', i\tau) = -iG(\mathbf{r}, \mathbf{r}', i\tau)G(\mathbf{r}, \mathbf{r}', -i\tau), \quad (17)$$

which is then transformed to imaginary frequency,

$$\chi^0(\mathbf{r}, \mathbf{r}', i\omega) = i \int_{-\infty}^{\infty} e^{-i\omega\tau} \chi^0(\mathbf{r}, \mathbf{r}', i\tau) d\tau. \quad (18)$$

This transform can be understood as Laplace transform followed by analytic continuation to the imaginary axis and effectively takes the form of a Fourier transform [121]. Next, the dielectric function ε can be calculated in imaginary frequency from the irreducible polarizability,

$$\varepsilon(\mathbf{r}, \mathbf{r}', i\omega) = \delta(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \chi^0(\mathbf{r}'', \mathbf{r}', i\omega), \quad (19)$$

using the Dirac delta function $\delta(\mathbf{r}, \mathbf{r}')$ and the Coulomb interaction $v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$. The screened Coulomb interaction can be computed from the inverse dielectric function,

$$W(\mathbf{r}, \mathbf{r}', i\omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', i\omega) v(\mathbf{r}'', \mathbf{r}'). \quad (20)$$

It is convenient in *GW* implementations to split the screened interaction W into the bare Coulomb interaction v and the correlation part W^c ,

$$W^c(\mathbf{r}, \mathbf{r}', i\omega) = W(\mathbf{r}, \mathbf{r}', i\omega) - v(\mathbf{r}, \mathbf{r}'). \quad (21)$$

In the space-time method, W^c is required in imaginary time,

$$W^c(\mathbf{r}, \mathbf{r}', i\tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{i\omega\tau} W^c(\mathbf{r}, \mathbf{r}', i\omega) d\omega, \quad (22)$$

and the correlation self-energy is given as product of the Green's function and the screened Coulomb interaction,

$$\Sigma^c(\mathbf{r}, \mathbf{r}', i\tau) = iG(\mathbf{r}, \mathbf{r}', i\tau)W^c(\mathbf{r}, \mathbf{r}', i\tau). \quad (23)$$

The self-energy is then transformed to imaginary frequency,

$$\Sigma^c(\mathbf{r}, \mathbf{r}', i\omega) = i \int_{-\infty}^{\infty} e^{-i\omega\tau} \Sigma^c(\mathbf{r}, \mathbf{r}', i\tau) d\tau, \quad (24)$$

and we calculate its (n, n) -diagonal element,

$$\begin{aligned} \Sigma_n^c(i\omega) &= \langle \psi_n | \Sigma^c(i\omega) | \psi_n \rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \psi_n^*(\mathbf{r}) \Sigma^c(\mathbf{r}, \mathbf{r}', i\omega) \psi_n(\mathbf{r}'). \end{aligned} \quad (25)$$

The self-energy is then analytically continued to real frequency, i.e., we determine the fit parameters $a_{j,n}$ and $b_{j,n}$ of an N -parameter Padé approximant $P_n(i\omega)$ [5,172] to match $\Sigma_n^c(i\omega)$ of QP level n as closely as possible,

$$\Sigma_n^c(i\omega) \approx P_n(i\omega) = \frac{\sum_{j=1}^{(N-1)/2} a_{j,n} \cdot (i\omega)^j}{1 + \sum_{j=1}^{N/2} b_{j,n} \cdot (i\omega)^j}. \quad (26)$$

Based on the identity theorem for analytic functions [173], one evaluates P_n at real frequencies to compute the self-energy at real frequencies, $\Sigma_n^c(\omega) \approx P_n(\omega)$ [2,5].

Focusing on the G_0W_0 method already introduced before, we use KS orbitals to approximate the QP wavefunctions

and we compute G and W only once using KS orbitals and KS eigenvalues from Eqs. (16)–(20). The QP energies $\varepsilon_n^{G_0W_0}$ can finally be calculated by solving the QP equation (7).

The computational cost of the presented algorithm increases with $O(N^3)$ in the system size N . This is apparent from Eq. (16), which requires $O(N_{\text{grid}}^2(N_{\text{occ}} + N_{\text{vir}})) = O(N^3)$ number of floating point operations, where N_{grid} is the number of real-space grid points, N_{occ} the number of occupied KS orbitals, and N_{vir} the number of virtual KS orbitals.

In a standard *GW* algorithm, a computational bottleneck is evaluating the Adler-Wiser formula [174,175] for the irreducible polarizability in imaginary frequency,

$$\begin{aligned} \chi^0(\mathbf{r}, \mathbf{r}', i\omega) &= \sum_i^{\text{occ}} \sum_a^{\text{virt}} \frac{2(\varepsilon_i - \varepsilon_a)}{(\varepsilon_i - \varepsilon_a)^2 + \omega^2} \\ &\times \psi_i(\mathbf{r}) \psi_a^*(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_a(\mathbf{r}'). \end{aligned} \quad (27)$$

This computation requires $O(N_{\text{grid}}^2 N_{\text{occ}} N_{\text{virt}}) = O(N^4)$ operations, and is thus computationally more demanding than the whole low-scaling algorithm (16)–(24) for a large system.

The drawback of algorithm (16)–(24) is that it requires very fine real-space grids, in particular when evaluating Coulomb interactions in Eqs. (19) and (20). This is why the original *GW* space-time method [120] used a plane-waves basis for the calculation of $\varepsilon(i\omega)$ and $W(i\omega)$. Then, the $O(N^3)$ -scaling convolutions (19) and (20) in real space transform into $O(N^2)$ multiplications in the plane-wave basis. The inversion of $\varepsilon(i\omega)$ remains as cubic-scaling step. For the low-scaling *GW* implementation used in this study [134], Eq. (16)–(24) have been reformulated in a Gaussian basis set resulting in effective $O(N^2)$ scaling [128,134].

V. REFERENCE GW CALCULATIONS WITH CONTOUR DEFORMATION

In the low-scaling *GW* space-time method, one major challenge regarding numerical precision is the analytic continuation of $\Sigma^c(i\omega)$ to $\Sigma^c(\omega)$. A numerically more precise procedure for computing $\Sigma^c(\omega)$ is the contour deformation (CD) [2,27,176–178]. The starting point of CD is Eq. (23), formulated in real frequency [2]

$$\Sigma^c(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int_{-\infty}^{\infty} G(\mathbf{r}, \mathbf{r}', \omega + \omega') W^c(\mathbf{r}, \mathbf{r}', \omega') d\omega'. \quad (28)$$

Because of the pole structure of G and W on the real-frequency axis, the numerical integration of Eq. (28) is potentially unstable [2]. One way to circumvent this problem is to rewrite Eq. (28) with a contour integral,

$$\begin{aligned} \Sigma^c(\mathbf{r}, \mathbf{r}', \omega) &= \frac{i}{2\pi} \oint d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') W^c(\mathbf{r}, \mathbf{r}', \omega') \\ &\quad - \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' G(\mathbf{r}, \mathbf{r}', \omega + i\omega') W^c(\mathbf{r}, \mathbf{r}', i\omega'), \end{aligned} \quad (29)$$

where the closed integral comprises the real axis, two arcs and the imaginary axis. The closed integral can be calculated

using Cauchy's residue theorem, while the imaginary axis can be integrated numerically since the problematic pole structure of G and W is restricted to the real frequency axis [2]. QP energies from CD follow from solving the QP equation (7).

