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Benchmark of GW Methods for Core-Level Binding Energies

Jiachen Li, Ye Jin, Patrick Rinke, Weitao Yang, and Dorothea Golze*

1. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a standard characterization tool for materials,1 liquids,2,3 and molecules.4 In XPS, the core-level binding energies (CLBEs) are measured, which are element-specific but also sensitive to the chemical environment.5 However, establishing the link between the measured spectrum and the atomic structure is challenging, in particular for complex materials with heavily convoluted XPS signals.6,7 Guidance from theory is thus often necessary to interpret XPS spectra.

Theoretical XPS methods can be distinguished into delta and response approaches. In delta-based methods, the CLBE is computed as the total energy difference between the neutral and core-excited system. These calculations can be performed at different levels of theory, for example, with high-level wave function methods, such as delta coupled cluster (ΔCC)8,9 or with Kohn–Sham density functional theory10−12 (KS-DFT). The most popular DFT-based approach is the delta self-consistent field (ΔSCF) method,13 which has been thoroughly benchmarked.14−20 While high accuracy can be achieved with these approaches, the explicit optimization of a core-ionized wave function leads to conceptual problems, for example, regarding periodicity, constraining spin–orbit coupled states or, in the case of DFT, deteriorating accuracy for larger structures, which was already discussed and demonstrated elsewhere.21−25

An explicit orbital optimization of core-ionized systems and the related conceptual issues are avoided in response theories, where electron propagators are applied to transform the ground into an excited state. Recently, wave function-based methods, such as linear response and equation-of-motion CC methods26−29 and the algebraic diagrammatic construction method,28 were reassessed for absolute CLBEs, yielding partly promising results. Another promising approach in the realm of response methods is the GW approximation30−32 to many-body perturbation theory, which is derived from Hedin’s equation33 by omitting the vertex correction. The GW approximation is considered the “gold standard” for the computation of band structures of materials,34,35 but it has also been successfully applied to valence excitations of molecules.34,35−37

Due to its primary application to solids, GW was traditionally implemented in plane wave codes that typically use pseudo-potentials for the deeper states. With the increasing availability of the GW method in localized basis set codes,38−45 core states moved into focus. CLBE calculations have emerged as a recent trend in GW.32,44,45−51 By extension to the Bethe–Salpeter equation (BSE@GW), also K-edge transition energies measured in X-ray absorption spectroscopy can be calculated.52 These studies focused primarily on molecules. However, GW is one of the most promising methods for core-level predictions of materials because the scaling with respect to system size is generally smaller than for wave

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function-based response methods and the method is well established for periodic structures. In addition, GW implementations for localized basis sets are advancing rapidly. Recently, periodic implementations \(^{44,55,66}\) and low-scaling GW algorithms with \(O(N^3)\) complexity emerged in localized basis set formulations.\(^{67-70}\)

The application of GW to core states is more difficult than for valence states. We showed that more accurate and computationally more expensive techniques for the frequency integration of the self-energy are required compared to valence excitations.\(^{71} \) Furthermore, we found that the standard single-shot \(G_0W_0\) approach performed on top of DFT calculations with generalized gradient approximations (GGAs) or standard hybrid functionals fails to yield a distinct solution, which is caused by a loss of spectral weight in the quasiparticle (QP) peak.\(^{49}\) We demonstrated that eigenvalue self-consistency in \(G\) or using a hybrid functional with 45% exact exchange as the starting point for the \(G_0W_0\) calculation restores the QP main excitation. Including also relativistic corrections,\(^{50}\) an agreement of 0.3 and 0.2 eV with respect to experiment was reported for absolute and relative CLBEs, respectively.\(^{49}\)

While \(G_0W_0\) is the computationally least expensive GW flavor, it strongly depends on the density functional approximation (DFA). Tuning the exchange in the hybrid functional to, for example, 45% is conceptually unappealing and introduces undesired small species dependencies, as discussed more in detail in this work. Self-consistency reduces or removes the dependence on the underlying DFT functional but significantly increases the computational cost. The computationally least expensive self-consistent schemes are the so-called eigenvalue self-consistent approaches, where the eigenvalues are iterated in the Green’s function \(G\) (evGW\(_0\)) or alternatively in \(G\) and the screened Coulomb interaction \(W\) (evGW).\(^{71}\) Higher-level self-consistency schemes, such as fully self-consistent GW\(^{64,65,66}\) (scGW) and QP self-consistent GW\(^{64}\) (qsGW), remove, unlike evGW\(_0\) or evGW, the starting point dependence completely. However, these higher-level self-consistency schemes are much more expensive and not necessarily better because of the inherent underscreening due to the missing vertex correction.\(^{65,66}\)

Recently, we proposed the renormalized singles (RS) Green’s function approach, denoted as \(G_{RS}W_0\), to reduce the starting point dependence in GW.\(^{71}\) The RS concept was developed in the context of the random phase approximation (RPA) for accurate correlation energies\(^{68,69}\) and termed renormalized single excitation (RSE) correction. Following standard perturbation theory, SEs contribute to the second-order correlation energy. It was shown that their inclusion significantly improves binding energies (BES).\(^{68,69}\) The RS Green’s function approach extends the RSE idea from correlation energies to GW QP energies. In the \(G_{RS}W_0\) scheme, the RS Green’s function is used as a new starting point and the screened Coulomb interaction is calculated with the KS Green’s function. For valence excitations, we found that this renormalization process significantly reduces the starting point dependence and provides improved accuracy over \(G_0W_0\).\(^{71}\) The mean absolute errors (MAEs) obtained from the \(G_{RS}W_0\) approach with different DFAs are smaller than 0.2 eV for predicting ionization potentials of molecules in the GW100 set.\(^{67}\) Unlike the self-consistent schemes, the RS Green’s function method hardly increases the computational cost compared to \(G_0W_0\).

```latex
\begin{equation}
\epsilon_n^{WP} = \epsilon_n^0 + \text{Re}(\psi_n^0(S_n^{WP}) - \psi_n) = \epsilon_n^0 + \text{Im}(\psi_n^0(S_n^{WP}) - \psi_n)
\end{equation}
```

where \(\psi_n^0\) are the KS molecular orbitals (MOs) and \(v^{WP}\) is the WS exchange–correlation potential. We use \(i, j\) for occupied orbitals, \(a, b\) for virtual orbitals, and \(m, n\) for general orbitals. We omitted the spin index in all equations for simplicity and use the notation \(S_n = \psi_n^0(S_n^{WP})\) and \(v_n^{WP} = \psi_n^0(S_n^{WP})\) in the following. We can directly obtain the CLBE of state \(n\) from the QP energies because they are related by CLBEs = \(-\epsilon_n^{WP}\).

The self-energy \(\Sigma\) is given by

```latex
\begin{equation}
\Sigma(r, r', \omega) = \frac{i}{2\pi} \sum a \omega g_0(r, r', \omega + a')W_0(r, r', \omega')e^{i\omega\eta}
\end{equation}
```

where the noninteracting KS Green’s function is denoted \(G_0\) and the screened Coulomb interaction \(W_0\). \(\eta\) is a positive infinitesimal. The KS Green’s function reads

```latex
\begin{equation}
G_0(r, r', \omega) = \sum m \omega - \epsilon_m^0 - \eta\text{sgn}(\epsilon_m - \epsilon_0^0)
\end{equation}
```

where \(\epsilon_m^0\) is the Fermi energy. The screened Coulomb interaction is calculated at the level of the RPA as

```latex
\begin{equation}
W_0(r, r', \omega) = \int dr'' e^{-i\omega(r, r', \omega)v(r, r')}
\end{equation}
```

Recently, we employed the concept of RS in a multi-reference DFT approach for strongly correlated systems.\(^{71}\) We also used the RS Green’s function in the T-matrix approximation (\(G_{RS}T_{RS}\)).\(^{71}\) The T-matrix method scales formally as \(O(N^6)\) with respect to system size \(N\).\(^{71,72}\) with reduced scaling possible using effective truncation of the active space.\(^{71}\) In addition to the high computational cost, the performance of \(G_{RS}T_{RS}\) for core levels is not particularly impressive. The error with respect to experiment is 1.5 eV for absolute and 0.3 eV for relative CLBEs.\(^{71}\) In the present work, we focus thus on RS GW approaches for core levels.

In this work, we benchmark GW approaches, which we consider computationally affordable and suitable for large-scale applications. This includes \(G_0W_0\) with tuned starting points, the eigenvalue self-consistent schemes evGW\(_0\) and evGW, and two new methods that we introduce in this work. One is based on the so-called Hedin shift\(^{74}\) and can be understood as approximation of the evGW\(_0\) method. We refer to this scheme as \(G_{MS}W_0\). The other is a different flavor of the RS Green’s function approach, where the screened Coulomb interaction is also computed with the RS Green’s function (\(G_{RS}W_{RS}\)).

The remainder of this article is organized as follows: we introduce the different GW approaches in Section 2 and give the computational details for our calculations in Section 3. The solution behavior of the different methods is discussed in Section 4.1 by comparing self-energy matrix elements and spectral functions. In Section 4.2, results are presented for the CORE65 benchmark set and in Section 4.3 for the ethyl trifluoroacetate (ETFA) molecule. The computational cost for the different GW flavors is discussed in Section 4.4, and we finally draw conclusions in Section 5.

2. THEORY

2.1. Single-Shot \(G_0W_0\) Approach. The most popular GW approach is the single-shot \(G_0W_0\) scheme, where the GW QP energies are obtained as corrections to the KS eigenvalues \(\epsilon_n^0\)

```latex
\begin{equation}
\epsilon_n^{WP} = \epsilon_n^0 + \text{Re}(\psi_n^0(S_n^{WP}) - \psi_n) = \epsilon_n^0 + \text{Im}(\psi_n^0(S_n^{WP}) - \psi_n)
\end{equation}
```

where \(\psi_n^0\) are the KS molecular orbitals (MOs) and \(v^{WP}\) is the WS exchange–correlation potential. We use \(i, j\) for occupied orbitals, \(a, b\) for virtual orbitals, and \(m, n\) for general orbitals. We omitted the spin index in all equations for simplicity and use the notation \(S_n = \psi_n^0(S_n^{WP})\) and \(v_n^{WP} = \psi_n^0(S_n^{WP})\) in the following. We can directly obtain the CLBE of state \(n\) from the QP energies because they are related by CLBEs = \(-\epsilon_n^{WP}\).

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\Sigma(r, r', \omega) = \frac{i}{2\pi} \sum a \omega g_0(r, r', \omega + a')W_0(r, r', \omega')e^{i\omega\eta}
\end{equation}
```

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\begin{equation}
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\end{equation}
```

where \(\epsilon_m^0\) is the Fermi energy. The screened Coulomb interaction is calculated at the level of the RPA as

```latex
\begin{equation}
W_0(r, r', \omega) = \int dr'' e^{-i\omega(r, r', \omega)v(r, r')}
\end{equation}
```
where \( \epsilon(\mathbf{r},\mathbf{r}',\omega) \) is the dielectric function and \( v(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'| \) the bare Coulomb interaction.

The calculation of the self-energy matrix elements \( \Sigma_n \) is split into a correlation part \( \Sigma^c \) and an exchange part \( \Sigma^x \), that is, \( \Sigma_n = \Sigma^c_n + \Sigma^x_n \). The HF-like exchange part \( \Sigma^x_n \) is given by

\[
\Sigma^x_n = -\sum_{i}^{\text{occ}} \langle \psi_i^0 \psi_i^0 | V^x \psi_i^0 \psi_i^0 \rangle
\]

(5)

The correlation part \( \Sigma^c \) is computed from \( W^{\Sigma} = W_0 - \nu \) and is the part that we plot in Section 4.1 to investigate the GW solution behavior. The correlation part in its fully analytic form is given by

\[
\Sigma^c_n(\omega) = \sum_{m} \sum_{s} \frac{|\langle \psi_m^0 | \psi_n^0 \rangle|^2}{\omega - \epsilon_n^0 + (\Omega^0_m - i\eta)\text{sgn}(\epsilon_n^0 - \epsilon_m^0)}
\]

(6)

where \( \Omega^0_m \) are charge neutral excitations at the RPA level and \( \rho_n^0 \) are the corresponding transition densities. The fully analytic form of \( \Sigma^c_n \) directly shows the pole structure of the self-energy and is illustrative to understand the solution behavior of GW.

However, the evaluation of \( \Omega^0_m \) scales with \( O(N^2) \). In practice, the correlation self-energy is usually evaluated with a reduced scaling by using techniques such as analytical continuation or the contour deformation; see ref 31 for an overview of frequency integration techniques.

The QP energies can be obtained by solving eq 1, which is typically the computationally least expensive approach. In this work, we additionally employ two alternative approaches to obtain further insight into the physics and suitability of the different GW approaches. The first is the graphical solution of eq 1, where we plot the self-energy matrix elements \( \Sigma_n \) and determine the QP solution by finding the intersections with the straight line \( \omega = \epsilon_m^0 + \epsilon_n^0 - \Sigma_n \). The presence of several intersections would indicate that more than one solution exists.

The second, computationally even more expensive alternative, is the computation of the spectral function, which is given by

\[
A(\omega) = \frac{1}{N} \sum_{m} \frac{|\text{Im}[\Sigma_n(\omega)]|^2}{[\omega - \epsilon_n^0 - (\text{Re}[\Sigma_n(\omega)] - \epsilon_m^0)]^2 + |\text{Im}[\Sigma_n(\omega)]|^2}
\]

(7)

The spectral function is related to the photocurrent, which is the experimental observable in photoemission spectroscopy, as discussed in, for example, refs 31 and 75. In eq 7, we include also the imaginary part of the complex self-energy, which gives us direct access to the spectral weights and satellite spectrum.

The GW formalism is primarily applied to closed-shell systems, but the treatment of open shell systems is also possible to some extent. Open shell systems are often multireference problems, while the KS Green’s function \( G_0 \) assumes a nondegenerate ground state characterized by a single Slater determinant. If a particular ground state is a sum of several Slater determinants, the GW approach is not applicable and a multiconfiguration method should be used instead. If it is possible to choose among the multiple ground states of the open shell systems one that evolves into a single Slater determinant, for example, the triplet state of \( O_2 \), then our definition of \( G_0 \) and thus Dyson’s equation are valid. As shown in ref 76, the QP multiplet splittings of valence excitations are correctly predicted by GW if the preceding spin-polarized KS-DFT calculations provide a sufficient approximation of the particular ground states of the open shell system. While the multiplet splittings of open shell valence levels can be rather complex, the 1s excitations give rise to a simple doublet with a weaker line at higher BE and a stronger one at lower BE. So far, we only investigated the \( O_2 \) molecules and found that GW performed very well for the splitting of the O 1s lines.

2.2. Eigenvalue Self-Consistent GW Schemes. Including self-consistency in Hedin’s GW equations is a widely used strategy to go beyond \( G_0W_0 \). scGW\(^{25,63} \) is conceptually the purest approach but also the most expensive one. To reduce the computational demands, different lower-level self-consistent schemes were developed. The simplest approach is an eigenvalue self-consistent scheme, which comes in two different flavors. The first one is to iterate the eigenvalues only in \( G \) and keep \( W \) fixed at the \( W_0 \) level. This scheme is referred to as the evGW\(_0 \) approach. In evGW\(_0 \) we start by updating the KS eigenvalues in the Green’s function with the \( G_0W_0 \) QP energies, re-evaluate the QP equation (see eq 1), and iterate until self-consistency in \( G \) is reached. The Green’s function in the eigenvalue self-consistent scheme reads

\[
G_{\text{ev}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{m} \frac{\psi_m^0(\mathbf{r})\psi_m^0(\mathbf{r}')}{\omega - \epsilon^0_m + \text{sgn}(\epsilon^c_{\mathbf{r}} - \epsilon^0_m)}
\]

(8)

with \( \epsilon^0_m = \epsilon^0_m + \Delta \epsilon_m \) where \( \Delta \epsilon_m \) is the GW correction, see eq 1. The second flavor is evGW\(_0 \), where the KS eigenvalues are updated not only in \( G \) but also in the screened Coulomb interaction \( W \). The eigenvalue self-consistent calculations are computationally significantly more expensive than a \( G_0W_0 \) calculation, in particular in combination with the accurate self-energy integration techniques that are required for core levels.\(^{22} \) The computational demands are large because, \( G \), the screened Coulomb interaction \( W \) (in the case of evGW\(_0 \)), and the self-energies have to be built repeatedly. In addition, eq 1 must be solved not only for the states of interest but for all states.

2.3. GW with the Hedin Shift. The cost of an evGW\(_0 \) scheme can be drastically reduced by using a global shift \( \Delta H \) instead of an individual shift \( \Delta \epsilon_m \) for each state \( m \). This scheme was first introduced by Hedin\(^{19} \) and is referred to as \( G_{\text{Hedin}}W_0 \) in the following. The \( G_{\text{Hedin}}W_0 \) approach was discussed several times in the literature,\(^{17,77-79} \) and the effect of evGW\(_0 \) and \( G_{\text{Hedin}}W_0 \) on the self-energy structure has been discussed for valence states in ref 31. In the Hedin-shift scheme, the Green’s function transforms into

\[
G_{\text{Hedin}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{m} \frac{\psi_m^0(\mathbf{r})\psi_m^0(\mathbf{r}')}{\omega - \epsilon^0_m + \Delta H - \text{sgn}(\epsilon^c_{\mathbf{r}} - \epsilon^0_m)}
\]

(9)

where \( G_0(\omega - \Delta H) = G_{\text{Hedin}}(\omega) \). The QP equation with the Hedin-shift scheme then becomes

\[
\epsilon^\text{QP}_m = \epsilon^0_m + \text{Re}[\psi_m^0|\Sigma^\text{QP} - \Delta H] - v^\text{xc}\psi_m^0
\]

(10)

Traditionally, \( \Delta H \) is determined with respect to the Fermi level of \( G_0 \) for metals or the valence band maximum for gapped solid-state systems. For the molecular case, \( \Delta H \) is evaluated with respect to the highest occupied MO (HOMO) by introducing the self-consistency condition \( \epsilon^\text{QP}_\text{HOMO} = \epsilon^0_{\text{HOMO}} + \Delta H \), which is inserted in eq 10 and yields

\[
\Delta H = \text{Re}[\Sigma^\text{Hedin}_{\text{HOMO}}(\epsilon_{\text{HOMO}})] - v^\text{xc}_{\text{HOMO}}
\]

(11)

As demonstrated in ref 31, evGW\(_0 \) and \( G_{\text{Hedin}}W_0 \) lead to a shift of the pole structure of the self-energy matrix elements \( \Sigma_n \) to
more negative frequencies. For $\Sigma_{\text{ROMO}}(\omega)$, the shift is similar for evGW$_0$ and $G_{\text{HOMO}}W_0$, yielding practically the same $\epsilon^\text{QP}_{\text{ROMO}}$.