The scaling for evaluating the self-energy from CD is $O(N^4)$ for a single valence excitation [27], which is an order higher than the $O(N^3)$ scaling of the GW space-time method. CD is numerically highly accurate. It was shown that CD reproduces the exact self-energy structure by comparing with fully analytic solutions obtained by evaluating Eq. (2) [27]. We therefore use the CD approach as reference to assess the numerical precision of our low-scaling GW algorithm. More details on CD can be found in Refs. [2,27].

VI. COMPUTATIONAL DETAILS

A. Low-scaling GW calculations using CP2K

The low-scaling GW space-time algorithm used in this paper [134] is implemented in the CP2K software package [179,180]. CP2K employs a Gaussian basis set for representing KS orbitals. We use the Gaussian and augmented plane-waves scheme (GAPW) [181] in CP2K, which allows for all-electron calculations. The low-scaling G_0W_0 implementation [134] is a reformulation of the space-time method [120] in a Gaussian basis set, where sparsity is introduced by combining a global resolution-of-the-identity (RI) scheme with a truncated Coulomb metric [146,147].

For expanding KS orbitals, we use the def2-QZVP basis set [182] with an RI-cc-pV5Z auxiliary basis [183]. We choose a minimax time-frequency grid [124,148,149,184] with 30 points for all low-scaling GW calculations. For the RI with the truncated Coulomb metric we set a truncation radius of 3 Å [146,147]. We compute two- and three-center integrals over Gaussians using recursive, analytical schemes [185,186]. The self-energy is analytically continued from imaginary frequency to the real frequency using a Padé model [5,172] with 16 parameters. We broaden the spectral functions using $\eta = 1 \text{ mHa} = 27.2 \text{ meV}$ in Eq. (5).

B. Reference GW calculations with contour deformation using FHI-aims

We use the CD- GW algorithm [27] as implemented in the FHI-aims software package [187]. FHI-aims is an all-electron electronic structure code using numerical atom-centered orbitals (NAO) for expanding KS orbitals [187]. We use the Gaussian def2-QZVP [182] basis set, which can be also represented as NAO basis, and an automatically generated RI basis set. In the CD, we employ a modified Gauss-Legendre grid [188] for the evaluation of the imaginary-frequency integral term, setting the number of frequency points to 2000 to obtain benchmark quality. The broadening parameter [27] is set to a rather large value $\eta = 4 \text{ mHa} = 108.8 \text{ meV}$ to facilitate the convergence in the evG_0W_0 case. The only exception is that for Fig. 1, we use a smaller broadening of 1 mHa to obtain sharp and well-separated peaks in the spectral function. The broadening of peaks in the spectral function resulting from

CD differs from that of analytic continuation, as outlined in Ref. [27]. Therefore it is difficult to directly compare peak widths and heights in the spectral function between CD and analytic continuation.

VII. LOW-SCALING G_0W_0 @PBE CALCULATIONS ON O_3 , BeO, MgO, BN, CuCN

In this section we present low-scaling G_0W_0 @PBE calculations on the five molecules, O_3 , BeO, MgO, BN, and CuCN, and we will discuss the challenges that occurred.

It was already observed in the original GW100 study [5] that computing the G_0W_0 @PBE HOMO energy of O_3 , BeO, MgO, BN, and CuCN posed a significant numerical challenge. In the analytic continuation, this challenge was addressed by employing a 128-pole function to fit $\Sigma_{\text{HOMO}}^c(i\omega)$ for obtaining $\Sigma_{\text{HOMO}}^c(\omega)$ along the real-frequency axis. This high-precision fit was essential for accurately computing the G_0W_0 @PBE HOMO energy from the QP equation (7) for the five aforementioned molecules. For all other 95 molecules, a 16-pole fit on Σ_{HOMO}^c was sufficient for accurately computing the G_0W_0 @PBE HOMO energy.

GW space-time algorithms require in general three transforms between imaginary time and imaginary frequency, as discussed in Sec. IV. These transforms are executed numerically using discrete time and frequency grids. The functions in imaginary time and frequency usually have long tails and localized features. The usual fast Fourier transform with homogeneously spaced integration grids would need a large number of discrete time or frequency points. Instead, a nonequidistant Fourier transform can reduce the number of time and frequency points drastically [124,149]. Nonequidistant grids can be set up through various techniques aimed at identifying discrete points that are optimal in a certain sense. Such approaches include the minimax approximation [124,128,134,148,149,189–192] or least-square quadratures [130,193–197]. Both algorithms have in common that they are numerically ill conditioned and grid generation is typically restricted to less than 100 grid points. For instance, the recently introduced GreenX library [148] offers minimax time and frequency grids, each containing up to 34 points [148,149,198]. Consequently, when utilizing time and frequency grids from the GreenX library, the number of parameters available for fitting $\Sigma^c(i\omega)$ is limited to 34. This is not sufficient for accurately computing the G_0W_0 @PBE HOMO energy of the five challenging molecules, O_3 , BeO, MgO, BN, CuCN, [128,134,149], which required a fit with a 128-pole model [5], that requires at least 128 imaginary-frequency points.

We now use our low-scaling GW implementation [134] to compute the G_0W_0 @PBE self-energy and spectral function. The results for the MgO molecule are shown as violet traces in Figs. 2(a) and 2(c). Low-scaling GW [134] fails to reproduce the shallow self-energy pole at $\omega_{\text{pole}} \approx -6.91 \text{ eV}$ [Fig. 2(a) and zoom in Fig. 1(b)], which results in a single peak of the spectral function at $\omega \approx -6.9 \text{ eV}$ [Fig. 2(c)] instead of the split peak present in the reference CD calculation [Fig. 2(c)]. The same failure in computing the self-energy has been observed in the original paper, Ref. [5] (Fig. 13), when using analytical continuation with a 16-pole approximant to the

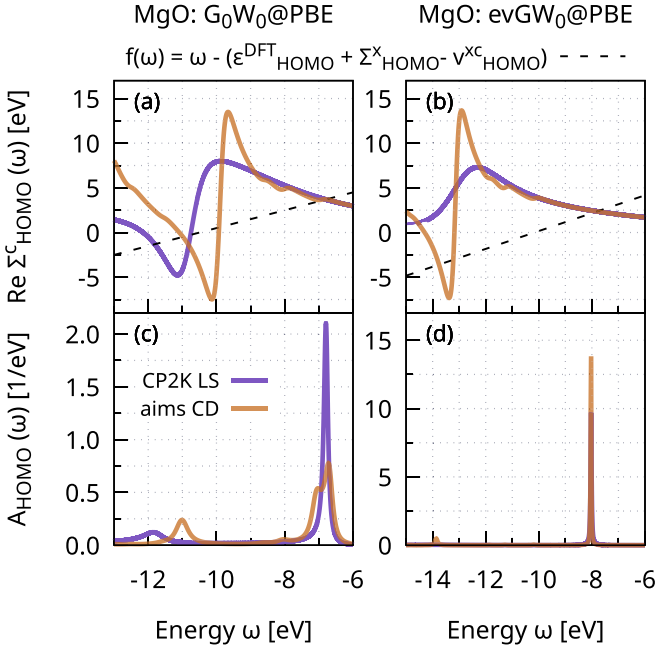


FIG. 2. Real part of the HOMO self-energy $\Sigma_{\text{HOMO}}^c(\omega)$ [G_0W_0 @PBE in (a) and $\text{ev}G_0W_0$ @PBE in (b)] and the HOMO contribution to the spectral function $A_{\text{HOMO}}(\omega)$ [Eq. (5), G_0W_0 @PBE in (c) and $\text{ev}G_0W_0$ @PBE in (d)] for the molecule MgO; computed from low-scaling GW in the CP2K package [134] (“CP2K LS”; violet traces) and from the highly accurate CD as implemented in FHI-aims [27] (“aims CD”; brown traces). $\text{Re}\Sigma_{\text{HOMO}}^c(\omega)$ and $A(\omega)$ for the other four numerically challenging molecules BeO, O_3 , BN, CuCN from the GW100 test set [5] are available in Figs. 6 and 7 for G_0W_0 @PBE and $\text{ev}G_0W_0$ @PBE in the Appendix.