For core states, we found that the shift $\Delta H$ computed as in eq 11 is much smaller than the one from evGW$_0$. Taking the H$_2$O molecule as an example, the evGW$_0$ shift of the self-energy poles with respect to $G_{\text{HOMO}}W_0$ is in the range of $-6$ eV for the HOMO, whereas it is in the range of $-30$ eV for the oxygen 1s state. Generally, we found that the evGW$_0$ shifts get progressively larger with increasing BE. Therefore, we propose here a modification of the Hedin approach, where we determine an $n$-specific shift $\Delta H_n$ for the (core) state $n$ of interest. $\Delta H_n$ is determined as

$$\Delta H_n = \text{Re}\Sigma_n(\epsilon_n^0) - \nu_n^\text{xc}$$

(12)

and the QP equation transforms then to

$$\epsilon^\text{QP}_n = \epsilon_n^0 + \text{Re}\Sigma_n(\epsilon_n^0 - \Delta H_n) - \nu_n^\text{xc}$$

(13)

$\Delta H_n$ is still a global shift, which is, however, specific for the respective (core) state of interest. For example, to obtain $\epsilon^\text{QP}$ for the CO molecule, we solve eq 13 with $\Delta H_{\text{HOMO}}$ whereas we solve it with $\Delta H_{\text{O1s}}$ for $\epsilon^\text{QP}_{\text{O1s}}$. In the case of HCOOH, we determine $\Delta H_n$ for each $n$ separately.

The flowchart of a $G_{\text{HOMO}}W_0$ calculation is shown in Figure 1. In a $G_{\text{HOMO}}W_0$ calculation of state $n$, we calculate $\Delta H_n$ once, insert it in eq 13, and iterate the latter as in a regular $G_{\text{HOMO}}W_0$ calculation. The shift $\Delta H_n$ is kept constant during the iteration of the QP equation. Compared to a $G_{\text{HOMO}}W_0$ calculation, the computation of $\Delta H$ is the only computational overhead that we introduce. The computational cost of a $G_{\text{HOMO}}W_0$ calculation is thus practically the same as for a $G_{\text{HOMO}}W_0$ calculation.

We point out that the Hedin shift is not an arbitrary scissor shift of the KS eigenvalues $\epsilon_n^0$, where the energies of the occupied and virtual states are shifted down and up, respectively. (i) The eigenvalues $\epsilon_n^0$ are still used to construct $W_0$. The shift is only applied in $G_n$ and its sign is, unlike in a scissor shift approach, independent on the occupation of state $m$ in eq 9. (ii) More importantly, the expression for $\Delta H_n$ is derived by enforcing self-consistency for the energy of state $n$. The motivation for the Hedin shift and its derivation was comprehensively discussed for the valence case in the literature,74,77,79 and is therein also referred to as “alignment of the chemical potential” or “adjusting the energy scale of $G_n$.

The Hedin shift can be understood as the simplest step toward self-consistency and viewed as one-diagonal element correction in the context of the evGW$_0$ method. In evGW$_0$, we replace the KS energies $\epsilon_n^0$ in eq 3 by $\epsilon_n^\text{QP} = \epsilon_n^0 + \Delta \epsilon_n^\text{G}$, see eq 8, where $m$ is an index that runs over all occupied and virtual states and $\Delta \epsilon_n^\text{G}$ is the GW correction. In the $G_{\text{HOMO}}W_0$ approach that we propose here, we aim to approximate the element $\Delta \epsilon_n^\text{G}$ which has the largest contribution, by $\Delta H_n$ and neglect the rest. We found that the element $\Delta \epsilon_n^\text{G}$ where $n$ is the state of interest, is (by far) the most relevant one. This is the motivation for determining a state-specific shift $\Delta H_n$ and using eq 12 instead of eq 11 for our core-level calculations.

2.4. RSEs in RPA. The RS Green’s function approach is based on the same idea as the RSE corrections in RPA. Since we consider the introduction of the RS concept more illustrative for total than QP energies, we will briefly summarize the key equations derived by Ren et al.68,69,80 in the context of Rayleigh–Schrödinger perturbation theory (RSPT), before proceeding with the RS Green’s function approaches in Section 2.5.

In RSPT, the interacting N-electron Hamiltonian $\hat{H}$ is partitioned into a noninteracting mean-field Hamiltonian $\hat{H}_0$ and an interacting perturbation $\hat{H}'$.

$$\hat{H}_0 = \sum_i \hat{h}_i^0(j) = \sum_{j=1}^N \left[ -\frac{1}{2} \nabla_j^2 + v_{\text{ext}}(\mathbf{r}_j) + v_{\text{Hxc}}^j \right]$$

(14)

$$\hat{H}' = \sum_{j<k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} - \sum_{j=1}^N v_{\text{Hxc}}^j$$

(15)

where $\hat{h}_i^0$ is the single-particle Hamiltonian of the mean-field reference. The Hamiltonian $\hat{H}_0$ includes the kinetic term, the external potential $v_{\text{ext}}$ and the mean-field potential $v_{\text{Hxc}}^j$. The latter can be the single-particle potential from HF or KS-DFT and contains the Hartree and exchange–correlation terms. Following standard perturbation theory, single excitations (SEs) contribute to the second-order correlation energy and are given by

$$E_{\text{SE}}^n = \sum_{i} \sum_{a}^\text{occ} \sum_{d}^\text{virt} \left[ \langle \Psi_0^i | \hat{H} | \Psi_0^d \rangle \right]^2 = \sum_{i} \sum_{a}^\text{occ} \sum_{d}^\text{virt} \left[ \langle \Psi_0^i | \hat{H} | \Psi_0^d \rangle \right]^2$$

(16)

$$= \sum_{i} \sum_{d}^\text{occ} \sum_{a}^\text{virt} \left[ \langle \Psi_0^i | \hat{H} | \Psi_0^d \rangle \right]^2$$

(17)

where $\langle \Psi_0^i \rangle$ is the Slater determinant for the ground-state configuration and $\langle \Psi_0^d \rangle$ for the singly excited configuration. The
orbitals $\psi^{0}_{i/a}$ and corresponding orbital energies $\epsilon^{0}_{i/a}$ are the ones of the $\hat{h}$ ($\hat{f}$) operator. The derivation of eq 17 from eq 16 is given in detail in the Supporting Information of ref 68. As evident from eq 17, the single correction vanishes if $\psi^{\text{Hxc}}$ is the HF mean-field potential, which is a consequence of Brillouin’s theorem.41

The energy $E^{\text{RS}}$ is only the second-order correction to the correlation energy, as shown in Figure 2. The infinite summation of the higher-order diagrams yields the RSE correction. The derivation of the RSE correlation energy is given in detail in ref 69. To summarize briefly the procedure, the Fock matrix is evaluated with the KS orbitals. Subsequently, the occupied and unoccupied blocks of this matrix are diagonalized separately (subspace diagonalization), which yields a new set of (RS) eigenvalues and orbitals. Replacing $\psi^{0}_{i/a}$ and $\epsilon^{0}_{i/a}$ in eq 17 with the RS eigenvalues and orbitals yields the RSE correlation energy.