self-energy. When using a 128-pole approximant for analytical continuation all poles of the self-energy were correctly reproduced [5]. The low-scaling GW implementation [134] is currently restricted to at most 34 imaginary-frequency points, and thus 34 fit parameters for analytic continuation. The Padé model is thus not flexible enough to accurately reproduce the G_0W_0 @PBE self-energy matrix elements for the HOMO of MgO. The same observation is made for O_3 , BeO, BN, and CuCN (Fig. 6 in the Appendix).

As discussed in Secs. II and III, the multiple solutions at the G_0W_0 @PBE level of theory are an artifact caused by the lack of eigenvalue self-consistency in G . Therefore, we should disregard the unphysical multi-solution G_0W_0 @PBE calculations and instead investigate whether we can obtain numerically precise $\text{ev}G_0W_0$ HOMO QP energies using low-scaling GW [28,33].

VIII. NUMERICALLY PRECISE LOW-SCALING $\text{ev}G_0W_0$ CALCULATIONS ON O_3 , BeO, MgO, BN, CuCN

Following the discussion in Sec. III, $\text{ev}G_0W_0$ @PBE ensures that poles of the self-energy are separated from frontier QP energies. This cures the unphysical and numerically challenging multisolution issue of the HOMO at the G_0W_0 @PBE level and we thus explore $\text{ev}G_0W_0$ to calculate the spectral function of the five molecules O_3 , BeO, MgO, BN, CuCN. The spectral function A_{HOMO} for the MgO molecule at the $\text{ev}G_0W_0$ @PBE

TABLE II. $\text{ev}G_0W_0$ @PBE HOMO energy, $\epsilon_{\text{HOMO}}^{\text{ev}G_0W_0\text{@PBE}}$ and spectral weight Z_{HOMO} of the HOMO peak, computed from CD [27] and from low-scaling (LS) GW [134] for the five multisolution cases from the GW100 set using a def2-QZVP basis set. The spectral weight Z has been computed according to Eq. (A4). As comparison, we also show the G_0W_0 @PBE HOMO energy [5], the CCSDT(T) ionization potential [63] (computed using a def2-TZVPP basis set) and the experimental vertical ionization potential (IP).

	O_3	BeO	MgO	BN	CuCN
$ \epsilon_{\text{HOMO}}^{\text{ev}G_0W_0\text{@PBE}} $ (CD)	12.667	10.141	8.039	11.695	10.663
$ \epsilon_{\text{HOMO}}^{\text{ev}G_0W_0\text{@PBE}} $ (LS)	12.649	10.134	8.030	11.685	10.649
Z_{HOMO} (CD)	0.83	0.85	0.68	0.85	0.79
Z_{HOMO} (LS)	0.88	0.78	0.68	0.85	0.80
$ \epsilon_{\text{HOMO}}^{G_0W_0\text{@PBE}} $ [5]	11.39	8.62	6.66	11.01	9.42
CCSD(T) [63]	12.71	9.94	7.91	11.98	10.85
IP (exp.)	12.73 [5]	10.10 [5]	8.01 [199]		

level is shown in Fig. 2(d). Only a single QP peak in the spectral function is present at $\omega = 8.03$ eV. The QP peak computed from the low-scaling algorithm [134] and the CD [27] match in position (within 9 meV) and spectral weight (within 1%, Table II).

We investigate the drastic difference between the spectral function computed with G_0W_0 and $\text{ev}G_0W_0$ by inspecting the respective self-energies, Figs. 2(a) and 2(b). For the $\text{ev}G_0W_0$ self-energy [Fig. 2(b)] the poles are shifted by ~ 2 eV towards lower energy compared to the G_0W_0 self-energy [Fig. 2(a)]. The $\text{ev}G_0W_0$ self-energy does not exhibit poles at the HOMO QP energy of 8.03 eV [Fig. 2(b)]. This is expected, as for $\text{ev}G_0W_0$, self-energy poles are separated from the HOMO QP energy by at least the lowest RPA excitation energy Ω_1^{RPA} , as discussed in Sec. III. The consequence is that there is only a single crossing point of the self-energy and the dashed straight line $f(\omega)$, Eq. (8), close to $\omega = 8.03$ eV. The slope of the self-energy is small at this crossing point such that the associated spectral weight is close to one. The same is observed for the other four molecules (Fig. 7 in the Appendix).

We report the total spectral function $A(\omega)$ for all five challenging molecules, O_3 , BeO, MgO, BN, CuCN, from $\text{ev}G_0W_0$ in Fig. 3. For all molecules, the HOMO peak positions of low-scaling GW [134] and CD [27] agree well, the mean absolute deviation is only 12 meV (Table II). The width of the QP peaks differ between low-scaling GW and the CD; the reason is the inherently different definition of the broadening parameter η in the two algorithms, cf. Eq. (5) and Ref. [27].

Our paper shows that low-scaling space-time $\text{ev}G_0W_0$ @PBE is numerically precise for O_3 , BeO, MgO, BN, CuCN. The improvement compared to the G_0W_0 @PBE is due to the fact that $\text{ev}G_0W_0$ @PBE yields well-defined QP valence peaks, whereas G_0W_0 @PBE exhibits unphysical, erroneous multisolution behavior as discussed in Secs. II and III. The failure of G_0W_0 @PBE also reflects in Table II: $\text{ev}G_0W_0$ @PBE HOMO energies show significantly better agreement with CCSD(T) calculations and experimental ionization potentials compared to G_0W_0 @PBE HOMO

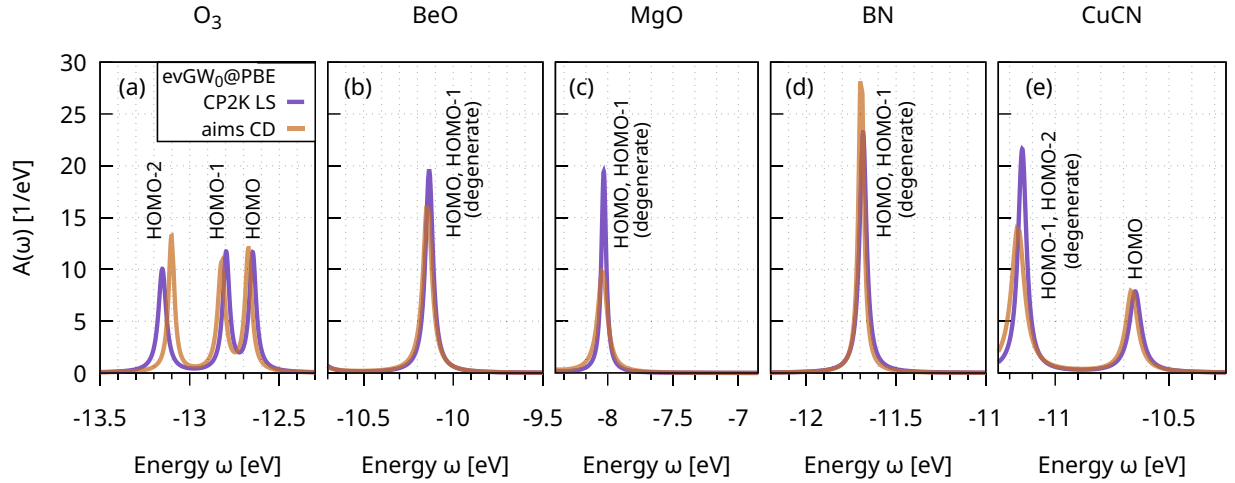


FIG. 3. [(a)–(e)] $evGW_0@PBE$ spectral function for five numerically challenging molecules (O_3 , BeO , MgO , BN , $CuCN$) computed from low-scaling GW [134] (CP2K LS) and from CD [27] (aims CD). Peak positions and spectral weight of the HOMO peaks are listed in Table II. $G_0W_0@PBE$ and $G_0W_0@PBE0$ spectral functions are shown in Figs. 4 and 5. Graphical solutions of the QP equation (7) are also shown in the Appendix, Figs. 6–8 for $G_0W_0@PBE$, $evGW_0@PBE$, and $G_0W_0@PBE0$, respectively.

energies. Therefore, it is not reasonable to invest effort in developing low-scaling GW methods, which can recover the $G_0W_0@PBE$ solution for these five molecules, as it is an insufficient level of theory from the outset. It was also shown for solids that $evGW_0@PBE$ outperforms $G_0W_0@PBE$ for computing accurate bandgaps, see discussion in Refs. [83] and [[2], p. 29]. $evGW_0@PBE$ is thus suitable for both molecules and solids making it ideal for studying complex, disordered systems such as molecules on surfaces or interfaces. In case of issues related to PBE orbitals used in $evGW_0@PBE$, one might also refer to $evGW_0@HSE06$ [200,201] for complex systems. [33,167].

Another way of partial self-consistency is the $evGW$ scheme. Our low-scaling algorithm is also expected to reproduce $evGW@PBE$ results well since the multi-solution issue is resolved by eigenvalue self-consistency in G . However, $evGW@PBE$ tends to underscreen, a phenomenon that is less noticeable for molecular frontier orbitals but becomes more apparent for deeper states [33]. This underscreening is particularly evident in solids, where it has been shown that $evGW@PBE$ produces bandgaps that are too large compared to experimental values [2,83]. The effectiveness of $evGW_0@PBE$ arises from a fortunate error cancellation: While the PBE approximation typically underestimates the fundamental gap, using PBE eigenvalues in W leads to an overscreened potential. This overscreening in W counteracts the underscreening caused by the absence of vertex corrections, which is another way of expressing the analysis in Appendix B.

IX. NUMERICALLY PRECISE LOW-SCALING $G_0W_0@PBE0$ CALCULATIONS ON O_3 , BeO , MgO , BN , $CuCN$

The HOMO QP energies at the $G_0W_0@PBE0$ level are given in Table III. The low-scaling algorithm reproduces the QP energies from CD within 9 meV and the spectral weights within 0.01. The total spectral functions $A(\omega)$ displayed in Fig. 4 follows also closely the CD reference. This align-

ment occurs because the poles in the real part of Σ_{HOMO}^c shift by 2–3 eV towards more negative frequencies (Fig. 8 in the Appendix), similar to what is observed in $evGW_0@PBE$ calculations. This shift is attributed to the fact that ε_i^{DFT} (i : occ. index) are more negative at the PBE0 than the PBE level, and Ω_s^{RPA} also increases, see Table I. The pole positions $\varepsilon_i^{DFT} - \Omega_s^{RPA}$ are thus moving to the left on our energy scale. The pole at -6.91 eV, which was the culprit for the two solutions at the $G_0W_0@PBE$ level, shifts now to $\varepsilon_{HOMO-2}^{PBE0} - \Omega_s^{RPA@PBE0} = -9.70$ eV. A proper separation between satellite and QP peak is consequently also achieved at the $G_0W_0@PBE0$ level and we obtain also a unique QP solution for all five molecules. This confirms the observation from our $evGW_0@PBE$ study from Sec. VIII: our low-scaling GW algorithm [134] is numerically precise if a well-defined QP peak is present.

G_0W_0 calculations starting from a hybrid functional with a larger fraction of exchange is common for molecules [2]. It was shown that 25% of exact exchange, as used in PBE0, is optimal to minimize the deviation from CCSD(T) for frontier orbitals [153]. However, for our five molecules, the $G_0W_0@PBE0$ QP energies reported in Table III show worse agreement with CCSD(T) and experimental ionization

TABLE III. $G_0W_0@PBE0$ HOMO energy, $\varepsilon_{HOMO}^{G_0W_0@PBE0}$ and spectral weight Z_{HOMO} of the HOMO peak, computed from CD [27] and from low-scaling (LS) GW [134] for all five difficult molecules from the GW100 set using a def2-QZVP basis set. The spectral weight Z has been computed according to Eq. (A4).

	O_3	BeO	MgO	BN	$CuCN$
$ \varepsilon_{HOMO}^{G_0W_0@PBE0} $ (CD)	12.566	9.646	7.459	11.545	10.253
$ \varepsilon_{HOMO}^{G_0W_0@PBE0} $ (LS)	12.557	9.643	7.454	11.542	10.230
Z_{HOMO} (CD)	0.81	0.76	0.67	0.83	0.81
Z_{HOMO} (LS)	0.81	0.77	0.67	0.83	0.81

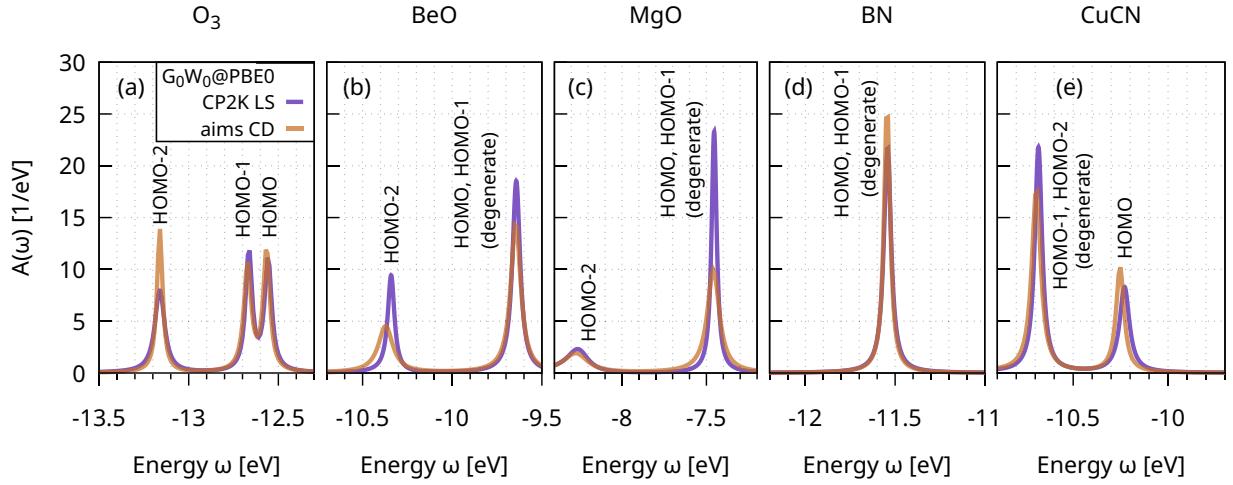


FIG. 4. [(a)–(e)] G_0W_0 @PBE0 spectral function for O_3 , BeO, MgO, BN, CuCN computed from low-scaling GW in CP2K [134] (CP2K LS) and from CD in FHI-aims [27] (aims CD).