25. RS Green’s Function GW Approaches. In analogy to the RPA RSE correction, the RS Green’s function $G^{\text{RS}}$ is designed as an effective noninteracting reference system that includes all the single contributions. The RS Green’s function is defined as

$$G^{\text{RS}}_{\omega}^{-1} = G^{\text{H}}_{\omega}^{-1} - P(\Sigma^{\text{H}}[G^{\text{H}}_{\omega}] - \nu^{\text{Hxc}})P - Q(\Sigma^{\text{H}}[G^{\text{H}}_{\omega}] - \nu^{\text{Hxc}})Q$$  

(18)

where $P = \sum^{\text{occ}} |\psi^{0}_{i} \rangle \langle \psi^{0}_{i}|$ is the projection into the occupied orbital space and $Q = 1 - P$ is the projection into the virtual orbital space. $\Sigma^{\text{H}}[G^{\text{H}}_{\omega}]$ refers to a HF-like self-energy constructed with $G^{\text{H}}_{\omega}$ which is usually the KS Green’s function. $\Sigma^{\text{H}}$ is the sum of the Hartree self-energy $\Sigma^{\text{H}}$ and the exchange self-energy $\Sigma^{\text{ex}}$, that is, $\Sigma^{\text{H}}_{\text{HK}} = \Sigma^{\text{H}} + \Sigma^{\text{ex}}$, where $\Sigma^{\text{H}} = \sum^{\text{occ}} (\langle \psi^{0}_{i} | \hat{h} | \psi^{0}_{j} \rangle - \delta_{ij})$ and $\Sigma^{\text{ex}} = -\sum^{\text{occ}} (\langle \psi^{0}_{i} | \hat{H}_{\text{ex}} | \psi^{0}_{j} \rangle - \delta_{ij}).$ Note that both are built with the mean-field orbitals $\psi^{0}_{i}$ provided by, for example, KS-DFT. $\nu^{\text{Hxc}}$ is the single-particle Hartree-exchange–correlation potential defined in eq 14. If the potential $\nu^{\text{Hxc}}$ is the one from HF and if $G^{\text{H}}$ is the HF Green’s function, then the second and third terms on the right-hand side of eq 18 vanish and $G^{\text{RS}}$ corresponds to the HF Green’s function, which is again a consequence of Brillouin’s theorem. $G^{\text{RS}}$ includes the single contributions, which are one source of the starting point dependence. As we showed previously,47 the dependence on the DFA is therefore reduced in the $G^{\text{RS}}W_0$ scheme. As for $G^{\text{RS}}W_0$, the primary use case of the RS approach are closed-shell systems for the same reasons discussed in Section 2.1 and due to the restriction of Brillouin’s theorem to the closed-shell case. While not part of this work, we expect nevertheless that simple spin splittings as observed for 1s excitations can be captured by the RS approach.

The RS Green’s function is given as the solution of the two projected equations in the occupied orbital subspace67

$$P(G^{\text{RS}}_{\omega})P = P(G^{\text{H}}_{\omega})P + P(\Sigma^{\text{H}}[G^{\text{H}}_{\omega}] - \nu^{\text{Hxc}})P$$  

(19)

and the virtual orbital subspace

$$Q(G^{\text{RS}}_{\omega})Q = Q(G^{\text{H}}_{\omega})Q + Q(\Sigma^{\text{H}}[G^{\text{H}}_{\omega}] - \nu^{\text{Hxc}})Q$$  

(20)

In practice, $G^{\text{RS}}$ is obtained by a similar subspace diagonalization procedure as used for the RSE total energy corrections. The KS density matrix is used to construct the HF Hamiltonian $\hat{H}^{\text{HF}}$, which defines the RS Hamiltonian $\hat{H}^{\text{RS}} = \hat{H}^{\text{HF}}[G^{\text{RS}}]$. The equations for the occupied

$$P(\hat{H}^{\text{HF}}[G^{\text{RS}}])P|\psi^{\text{RS}}_{i} \rangle = |\epsilon^{\text{RS}}_{i} \rangle |\psi^{\text{RS}}_{i} \rangle$$  

(21)

and virtual subspace

$$Q(\hat{H}^{\text{HF}}[G^{\text{RS}}])Q|\psi^{\text{RS}}_{a} \rangle = |\epsilon^{\text{RS}}_{a} \rangle |\psi^{\text{RS}}_{a} \rangle$$  

(22)

are diagonalized separately.65 The subspace diagonalization yields the RS eigenvalues $\epsilon^{\text{RS}}_{i}$ and corresponding eigenvectors $|\psi^{\text{RS}}_{i} \rangle$ and is performed only once. The RS Hamiltonian can be reduced to the HF$_{\text{diag}}$ method38 if only diagonal elements in eqs 21 and 22 are used. It has been shown that the $G^{\text{RS}}W_0$(HF$_{\text{diag}}$) method predicts accurate valence QP energies of molecular systems.88

The RS Green’s function is computed with the RS eigenvalues and orbitals

$$G^{\text{RS}}_{\omega}(r, r', \alpha) = \sum_{m} \frac{|\psi^{\text{RS}}_{m}(r') \rangle \langle \psi^{\text{RS}}_{m}(r)|}{\omega - \epsilon^{\text{RS}}_{m} - i\eta \text{sgn}(\epsilon^{\text{RS}}_{m} - \epsilon^{\text{RS}}_{m})}$$  

(23)

and is diagonal in the occupied subspace and the virtual subspace.

In the $G_{\omega}W_0$ approach,67 the RS Green’s function is used as a new starting point and the screened interaction is calculated with the KS Green’s function. The correlation part of the $G_{\omega}W_0$ self-energy is67

$$\Sigma_{\omega}^{\text{GW}_0}(\omega) = \sum_{m} \frac{|\psi^{0}_{m} \rangle \langle \psi^{0}_{m}|}{\omega - \epsilon^{0}_{m} + (\Omega^{0}_{m} - i\eta)\text{sgn}(\epsilon^{0}_{m} - \epsilon^{0}_{m})}$$  

(24)

where $\rho^{0}_{m}$ and $\Omega^{0}_{m}$ are the transition densities and the RPA excitation energies calculated with the KS Green’s function. Then, the QP equation for $G_{\omega}W_0$ is

$$\epsilon_{n}^{\text{QP}} = \epsilon_{n}^{0} + \text{Re}(\langle \psi^{0}_{n} | \Sigma^{\text{GW}_0} | \psi^{0}_{n} \rangle) - v_{x0}^{0} |\psi^{0}_{n} \rangle$$  

(25)

Note that eqs 24 and 25 are slightly different from the original QP equation for $G_{\omega}W_0$67 where we used the RS eigenvectors $|\psi^{\text{RS}}_{n} \rangle$. Here, we use for simplicity the KS instead of the RS orbitals because we found that the difference induced upon using RS orbitals is marginal.67 Since we use the KS orbitals, the exchange part of the $G_{\omega}W_0$ self-energy is the same as in $G_{\omega}W_0$, see eq 5.
Core-level calculations were performed at the G0W0, evGW0, GΔH0, evGW, and GRSWRS computed at the cc-pVQZ level. (a) Spectral function A(\(\omega\)) (eq 7) from G0W0 using starting points with no exact exchange or a low amount. (b,c) Real part of the correlation self-energy \(\Sigma^c(\omega)\) in evGW0@PBE, GΔH0, and evGW@PBE. Diagonal matrix elements Re \(\Sigma^c(\omega)\) = \(\langle \psi_n^0 | \Sigma^c(\omega) | \psi_n^0 \rangle\) for the oxygen 1s orbital. The intersection with the red line is the graphical solution of eq 1. The vertical gray-dashed line indicates the QP solution of this graphical solution, and \(\Delta\) indicates the shift with respect to G0W0@PBE (gray). (d) Spectral functions in evGW0@PBE, GΔH0@PBE, evGW@PBE, and G0W0@PBE\(h(\alpha=0.45)\). (e) Self-energy matrix elements Re \(\Sigma^c(\omega)\) in GRSWRS@PBE (green) compared to G0W0@PBE (gray). (f) Spectral functions A(\(\omega\)) in GRSWRS with different starting points.

In this work, we introduce a new approach that uses the RS Green’s function as a new starting point and also calculates the Green’s function as a new starting point and also calculates the self-energy becomes

\[
\Sigma^c_{\text{GRS-WRS}}(\omega) = \sum_m \sum_s \left( \omega - \epsilon_m^{\text{RS}} - (\Omega_m^{\text{RS}} - i\eta) \right) \text{sgn}(\epsilon_m^{\text{RS}} - \epsilon_s^{\text{RS}}) \]

(26)

where \(\rho_s^{\text{RS}}\) and \(\Omega_s^{\text{RS}}\) are the transition densities and the RPA excitation energies calculated with the RS Green’s function. Then, the QP equation for the GRSWRS approach follows as

\[
\epsilon_s^{\text{QP}} = \epsilon_s^{0} + \text{Re}\langle \psi_s^0 | \Sigma_{\text{GRS-WRS}}^{\text{QP}}(\epsilon_s^{\text{QP}}) - \nu_m^{\text{GRS-WRS}}(\epsilon_s^{\text{QP}}) \rangle
\]

(27)

The construction of the RS Green’s function scales only as \(O(N^3)\) with respect to system size \(N\). The overall scaling of GRSWRS depends on the frequency integration technique that is used, which will be discussed more in detail in Section 4.4.

3. COMPUTATIONAL DETAILS

Core-level calculations were performed at the G0W0, evGW0, evGW, GΔH0, and GRSWRS levels for the CORE65 benchmark set, which contains 65 1s excitation energies of 32 small molecules (30 \(\times\) C 1s, 21 \(\times\) O 1s, 11 \(\times\) N 1s, and 3 \(\times\) F 1s).

Geometries and experimental reference values were taken from ref 49. Additionally, we studied the ETFA molecule. The structure of the latter was obtained upon request from the authors of ref 18 and is available in the Supporting Information.

The G0W0, evGW0, evGW, and GΔH0 calculations were carried out with the FHI-aims program package, which is based on numeric atom-centered orbitals (NAOs). The G0W0 and evGW0 data were extracted from our previous work, while the evGW and GΔH0 data were generated for this benchmark study. In the FHI-aims calculations, the contour deformation technique is used to evaluate the self-energy using a modified Gauss–Legendre grid with 200 grid points for the imaginary frequency integral part. The GRSWRS calculations were performed with the QM4D program. In QM4D, the GW self-energy integral is calculated fully analytically, see eq 6. In FHI-aims and also in QM4D, the QP equation is always solved iteratively.