potentials (Table II) compared to $evGW_0$ @PBE. In addition, the G_0W_0 @PBE0 approach is not extendable beyond molecular frontier orbitals: For deeper states, the amount of exact exchange needs to be progressively increased as excitation energies increase [28,202]. For solids, G_0W_0 @PBE0 overestimates band gaps by more than 0.5 eV [203]. The G_0W_0 @PBE0 behavior can be traced to the overestimation of excitation energies Ω_s of many-electron systems at the RPA@PBE0 level, see Table I, Appendix B and the discussion in the literature, for example in Ref. [2]. Since $\Omega_s^{RPA@PBE0}$ energies are too large, the poles in the self-energy are shifted approximately to the same frequency range as for $evGW_0$ @PBE in case of the HOMO. However, it also leads to an under-screening in W , which affects the long-range interactions in solids more significantly than in finite molecular systems.

X. CONCLUSIONS

In summary, our study revisits low-scaling GW calculations on molecules O_3 , BeO, MgO, BN, and CuCN from the GW100 benchmark set. Previous studies [134,149] encountered numerical challenges, particularly with the computation of the G_0W_0 @PBE HOMO energy for these molecules from low-scaling GW. These challenges arise from unphysical, erroneous multiple solutions of the quasiparticle equation at the G_0W_0 @PBE level, which can be traced back to an insufficient separation between quasiparticle peak and satellite positions caused by the too high PBE eigenvalues of occupied Kohn-Sham orbitals and the lack of eigenvalue-selfconsistency in G . This suggests that G_0W_0 @PBE calculations of the HOMO of O_3 , BeO, MgO, BN, and CuCN should be disregarded. Applying self-consistency in the Green's function ($evGW_0$) or using a hybrid functional as starting point for the G_0W_0 calculation separates QP peak and satellite leading to a single HOMO QP peak and small satellite weights. Low-scaling GW computations yield numerically precise $evGW_0$ and G_0W_0 @PBE0 HOMO energies of O_3 , BeO, MgO, BN, and CuCN, with a mean absolute deviation in the order of only 10 meV from reference

calculations. We thus demonstrate that low-scaling GW is well suited for computing frontier quasiparticle energies.

Inputs and outputs of all calculations reported in this paper are available in a NOMAD repository [204] and in a Github repository [205]. The low-scaling GW algorithm [134] used in this paper is available in the open-source package CP2K [179,180].

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APPENDIX A: SPECTRAL FUNCTION AND SPECTRAL WEIGHT

In this Appendix, we derive Eq. (9) for the spectral weight Z_ε associated with a peak at energy ε of $A_n(\omega)$. The spectral weight is the integral of that peak,

$$Z_\varepsilon = \int_{\varepsilon-\Delta}^{\varepsilon+\Delta} A_n(\omega) d\omega \quad (A1)$$

$$= \int_{\varepsilon-\Delta}^{\varepsilon+\Delta} \frac{1}{\pi} \frac{|\gamma|}{(\omega - (\varepsilon + \text{Re}(\Sigma_n^c(\omega) - \Sigma_n^c(\varepsilon))))^2 + |\gamma|^2} d\omega. \quad (A2)$$

We use $\gamma = \text{Im } \Sigma_n^c(\omega) + \eta$ and we integrate over the interval $[\varepsilon - \Delta, \varepsilon + \Delta]$ with a parameter $\Delta > 0$ to exclude other peaks from the integration. We have used Eq. (5) and the QP equation (7) to arrive at the denominator in Eq. (A2).

To evaluate the integral (A2), we assume that $\text{Im } \Sigma_n^c(\omega)$ is independent of frequency and we use Taylor expansion of $\text{Re } \Sigma_n^c(\omega)$ around $\omega = \varepsilon$,

$$\text{Re}[\Sigma_n^c(\omega) - \Sigma_n^c(\varepsilon)] \approx \text{Re} \left. \frac{\partial \Sigma_n^c(\omega)}{\partial \omega} \right|_{\omega = \varepsilon} \cdot (\omega - \varepsilon). \quad (\text{A3})$$

Carrying out the integration (A2) gives the common approximate expression for the spectral weight,

$$Z_\varepsilon \approx \left[1 - \text{Re} \left. \frac{\partial \Sigma_n^c(\omega)}{\partial \omega} \right|_{\omega = \varepsilon} \right]^{-1}.$$

In practice, for Tables II and III, we determine the spectral weight Z of a peak in $A_{\text{HOMO}}(\omega)$ by fitting a Lorentz function

$$L(\omega) = Z \cdot \frac{1}{\pi} \frac{\gamma}{(\omega - \varepsilon_n^{G_0W_0})^2 + \gamma^2} \quad (\text{A4})$$

to $A_{\text{HOMO}}(\omega)$. We fix the position of the peak as the solution of the QP equation $\varepsilon_n^{G_0W_0}$, while the peak width γ and the spectral weight Z were fitted.

Note that in non-selfconsistent GW flavors like G_0W_0 or $\text{ev}GW_0$, the particle number is not conserved [170]. The violation is often in the order of 1% or less [170]. For fully self-consistent GW , the particle number is conserved, i.e., $\int_{-\infty}^{\infty} A_n^{GW}(\omega) d\omega = 1$.

APPENDIX B: EXCITATION ENERGIES Ω_s FROM CASIDA'S EQUATIONS

In TDDFT, Casida's equations [159,206] provide a framework for calculating electronic excitation energies Ω_s . Casida's formalism casts the TDDFT linear response problem into an eigenvalue problem,

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{pmatrix} = \Omega_s^{\text{TDDFT}} \begin{pmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{pmatrix}, \quad (\text{B1})$$

where Ω_s^{TDDFT} are the excitation energies, i.e., the energy difference of an excited-state energy and the ground-state energy. $(\mathbf{X}_s, \mathbf{Y}_s)$ are the eigenvectors of the excitation. The matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are given by

$$A_{ia,jb} = (\varepsilon_a^{\text{DFT}} - \varepsilon_i^{\text{DFT}}) \delta_{ij} \delta_{ab} + \langle ia | f_{\text{Hxc}} | jb \rangle, \quad (\text{B2})$$

$$B_{ia,jb} = \langle ia | f_{\text{Hxc}} | bj \rangle, \quad (\text{B3})$$

where $\varepsilon_i^{\text{DFT}}$ and $\varepsilon_a^{\text{DFT}}$ are KS orbital energies, δ_{ij} and δ_{ab} are Kronecker deltas, and $f_{\text{Hxc}} = f_{\text{H}} + f_{\text{xc}}$ is the Hartree-exchange-correlation kernel, which includes both the Hartree and exchange-correlation (xc) kernel.

TDDFT in Casida's formulation is exact in case the exact xc kernel is used. In practice one relies on approximations, for example the adiabatic local-density approximation [159], the

PBE functional [151], or the PBE0 functional [207]. This is important in GW calculations as the self-energy (2) depends on excitation energies. For small molecules, excitation energies Ω_s^{TDDFT} computed from one of these approximations are often quite similar [159]; for MgO, we have

$$\Omega_1^{\text{PBE}} = 0.67 \text{ eV} \approx \Omega_1^{\text{PBE0}} = 0.62 \text{ eV}, \quad (\text{B4})$$

see also Table I. In contrast, the HOMO-LUMO gaps of PBE and PBE0 differ substantially; we have for the MgO molecule

$$\varepsilon_{\text{LUMO}}^{\text{PBE}} - \varepsilon_{\text{HOMO}}^{\text{PBE}} = 0.50 \text{ eV}, \quad (\text{B5})$$

$$\varepsilon_{\text{LUMO}}^{\text{PBE0}} - \varepsilon_{\text{HOMO}}^{\text{PBE0}} = 2.47 \text{ eV}. \quad (\text{B6})$$

To better understand $\Omega_1^{\text{PBE}} \approx \Omega_1^{\text{PBE0}}$ and the big difference of the PBE and PBE0 HOMO-LUMO gap, we focus on large Coulomb interactions of densities with nonzero charge,

$$\langle nn | V | mm \rangle = \int d\mathbf{r} d\mathbf{r}' \frac{|\psi_n(\mathbf{r})|^2 |\psi_m(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (\text{B7})$$

that are present in the exact-exchange part of PBE0. For an occupied orbital i , the exact-exchange part of PBE0 contains the large interaction

$$\Delta_i = \beta \langle ii | V | ii \rangle \quad (\text{B8})$$

where $\beta = 0.25$ for PBE0. Δ_i reduces occupied KS orbital energies of small molecules in PBE0 compared to PBE,

$$\varepsilon_i^{\text{PBE0}} \approx \varepsilon_i^{\text{PBE}} - \Delta_i. \quad (\text{B9})$$

This reduction of occupied orbital energies in PBE0 is a primary contribution to the increased HOMO-LUMO gap in PBE0 compared to PBE.

Excitation energies from PBE and PBE0 are similar for small molecules, Eq. (B5). We trace this finding back to the diagonal matrix elements of $A_{ia,ia}$, Eq. (B2). In PBE, we have $\langle ia | f_{\text{Hxc}}^{\text{PBE}} | ia \rangle \approx 0$, such that $A_{ia,ia} \approx \varepsilon_a^{\text{PBE}} - \varepsilon_i^{\text{PBE}}$. In PBE0, we have for small molecules [159]

$$\langle ia | f_{\text{Hxc}}^{\text{PBE0}} | ia \rangle \approx -\beta \langle ii | V | aa \rangle \quad (\text{B10})$$

where $-\langle ii | V | aa \rangle$ is the Coulomb interaction of an electron in a previously empty orbital $\psi_a(\mathbf{r})$ with a hole in a previously occupied orbital $\psi_i(\mathbf{r})$. In case orbitals are delocalized over the whole molecule, the Coulomb interaction $\langle ii | V | aa \rangle$ is similar to the Coulomb interaction of $\psi_i(\mathbf{r})$ with itself, $\langle ii | V | aa \rangle \approx \langle ii | V | ii \rangle$. This allows us to use definition (B9)

$$\langle ia | f_{\text{Hxc}}^{\text{PBE0}} | ia \rangle \approx -\Delta_i, \quad (\text{B11})$$

such that we can estimate

$$A_{ia,ia}^{\text{PBE0}} \approx \varepsilon_a^{\text{PBE0}} - \varepsilon_i^{\text{PBE0}} - \Delta_i \approx \varepsilon_a^{\text{PBE}} - \varepsilon_i^{\text{PBE}} \approx A_{ia,ia}^{\text{PBE}}. \quad (\text{B12})$$

Our estimate (B12) rationalizes $\Omega_1^{\text{PBE}} \approx \Omega_1^{\text{PBE0}}$, Eq. (B4).

Equation (B12) can be also understood by recognizing that the self-interaction in the HOMO level of KS-DFT and

the absence of electron-hole Coulomb interaction in the xc kernel have similar magnitudes but opposite signs, leading to a mutual cancellation.

One often employs the RPA in *GW*, mainly for computational efficiency. In RPA, the xc kernel f_{xc} is neglected in Casida's equations,

$$\begin{pmatrix} \mathbf{A}^{\text{RPA}} & \mathbf{B}^{\text{RPA}} \\ -\mathbf{B}^{\text{RPA}} & -\mathbf{A}^{\text{RPA}} \end{pmatrix} \begin{pmatrix} \mathbf{X}_s^{\text{RPA}} \\ \mathbf{Y}_s^{\text{RPA}} \end{pmatrix} = \Omega_s^{\text{RPA}} \begin{pmatrix} \mathbf{X}_s^{\text{RPA}} \\ \mathbf{Y}_s^{\text{RPA}} \end{pmatrix}, \quad (\text{B13})$$

$$A_{ia,jb}^{\text{RPA}} = (\varepsilon_a^{\text{DFT}} - \varepsilon_i^{\text{DFT}}) \delta_{ij} \delta_{ab} + \langle ia | f_{\text{H}} | jb \rangle, \quad (\text{B14})$$

$$B_{ia,jb}^{\text{RPA}} = \langle ia | f_{\text{H}} | bj \rangle. \quad (\text{B15})$$

When using the PBE functional, RPA leaves the diagonal elements of $\mathbf{A}$ almost unchanged because $\langle ia | f_{xc}^{\text{PBE}} | ia \rangle \approx 0$,

$$A_{ia,ia}^{\text{RPA@PBE}} \approx \varepsilon_a^{\text{PBE}} - \varepsilon_i^{\text{PBE}} \approx A_{ia,ia}^{\text{PBE}} \approx A_{ia,ia}^{\text{PBE0}}. \quad (\text{B16})$$

Thus, PBE excitation energies change only little under RPA; for the MgO molecule, we have

$$\Omega_1^{\text{RPA@PBE}} = 0.82 \text{ eV} \approx \Omega_1^{\text{PBE}} = 0.67 \text{ eV}. \quad (\text{B17})$$

When applying the RPA with the PBE0 functional, the diagonal elements of $\mathbf{A}$ increase by $\approx \Delta_i$,

$$A_{ia,ia}^{\text{RPA@PBE0}} \stackrel{(\text{B14}),(\text{B12})}{\approx} \varepsilon_a^{\text{PBE0}} - \varepsilon_i^{\text{PBE0}} \approx A_{ia,ia}^{\text{PBE0}} + \Delta_i. \quad (\text{B18})$$

This increase translates to spuriously increased excitation energies in RPA@PBE0; again, for MgO, we have

$$\Omega_1^{\text{RPA@PBE0}} = 2.83 \text{ eV} \gg \Omega_1^{\text{PBE0}} = 0.62 \text{ eV}, \quad (\text{B19})$$

see also Table I.