For evGW0, evGW, and GΔH0, we used the Perdew–Burke–Ernzerhof (PBE) functional for the underlying DFT calculation, while the G0W0 calculations employ the PBE\(h(\alpha)\) hybrid functional with 45% exact exchange (\(\alpha = 0.45\)). The GRSWRS calculations were performed with PBE and three different hybrid functionals, namely, PBE0, PBEH(\(\alpha = 0.45\)), and B3LYP. Note that PBE0 corresponds to PBE\(h(\alpha = 0.25)\).

All GW results are extrapolated to the complete basis set limit using the Dunning basis set family cc-pVnZ. For a discussion of the basis set choice, we refer the reader to ref 52.
and the Supporting Information of ref 50. Following ref 49, the extrapolation is performed by a linear regression with respect to the inverse of the total number of basis functions. A four-point extrapolation with \( n = 3-6 \) is performed for \( G_0 W_o \), \( e v G W_o \), \( e v G W \), and \( G_{SH} W_o \). For \( G_0 W_{KS} \), we use only two points \( (n = 3, 4) \) due to computational limitations. We verified that this two-point extrapolation deviates only by 0.1 eV from the four-point scheme on average. The cc-pVnZ family consists of contracted Gaussian-type orbitals (GTOs), which can be considered as a special case of an NAO and are treated numerically in FHI-aims. Note that the cc-pVnZ basis sets are treated as spherical GTOs in FHI-aims, whereas in QM4D, they are processed as pure Cartesian GTOs. Both codes use the resolution-of-the-identity (RI) approach with the Coulomb metric (RI-V).44 In FHI-aims, the RI auxiliary basis sets are generated on-the-fly as described in ref 39. For the QM4D calculations, the corresponding RI basis sets for cc-pVTZ and cc-pVQZ from ref 95 were used.

Relativistic effects were included for all calculations as post-processing step following the approach in refs 49 and 50; that is, we performed a nonrelativistic GW calculation on top of a nonrelativistic KS-DFT calculation and added the corrective term derived in ref 50 to the GW QP energies. The magnitude of the corrections increases with the atomic number and ranges from 0.12 eV for C 1s to 0.71 eV for F 1s. The relativistic corrections were derived for a free neutral atom at the PBE level and were obtained by evaluating the difference between the 1s eigenvalues from the radial KS and the 4-component Dirac-KS equation.

### 4. RESULTS AND DISCUSSION

#### 4.1. Solution Behavior

In our previous work,49 we showed that standard \( G_0 W_0 \) calculations starting from a GGA functional, which are routinely applied to valence states, lead to an erroneous multi-solution behavior for deep core states. It is thus important to confirm that the respective GW flavors yield indeed a unique solution. Only looking at the QP energies obtained by iterating eq 1 is typically not enough to verify the latter. Detailed insight into the solution behavior of GW-based methods can be obtained by (i) plotting the real part of the correlation self-energy \( \Sigma \) and (ii) plotting the spectral function \( A(\omega) \) as defined in eq 7. In Figure 3, we investigate \( A(\omega) \) and the diagonal matrix elements \( \Sigma_{ii}(\omega) \) for the 1s oxygen orbital of a single water molecule. Results are shown for \( G_0 W_o \) and \( G_{KS} W_{KS} \) with different starting points [PBE, PBE0, B3LYP, PBEh(\( \alpha = 0.45 \))] as well as partial self-consistent schemes, namely, evGW\(_o\), evGW, and \( G_{SH} W_o \) using PBE for the underlying DFT calculation.

We start our discussion with the \( G_0 W_o \) spectral functions and self-energy elements displayed in Figure 3a,b,d, where we reproduced for convenience the \( G_0 W_0 @PBE \), \( G_0 W_0 @PBE0 \), and \( G_0 W_0 @PBEh(\alpha = 0.45) \) results, which are also presented in ref 49. Figure 3b shows the self-energy from a \( G_0 W_0 @PBE \) calculation (gray line), which exhibits many poles. The poles are broadened by the \( \eta \)-term in eq 3 and thus appear as spikes in the self-energy. For \( G_0 W_{KS} @PBE \), we find that the poles are located in the frequency region where the QP solution is expected (around \(-540 \) eV). As already outlined in Section 2.1, we can obtain the graphical solution of eq 1 by finding the intersections with the straight line \( \omega = \varepsilon_1^0 + \varepsilon_2^0 - \Sigma \). For \( G_0 W_0 \), we observe many intersections, which are all valid solutions of the QP equation. The corresponding spectral function in Figure 3a shows many peaks with equal spectral weight but no clear main peak that could be assigned to the QP excitation in contrast to the experiment, where a sharp peak at 539.7 eV\(^2\) is observed. A main peak starts to emerge for hybrid functional starting points, such as PBE0 (\( \alpha = 0.25 \)) and B3LYP (\( \alpha = 0.20 \)). However, \( G_0 W_0 @PBE0 \) and \( G_0 W_0 @B3LYP \) still yield an unphysical second peak, which carries a large fraction of the spectral weight.

As already discussed in ref 49, the reason for this unphysical behavior is the overlap of the satellite spectrum with the QP peak. Satellites are due to multielectron excitations that accompany the photoemission process, for example, shake-up satellites, which are produced when the core photoelectron scatters a valence shell electron to a higher unoccupied energy level.\(^97\) These peaks appear as series of smaller peaks at higher BEs than the QP energy. For molecules, the spectral weight of these peaks is orders of magnitudes smaller than for the main excitation.\(^97\) Satellites occur in frequency regions where the real part of the self-energy has poles. As demonstrated in, for example, ref 31, the imaginary part of the self-energy exhibits complementary peaks at these frequencies (Kramers–Kronig relation). According to eq 7, large imaginary parts lead to peaks with small spectral weight, that is, peaks with a satellite character.

The occurrence of pole features around the QP excitations for deep core states can best be understood by analyzing the denominator of the fully analytic expression of the self-energy given in eq 6. \( \Sigma(\omega) \) has poles on the real axis for \( \eta \rightarrow 0 \) at \( \epsilon_1^0 - \Omega \) (occupied states \( i \)) and \( \epsilon_2^0 + \Omega \) (virtual states \( a \)). For occupied states, the eigenvalues \( \epsilon_1^0 \) are too large (too positive), and the charge neutral excitations \( \Omega \) are underestimated at the PBE level. As a result, the poles \( \epsilon_1^0 - \Omega \) are at too positive frequencies and the satellite thus too close to the QP peak. For virtual states, the same reasoning holds for the poles \( \epsilon_2^0 + \Omega \) but with reversed sign, that is, the poles are at too small frequencies. The separation between satellites and QP peak is also too small for valence excitations. However, the problem gets progressively worse further away from the Fermi level since the absolute differences between PBE eigenvalues \( \epsilon_i^0 \) and the QP excitation increase. We demonstrated this for semiconductor states,\(^58\) for which a distinct QP peak is still obtained. However, for deep core states, the separation becomes finally so small that the satellites merge with the QP peak.

The proper separation between the QP excitation and satellites can be restored by using an evGW\(_o\) scheme. The evGW\(_o@PBE \) self-energy is shown in Figure 3b (reproduced from ref 49). Iterating the eigenvalues in G shifts the on-set of the pole structure too more negative frequencies. The overall pole structure is very similar to \( G_0 W_0 @PBE \) but shifted by a constant value of \( \Delta = -28.7 \) eV. The \( G_{SH} W_0 @PBE \) self-energy displayed in Figure 3b is almost identical to evGW\(_0@PBE \). The shift of the pole structure compared to \( G_0 W_0 @PBE \) is with \( \Delta = -28.8 \) eV only slightly larger than for evGW\(_0\). The rigid \( \Delta \) shift of the pole features can be understood as follows: in evGW\(_0\) and \( G_{SH} W_0 \) the KS eigenvalue \( \epsilon_i^0 \) is replaced with \( \epsilon_i^0 + \Delta \epsilon_m \) and \( \epsilon_i^0 + \Delta H_{1o} \) respectively, where \( \Delta \epsilon_m \) is the self-consistent GW correction for state \( m \) and \( \Delta H_{1o} \) its non-self-consistent approximation for the \( 1s \) state (see eq 12). The poles are consequently located at \( \epsilon_i^0 + \Delta \epsilon_m - \Omega \) and \( \epsilon_i^0 + \Delta H_{1o} - \Omega \). Since both corrections, \( \Delta \epsilon_m \) and \( \Delta H_{1o} \), are negative for PBE starting points, the poles, that is, satellites, move to more negative frequencies and are properly separated from the main excitation. The spectral function now exhibits a distinct QP peak as evidenced by Figure 3d.
While the main effect of $\text{evGW}_0$ and $G_{\Delta H}W_0@PBE$ for deep core levels is the correction of the spurious transfer of spectral weight to the satellites, it affects also the location of the QP peak. This has been graphically demonstrated for molecular valence states in Figure 25 of ref 31: by shifting the pole structure to more negative frequencies, the slope of $\text{Re}\Sigma^i$ will be flatter in the region where the QP excitation is expected. As a consequence, the intersection with the straight line $\omega = \epsilon^i + v^i_s - \Sigma^i$ ( = QP solution) will be at more negative frequencies compared to $G_0W_0@PBE$.