RPA excitation energies are used in the *GW* self-energy, see Eq. (2). It has already long been recognized that starting a G_0W_0 calculation from PBE0 features too large RPA@PBE0 excitation energies [2], see Eq. (B19) as an example. It is often recommended to use the PBE functional as starting point for *GW* calculations because of $\Omega_s^{\text{RPA@PBE}} \approx \Omega_s^{\text{PBE}}$. To cure the too high PBE eigenvalues of occupied KS orbitals in *G*, Eq. (2), it is often recommended to use *evGW*₀@PBE [2].

APPENDIX C: SELF-ENERGY AND SPECTRAL FUNCTION OF ALL MOLECULES O₃, BeO, MgO, BN, CuCN

We provide spectral function $A(\omega)$ of the previously challenging five molecules O₃, BeO, MgO, BN, CuCN computed from G_0W_0 @PBE (Fig. 5). We also show $\text{Re}(\Sigma_{\text{HOMO}}^c)$, $\text{Im}(\Sigma_{\text{HOMO}}^c)$, and A_{HOMO} [Eq. (5)] for O₃, BeO, MgO, BN, and CuCN computed from G_0W_0 @PBE, *evGW*₀@PBE, and G_0W_0 @PBE0 (Figs. 6–8).

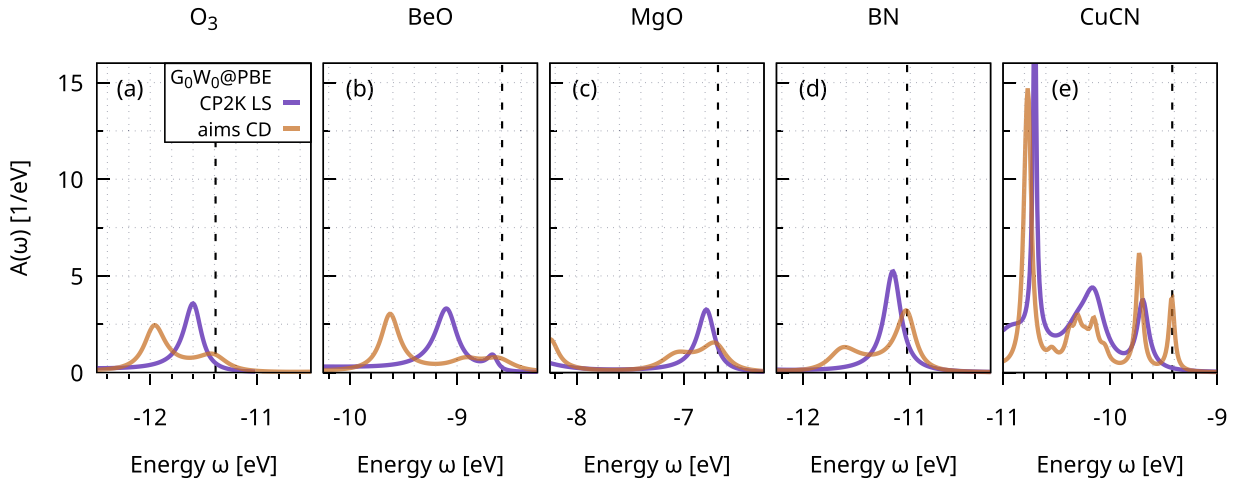


FIG. 5. [(a)–(e)] G_0W_0 @PBE spectral function for O₃, BeO, MgO, BN, CuCN computed from low-scaling *GW* in CP2K [134] (CP2K LS) and from CD in FHI-aims [27] (aims CD). The dashed lines indicate the G_0W_0 @PBE HOMO energy computed from FHI-aims and 128-parameter Padé continuation taken from the original GW100 study [5].

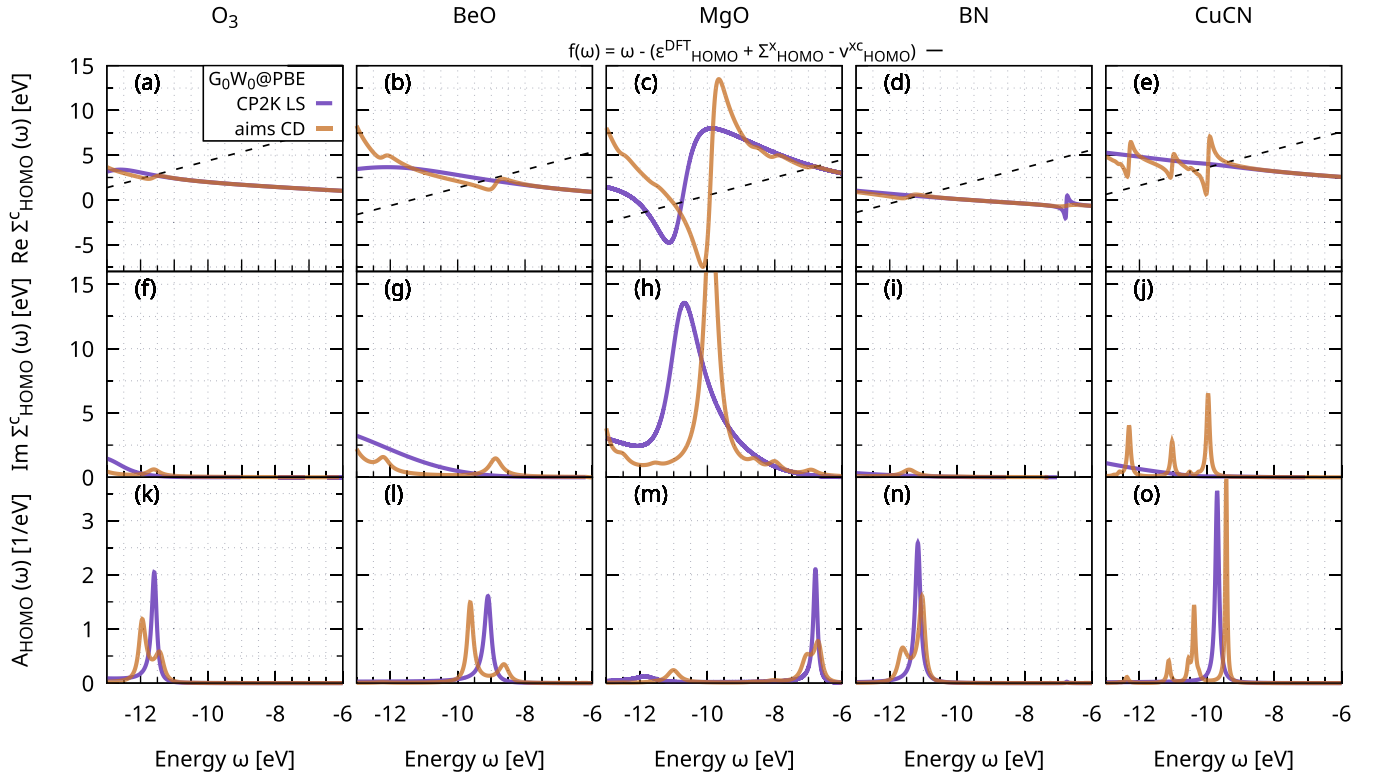


FIG. 6. (a)–(e) $\text{Re}(\Sigma_{\text{HOMO}}^c)$, (f)–(j) $\text{Im}(\Sigma_{\text{HOMO}}^c)$, and (k)–(o) A_{HOMO} [Eq. (5)] for O₃, BeO, MgO, BN, and CuCN computed from G₀W₀@PBE.