As discussed in detail previously, the effect of eigenvalue self-consistency can be mimicked in a $G_0W_0$ calculation by using a hybrid functional with a high amount of exact exchange $\alpha$. We showed that increasing $\alpha$ progressively shifts the pole features to more negative frequencies. For $\alpha = 0.45$, the $\text{evGW}_0@PBE$ self-energy is approximately reproduced, and the spectral function shows a distinct peak as displayed in Figure 3d. We note here again that values of $\alpha < 0.3$ do not yield a clear main peak and thus no unique solution, which is also demonstrated in Figure 3a.

The $\text{evGW}$ approach and the $G_{\Delta H}W_{\alpha}@PBE$ schemes lead to a significantly stronger shift of the pole features than $\text{evGW}_0@PBE$ or $G_{\Delta H}W_0@PBE$, as shown in Figure 3c,e. The spectral functions displayed in Figure 3d,f confirm that $\text{evGW}$ and $G_{RI}W_{RI}$ yield a distinct peak in the spectrum. The RS eigenvalues of the occupied orbitals are more negative, and the ones of the virtual orbitals are more positive than the KS eigenvalues. In addition, RPA evaluated with RS fundamental gaps provides larger excitation energies $\Omega$. In $G_{RI}W_{RI}$, the poles at $\epsilon^i + \Omega$ are shifted in the positive direction and the poles at $\epsilon^i - \Omega$ are shifted in the negative direction. Therefore, satellites from these poles are separated from the main peak. For $G_{RI}W_{RI}$ a unique solution is obtained for all starting points. As shown in Figure S1 (see Supporting Information), the $G_{RI}W_{RI}$ approach suffers from a multi-solution behavior in the deep core region and cannot be applied for core-level calculations.

### 4.2. CORE65 Benchmark
In the following, we discuss the CORE65 results for the GW schemes for which a physical solution behavior was confirmed in Section 4.1, namely, $\text{evGW}_0@PBE$, $\text{evGW}@PBE$, $G_0W_0@PBE\alpha = 0.45$, $G_{\Delta H}W_0@PBE$, and $G_{RI}W_{RI}$ with four different starting points [PBE, PBE0, B3LYP, and PBE($\alpha = 0.45$)]. The distribution of the errors with respect to experiment is shown in Figures 4 and 5 for the absolute CLBEs and the relative CLBEs, respectively. The corresponding MAE and the mean errors (MEs) are given in Table 1. The error of excitation $i$ is defined as error = CLBE$^\text{theory} - \text{CLBE}^\text{experiment}$.

Starting the discussion with the absolute CLBEs, we find that $\text{evGW}_0@PBE$, $G_0W_0@PBE\alpha = 0.45$, and $G_{\Delta H}W_0@PBE$ yield the best results with error distributions close to zero and MAEs of $\approx 0.3$ eV. The smallest overall MAE of $0.25$ eV is obtained with $G_{\Delta H}W_0@PBE$. Figure 4a,d shows that the errors from $\text{evGW}_0@PBE$ and $G_{\Delta H}W_0@PBE$ are tightly distributed but mostly negative; that is, the computed CLBEs are slightly underestimated. Generally, we find that the $G_{\Delta H}W_0@PBE$ scheme reproduces the $\text{evGW}_0@PBE$ results almost perfectly. The slight underestimation of the absolute CLBEs by $\text{evGW}_0@PBE$ and $G_{\Delta H}W_0@PBE$ might be due to insufficiencies in the cc-pVnZ basis sets, which are not captured by the extrapolation procedure. A very recent study with $G_0W_0@PBE\alpha$ showed that increasing the number of core functions by, for example, uncontracting the cc-pVnZ basis sets yields larger absolute CLBEs. The reported increase is in the range of $0.25$ to maximal $0.5$ eV, indicating that the CLBEs from $\text{evGW}_0$ and $G_{\Delta H}W_0@PBE$ are more accurate than the CLBEs from $\text{evGW}_0@PBE$ and $G_{\Delta H}W_0@PBE$.
Table 1. MAE and ME in eV with Respect to Experiment for Absolute and Relative CLBEs of the CORE65 Benchmark Set

<table>
<thead>
<tr>
<th>Core level</th>
<th>evGW@PBE</th>
<th>G\text{RS}W\text{RS}@PBE</th>
<th>G\text{RS}W\text{RS}@PBE0</th>
<th>B3LYP</th>
<th>PBEh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MAE</td>
<td>ME</td>
<td>MAE</td>
<td>ME</td>
<td>ME</td>
</tr>
<tr>
<td>C 1s</td>
<td>0.30</td>
<td>−0.29</td>
<td>0.33</td>
<td>−0.08</td>
<td>1.53</td>
</tr>
<tr>
<td>N 1s</td>
<td>0.30</td>
<td>−0.27</td>
<td>0.24</td>
<td>0.19</td>
<td>1.37</td>
</tr>
<tr>
<td>O 1s</td>
<td>0.32</td>
<td>−0.28</td>
<td>0.48</td>
<td>−0.40</td>
<td>1.70</td>
</tr>
<tr>
<td>F 1s</td>
<td>0.44</td>
<td>−0.44</td>
<td>0.83</td>
<td>−0.83</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>absolute CLBEs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>0.25</td>
<td>−0.20</td>
<td>4.88</td>
<td>4.88</td>
<td>5.32</td>
</tr>
<tr>
<td>N 1s</td>
<td>0.20</td>
<td>−0.13</td>
<td>3.97</td>
<td>3.97</td>
<td>4.50</td>
</tr>
<tr>
<td>O 1s</td>
<td>0.35</td>
<td>−0.31</td>
<td>5.91</td>
<td>5.91</td>
<td>6.24</td>
</tr>
<tr>
<td>F 1s</td>
<td>0.54</td>
<td>−0.54</td>
<td>6.56</td>
<td>6.56</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative CLBEs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>0.19</td>
<td>−0.02</td>
<td>0.40</td>
<td>0.39</td>
<td>0.43</td>
</tr>
<tr>
<td>N 1s</td>
<td>0.20</td>
<td>−0.07</td>
<td>0.36</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>O 1s</td>
<td>0.20</td>
<td>−0.06</td>
<td>0.56</td>
<td>0.56</td>
<td>0.66</td>
</tr>
<tr>
<td>F 1s</td>
<td>0.16</td>
<td>−0.16</td>
<td>0.16</td>
<td>−0.10</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The error for excitation i is defined as \(\varepsilon_i = CLBE^{\text{theory}} − CLBE^{\text{exp}}\). The relative CLBEs are the shifts with respect to a reference molecule, \(\Delta CLBE = CLBE − CLBE^{\text{ref,mol}}\). CH\(_4\), NH\(_3\), H\(_2\)O, and CH\(_2\)F have been used as reference molecules for C 1s, N 1s, O 1s, and F 1s, respectively.
alternative strategy is to compensate the underscreening by including vertex corrections, for example, to use the T-matrix formalism,\textsuperscript{30,71,72} where the two-point screened interaction $W$ is replaced with a four-point effective interaction $T$. However, methods such as the T-matrix are computationally much more expensive than $GW$ due to their higher complexity. We recently applied the $G_{RS}T_{RS}$ scheme to the CORE65 benchmark set.\textsuperscript{71} Comparing $G_{RS}W_{RS}$ and $G_{RS}T_{RS}$, the overestimation is indeed reduced by $G_{RS}T_{RS}$ which yields an ME of $\approx 1.5$ eV. However, the errors for the absolute CLBEs are still an order of magnitude larger than for computationally cheaper schemes such as ev$\Delta H_0$ or $G_{RS}W_{RS}$ which rely on a very fortunate error cancellation effect that leads to a balanced screening.

Furthermore, we find that the overestimation with $G_{RS}W_{RS}$ increases with the atomic number, that is, from the C 1s to the F 1s excitations. This species dependence is inherited from the KS-DFT calculation. As shown in Table S8 in the Supporting Information, the deviations of the CLBEs obtained from KS-DFT calculation. As shown in Table S9 in the Supporting Information), which shows the MAEs of the relative CLBEs from the KS-DFT eigenvalues. For all four functionals (PBE, PBE0, B3LYP, and ev$\Delta H_0$), we obtained the largest MAE at the KS-DFT level for C 1s excitations, which originate from the underlying DFT calculation, as evident from Table S9 (see Supporting Information), which shows the MAEs of the relative CLBEs from the KS-DFT eigenvalues. For all four functionals (PBE, PBE0, B3LYP, and ev$\Delta H_0$), we obtained the largest MAE at the KS-DFT level for C 1s excitations, which originate from the underlying DFT calculation, as evident from Table S9 (see Supporting Information), which shows the MAEs of the relative CLBEs from the KS-DFT eigenvalues.