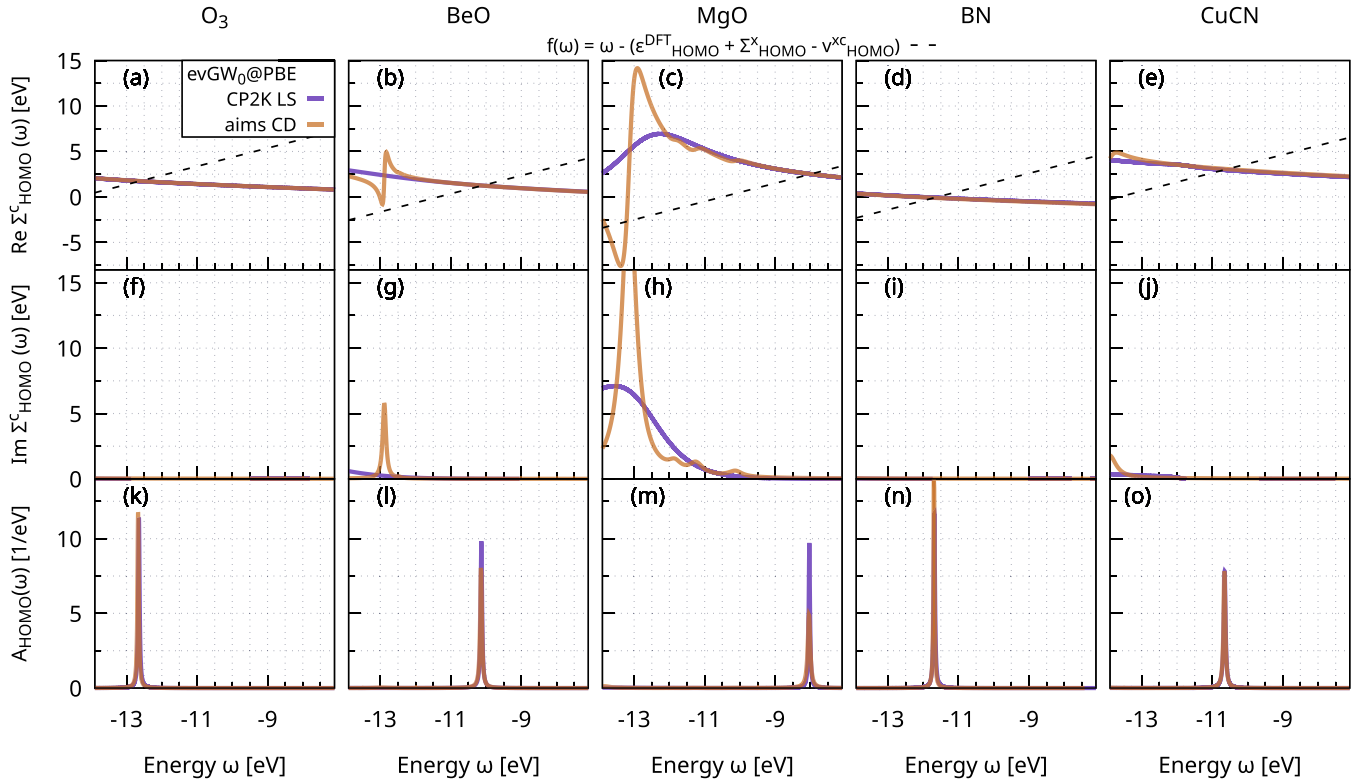


FIG. 7. (a)–(e) $\text{Re}(\Sigma_{\text{HOMO}}^c)$, (f)–(j) $\text{Im}(\Sigma_{\text{HOMO}}^c)$, and (k)–(o) A_{HOMO} [Eq. (5)] for O₃, BeO, MgO, BN, and CuCN computed from evGW₀@PBE.

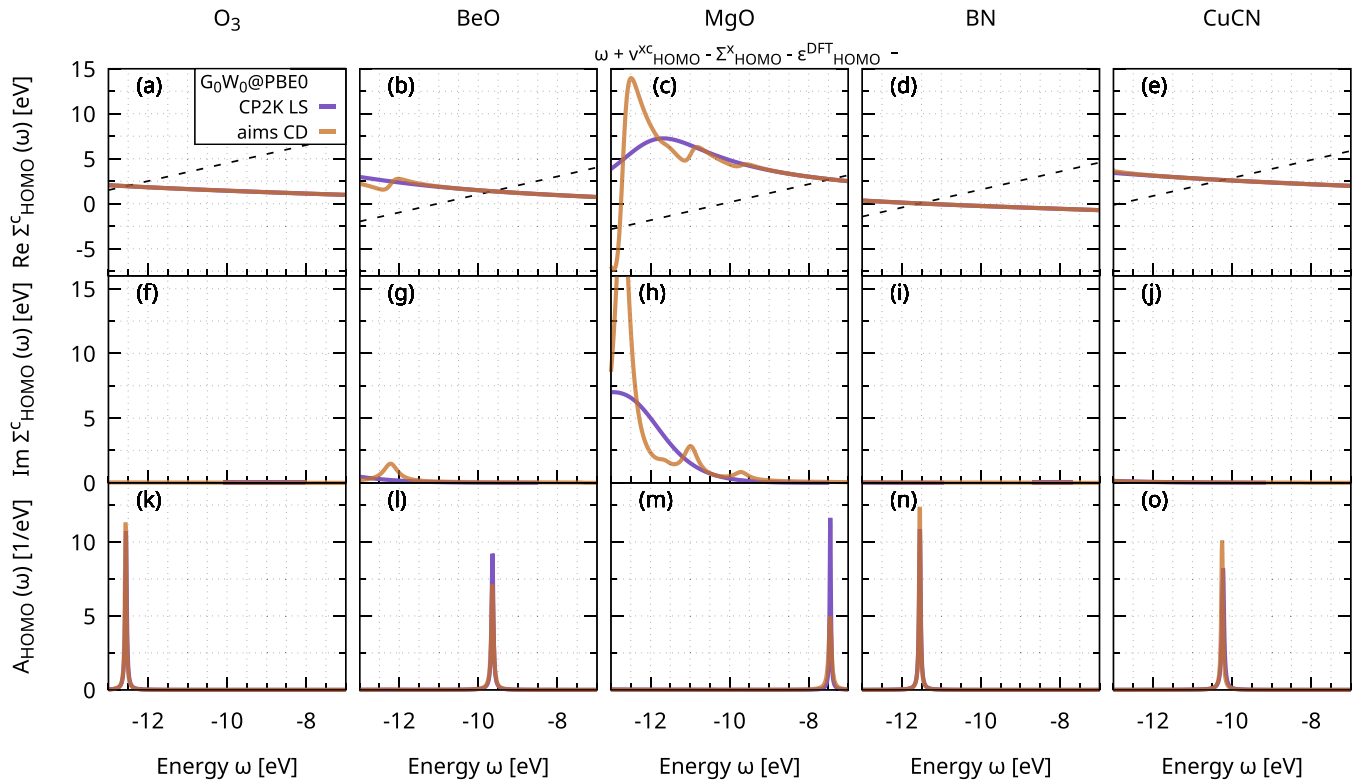


FIG. 8. (a)–(e) $\text{Re}(\Sigma_{\text{HOMO}}^c)$, (f)–(j) $\text{Im}(\Sigma_{\text{HOMO}}^c)$, and (k)–(o) A_{HOMO} [Eq. (5)] for O_3 , BeO , MgO , BN , and CuCN computed from G_0W_0 @PBE0.

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