Moving now to the relative CLBEs, we observe that $G_{RS}W_{RS}$ and $G_{RS}W_{RS}$ yield MAEs of $\approx 0.2 \pm 0.3$ eV, and $G_{RS}W_{RS}$ MAEs of $0.4 \pm 0.5$ eV, see Table 1. The errors of the relative CLBEs are centered and tightly distributed around zero for ev$\Delta H_0$ and ev$\Delta H_0$, and $G_{RS}W_{RS}$, see Table S8 in the Supporting Information. The perturbative schemes $G_{RS}W_{RS}$ and $G_{RS}W_{RS}$ slightly overestimate the relative CLBEs. The latter is evident from the positive MEs and the error distributions in Figure 4b–e, which are still not centered at zero but exhibit a small offset toward positive values. The RS results show a larger spread compared to $G_{RS}W_{RS}$ and the partial self-consistent schemes. Furthermore, outliers with errors $> 1$ eV are observed for $G_{RS}W_{RS}$ and in particular for $G_{RS}W_{RS}$. The largest outliers are primarily O 1s excitations, which originate from the underlying DFT calculation, as evident from Table S9 (see Supporting Information), which shows the MAEs of the relative CLBEs from the KS-DFT eigenvalues.

The chemical shifts between CLBEs of the same atomic type can be smaller than 0.5 eV for second row elements\textsuperscript{5} and even as small as 0.1 eV for C 1s.\textsuperscript{101} Therefore, the errors for absolute CLBEs from ev$\Delta H_0$ and $G_{RS}W_{RS}$ are too large to align or resolve experimental XPS spectra, for which reference data are not available. The most promising methods are ev$\Delta H_0$ and $G_{RS}W_{RS}$ in particular for $G_{RS}W_{RS}$. With MAEs between 0.2 and 0.3 eV for absolute and relative CLBEs, the accuracy is well within the chemical resolution required to interpret most XPS data. The disadvantage of the $G_{RS}W_{RS}$ scheme is the need for tuning the $\alpha$ parameter. In addition, the species dependence of $\alpha_{opt}$ for C–F cannot be completely removed and is expected to increase for heavier elements. For example, we found $\alpha_{opt} = 0.61$ for sulfur 1s excitations.\textsuperscript{74} Conversely, the accuracy of ev$\Delta H_0$ and $G_{RS}W_{RS}$ is species independent. In addition, the already very good agreement of ev$\Delta H_0$ and $G_{RS}W_{RS}$ with experiment might further improve with core-rich basis sets, as already mentioned before.

### 4.3. ETFA Molecule

We further examine the performance of the eight GW approaches, which we applied to the CORE65 benchmark set in Section 4.2, for C 1s excitations of the ETFA molecule, which is also referred to as the "ESCA molecule" in the literature.\textsuperscript{102} The ETFA molecule was synthesized to demonstrate the potential of XPS for chemical analysis in the late 1960s. It contains four carbon atoms in various chemical environments, see the inset of Figure 6a. The ETFA molecule

**Figure 6.** Comparison of the C 1s XPS spectrum of ETFA (a) for absolute CLBEs and (b) relative CLBEs obtained from ev$\Delta H_0$, $G_{RS}W_{RS}$, and $G_{RS}W_{RS}$. Dashed lines indicate the experimental ref 102.
presents a challenge because of the extreme variations of the chemical shifts, which range up to 8.0 eV and decrease from the CF$_3$ to the CH$_3$ end. The four C 1s signals are separated by several electronvolts due to the widely different electron-affinities of the substituents on the carbon atoms. ETFA is thus an important reference system and was very recently used to benchmark the performance of different functionals in ΔSCF calculations and GW approaches.

In equilibrium, ETFA exists in two dominating conformations (anti-anti and anti-gauche); that is, each peak in the spectrum is a superposition of the signals from both conformers. However, including the different conformations is primarily important when resolving the vibrational profiles of the peaks, which is not the scope of our benchmarking effort. The experimental conformational shifts are <0.1 eV. To ensure direct comparability with the computational data from ref 18, we include thus only the anti-anti conformer.

The first high-quality experimental spectrum of the free ETFA molecule in gas phase was reported in 1973, while new results were published by Travnikova et al. in 2012. Both results were referenced in the most recent studies. The newer results have a higher resolution and are significantly closer to the new experimental peak positions are reported in Tables 2 and 3. For the absolute CLBEs, the ETFA predictions are in line with the CORE65 benchmark results. evGW$_0$@PBE and G$_{\text{b}}$W$_0$@PBE slightly underestimate the CLBEs, while evGW$_0$@PBE and the RS schemes severely overestimate them, see Figure 6. G$_{\text{b}}$W$_0$@PBE(α = 0.45) also overestimates the C 1s energies slightly. As discussed in Section 4.2, this is due to the fact that α$_{\text{opt}}$ is slightly smaller than 0.45 for C 1s excitation. C 1s excitations are consequently slightly overestimated in G$_{\text{b}}$W$_0$@PBE. Table 3 reports the relative C 1s CLBEs for the ETFA molecule.

Table 2. Absolute C 1s CLBEs for the ETFA Molecule

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>ME</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
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<td>299.45</td>
<td>296.01</td>
<td>293.07</td>
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<tr>
<td>experiment 102</td>
<td>298.93</td>
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<td>291.47</td>
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<tr>
<td>evGW$_0$@PBE</td>
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</tr>
<tr>
<td>G$_{\text{b}}$W$_0$@PBE</td>
<td>0.56</td>
<td>0.54</td>
<td>0.30</td>
<td>0.16</td>
<td>0.39</td>
<td>0.39</td>
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<tr>
<td>G$_{\text{b}}$W$_0$@PBE</td>
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<td>−0.10</td>
<td>−0.02</td>
<td>−0.27</td>
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<tr>
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<td>1.01</td>
<td>1.35</td>
<td>1.40</td>
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<tr>
<td>G$_{\text{b}}$W$_0$@PBE</td>
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<td>3.70</td>
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<td>G$_{\text{b}}$W$_0$@PBE0</td>
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<td>4.53</td>
<td>4.65</td>
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<tr>
<td>G$_{\text{b}}$W$_0$@B3LYP</td>
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<tr>
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<td>ΔSCAN$^8$</td>
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<td>0.17</td>
<td>0.00</td>
<td>0.11</td>
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<tr>
<td>ΔCCSD(T)$^8$</td>
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<td>−0.31</td>
<td>−0.23</td>
<td>−0.28</td>
<td>0.28</td>
</tr>
</tbody>
</table>

The deviation Δ$_{\text{exp}}$ with respect to experiment and the corresponding ME and MAE are computed with the experimental data by Travnikova et al. (in bold), where error$^i$ = CLBE$^i$exp − CLBE$^i$th. The labels of the C atoms are given in the inset of Figure 6a. For the @PBEh calculations, we use α = 0.45.

In calculating the CLBEs of the ETFA molecule in gas phase, we use the experimental peak positions reported in Tables 2 and 3. Both results were referenced in the most recent studies. The newer results have a higher resolution and are significantly closer to the new experimental results. C 1s excitations are consequently slightly overestimated in G$_{\text{b}}$W$_0$@PBE. Table 3 reports the relative C 1s CLBEs for the ETFA molecule.

Table 3. Relative C 1s CLBEs for the ETFA Molecule

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>ME</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment 103</td>
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<td>4.81</td>
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<tr>
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<td>0.00</td>
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<td>0.36</td>
</tr>
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<td>G$_{\text{b}}$W$_0$@PBE</td>
<td>0.40</td>
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<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>G$_{\text{b}}$W$_0$@PBE</td>
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<td>−0.07</td>
<td>0.00</td>
<td>−0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>evGW$_0$@PBE</td>
<td>−0.47</td>
<td>−0.39</td>
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<td>0.00</td>
<td>−0.30</td>
<td>0.30</td>
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<tr>
<td>G$_{\text{b}}$W$_0$@PBE</td>
<td>−0.58</td>
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<td>G$_{\text{b}}$W$_0$@B3LYP</td>
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<td>G$_{\text{b}}$W$_0$@PBEh</td>
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<td>evGW$_0$@PBE</td>
<td>−0.32</td>
<td>−0.09</td>
<td>0.05</td>
<td>0.00</td>
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<tr>
<td>ΔSCAN$^8$</td>
<td>−0.32</td>
<td>−0.25</td>
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<tr>
<td>ΔCCSD(T)$^8$</td>
<td>−0.12</td>
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<td>−0.08</td>
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<td>−0.07</td>
<td>0.07</td>
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</tbody>
</table>

The deviation Δ$_{\text{exp}}$ with respect to experiment and the corresponding ME and MAE are computed with the experimental data by Travnikova et al. (in bold), where Δ$_{\text{exp}}$ = CLBE$^i$exp − CLBE$^i$th. The relative energies δCLBE are computed with respect to C4. The labels of the C atoms are given in the inset of Figure 6a. For the @PBEh calculations, we use α = 0.45.

PBEh, G$_{\text{b}}$W$_0$@PBE provides the best accuracy followed by evGW$_0$@PBE with an MAE of 0.27 and 0.36 eV, respectively, which is consistent with the conclusion for the CORE65 set benchmark.

Turning to the relative CLBEs, the three partial self-consistent schemes and G$_{\text{b}}$W$_0$@PBE yield MAEs around 0.3 eV, which is only slightly worse than the CORE65 MAEs for C 1s. G$_{\text{b}}$W$_0$@PBE, evGW$_0$@PBE, and G$_{\text{b}}$W$_0$@PBE overestimate all shifts, while G$_{\text{b}}$W$_0$@PBEh overestimates the shifts of the more “descreened” C atoms (C1 and C2), see Figure 6b. G$_{\text{RS}}$W$_{\text{RS}}$ also provides good shifts for ETFA. The RS schemes with the conventional hybrid functionals PBE0 and B3LYP yield, with MAEs below 0.1 eV, the best overall result of the 8 investigated schemes. Furthermore, except for G$_{\text{RS}}$W$_{\text{RS}}$ with hybrid starting points, we find that our predictions are worse progressively with the electronegativity of the substituents at the C atoms. The relative CLBEs of C1 (CF$_3$) and C2 (carbonyl) seem to be the ones that are more
4.4. Comparison of the Computational Cost. Comparing the computational cost of the five GW flavors employed in this work (\(G_0W_0\), \(G_{\Delta H}W_0\), \(G_{\text{RS}}W_{\text{RS}}\), evGW\(_{\text{0}}\), and evGW\(_{\text{W}}\)), the \(G_0W_0\) scheme is the computationally least expensive one. For core-level calculations, highly accurate frequency techniques are required,\(^{22}\) such as the fully analytic evaluation of the self-energy via eq 6 or the contour deformation. This increases the computational cost compared to valence excitations, where schemes like the analytic continuation\(^{15}(\text{AC})\) can be used. In conventional implementations, the AC scheme scales \(O(N^4)\) with respect to system size \(N\) but fails to reproduce the self-energy structure for deep core states.\(^{22}\) The scaling of the fully analytic approach (eq 6) is \(O(N^6)\) with respect to system size \(N\). The complexity of the contour deformation technique increases for core levels from \(O(N^4)\) (valence states) to \(O(N^6)\). A detailed analysis of the scaling behavior of the contour deformation approach can be found in ref 22. For both techniques, fully analytic approach and contour deformation, the polarizability, which is the computational most expensive step in the GW calculation, is explicitly constructed in each iteration step of eq 1 (the QP equation). Typically, the QP equation converges within 10 steps; that is, the self-energy must be computed 10 times.

The computational cost of \(G_{\Delta H}W_0\) at PBE is only slightly larger than for \(G_0W_0\). The Hedin shift \(\Delta H\) (see eq 12) is computed from \(\Sigma_\alpha\left(e_\alpha^0\right)^2\) once before the iteration of eq 13. Given that the latter converges also in 10 steps, the self-energy needs to be calculated 11 instead of 10 times.

The \(G_{\text{RS}}W_{\text{RS}}\) requires the subspace diagonalization of the RS Hamiltonian (eqs 21 and 22), which scales only \(O(N^3)\), which is at least two orders of magnitudes lower than the frequency integration of the self-energy. In practice, the computational cost of a \(G_{\text{RS}}W_{\text{RS}}\) calculation is only marginally larger than for a \(G_0W_0\) calculation.

The most expensive approaches discussed here are evGW\(_{\text{W}}\) and evGW. In evGW\(_{\text{W}}\), the eigenvalues are iterated in \(G\) (outer loop), and in each step of the outer loop, we iterate the QP equation, that is, eq 1, not only for the core state of interest but for all states. Assuming again that the iteration converges within 10 steps, this implies that even for small molecules we evaluate the self-energy in the evGW\(_{\text{W}}\) procedure several hundred times. evGW is even more expensive because \(W\) is rebuilt in each step.

For core-level calculations, the eigenvalue self-consistent schemes are restricted to molecules with less than 20–25 atoms, while \(G_0W_0\) at PBEh, \(G_{\Delta H}W_0\), and \(G_{\text{RS}}W_{\text{RS}}\) are equally applicable to larger systems. In our previous work,\(^{24}\) we computed CLBEs of structures of up to 110–120 atoms at the \(G_0W_0\) at PBEh level.

The comparison of the computational cost between \(G_0W_0\) at PBEh and \(\Delta\text{SCF}\) depends on (i) the system size due to the different scalings of both methods and (ii) the choice of the functional for the \(\Delta\text{SCF}\) calculations. A comprehensive assessment of the computational cost was given in our previous work,\(^{24}\) where we compared \(G_0W_0\) at PBEh to \(\Delta\text{Kohn–Sham}\) (\(\Delta\text{KS}\)) calculations with the PBE functional. \((\Delta\text{KS})\) is the projector augmented wave variant of the all-electron \(\Delta\text{SCF}\) method. We found that \(G_0W_0\) at PBEh is already \(\approx 50\) times more expensive for smaller molecules of around 20 atoms, while for isolated structures of \(\approx 100\) atoms the factor increases to 20,000. When using hybrid functionals...
for the $\Delta$SCF calculation, the computational cost of $G_0 W_0 \rho$ @ PBEh is similar to $\Delta$SCF for small molecules since the evaluation of the exchange is the computational bottleneck in both cases. With increasing system size, the higher-scaling steps in $G_0 W_0$ start to dominate. For structures with $\approx 100$ atoms, we estimate that $G_0 W_0 \rho$ @ PBEh is $1\text{-}2$ orders of magnitude more expensive than hybrid-based $\Delta$SCF calculations.

5. CONCLUSIONS

We have presented a benchmark study of different GW approaches for the prediction of absolute and relative CLBEs. In addition to the ev$G_0 W_0 \rho$ @ PBE and ev$G_0 W_0 \rho$ @ PBEh ($\alpha = 0.45$) methods, which were already investigated in ref 49, we have included ev$G_0 W_0 @$ PBE and two new methods, namely, $G_{\Delta H} W_0$ and $G_{\Delta H} W_{0S}$, in our study. $G_{\Delta H} W_0$ is an adaption of the "Hedin shift" to core levels and can be considered as computationally less expensive approximation to ev$G_0 W_0$. In the $G_{\Delta H} W_{0S}$ approach, the RS Green’s function is used as a new starting point and, in contrast to our previous work, also used to compute the screened Coulomb interaction. The purpose of introducing the RS scheme is to reduce the dependence on the starting point, and the method has thus been tested with four different DFAs (PBE, PBE0, B3LYP, and PBEh ($\alpha = 0.45$)).

By investigating the self-energy matrix elements and spectral functions, we have confirmed that ev$G_0 W_0 @$ PBE, ev$G_0 W_0 @$ PBEh, $G_{\Delta H} W_0 @$ PBE, $G_{\Delta H} W_{0S} @$ PBE, $G_{\Delta H} W_{0S} @$ PBEh, and $G_{\Delta H} W_{0S} @$ PBEh yield a unique solution. $G_{\Delta H} W_0$ schemes starting from a GGA or hybrid DFT calculation with a low amount of exact exchange do not yield a distinct QP solution. A meaningful physical solution can thus not be obtained with standard approaches such as $G_0 W_0 @$ PBE, $G_0 W_0 @$ PBEh, and $G_{\Delta H} W_0 @$ B3LYP for CLBEs.

We have studied the CORE65 benchmark set and the C 1s excitations of the ETFA molecule with all 8 approaches, for which a physically reasonable solution behavior was confirmed. For the CORE65 set, ev$G_0 W_0 @$ PBE, $G_{\Delta H} W_0 @$ PBEh, and $G_{\Delta H} W_0 @$ PBEh yield with MAEs of 0.30, 0.33, and 0.25 eV, respectively, the best results. ev$G_0 W_0$ and $G_{\Delta H} W_{0S}$ overestimate the absolute CLBEs by several electronvolts and are thus not suitable for the prediction of the absolute BEs. Nevertheless, the RS approaches significantly reduce the starting point dependence as intended. The relative CLBEs are reasonably reproduced with all methods, but in particular with the eigenvalue self-consistent schemes and $G_{\Delta H} W_0 @$ PBE (MAEs < 0.2 eV). The methods exhibit a similar performance for the ETFA molecule, except that the RS approaches with standard hybrid functionals yield here the best chemical shifts.

The $G_0 W_0 @$ PBEh ($\alpha$) approach was introduced in our previous work and computationally affordable alternative to ev$G_0 W_0$ that can mimic to some extent the effect of eigenvalue self-consistency in $G$. However, the $\alpha$-tuning is methodologically unsatisfying since the optimal $\alpha$ increases with the atomic number and an individual tuning for each element is in principle required and in fact mandatory for heavier elements. We therefore recommend to use the $G_{\Delta H} W_0 @$ PBE approach instead, which is in terms of computational cost comparable to $G_0 W_0$.

Finally, we found that ev$G_0 W_0 @$ PBE and $G_{\Delta H} W_0 @$ PBE systematically underestimate the experiment. Our comparison to the ETFA literature results and very recent work suggest that this slight but systematic underestimation can be cured by very large, core-rich basis sets, which might improve the agreement with experiment even further. Future work will consider this and focus on the development of compact and computationally efficient NAO basis sets for core-level GW calculations.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.2c00617.

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(85) See http://www.qm4d.info for an in-house program for QM/MM simulations (last accessed: June 1, 2022).


