Self-consistent $GW$: an all-electron implementation with localized basis functions

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This paper describes an all-electron implementation of the self-consistent $GW$ (sc-$GW$) approach – i.e. based on the solution of the Dyson equation – in an all-electron numeric atom-centered orbital (NAO) basis set. We cast Hedin’s equations into a matrix form that is suitable for numerical calculations by means of i) the resolution of identity technique to handle 4-center integrals; and ii) a basis representation for the imaginary-frequency dependence of dynamical operators. In contrast to perturbative $G_0W_0$, sc-$GW$ provides a consistent framework for ground- and excited-state properties and facilitates an unbiased assessment of the $GW$ approximation. For excited-states, we benchmark sc-$GW$ for five molecules relevant for organic photovoltaic applications: thiophene, benzothiazole, 1,2,5-thiadiazole, naphthalene, and tetrathiafulvalene. At self-consistency, the quasi-particle energies are found to be in good agreement with experiment and, on average, more accurate than $G_0W_0$ based on Hartree-Fock (HF) or density-functional theory with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Based on the Galitskii-Migdal total energy, structural properties are investigated for a set of diatomic molecules. For binding energies, bond lengths, and vibrational frequencies sc-$GW$ and $G_0W_0$ achieve a comparable performance, which is, however, not as good as that of exact-exchange plus correlation in the random-phase approximation (EX+crPA) and its advancement to renormalized second-order perturbation theory (rPT2). Finally, the improved description of dipole moments for a small set of diatomic molecules demonstrates the quality of the sc-$GW$ ground state density.

Many-body perturbation theory (MBPT) in the $GW$ approach for the electron self-energy provides a natural framework for an $ab$ $initio$, parameter-free description of photo-ionization processes and charged excitations. In recent years, the $GW$ approach has become a popular method for the computation of band gaps and charged excitations for extended and finite systems. In numerical implementations, following Hybertsen and Louie it is standard practice to treat the $GW$ self-energy as a single-shot perturbation ($G_0W_0$) acting on a Kohn-Sham (KS) or Hartree-Fock (HF) reference system. Thus, excitation energies are evaluated from first-order Feynman-Dyson perturbation theory as corrections to a set of single-particle eigenvalues.

The popularity of the $G_0W_0$ approximation stems from the substantial reduction in the complexity of Hedin’s equations at first-order perturbation theory: the KS or HF eigenstates from a self-consistent field calculation can be used as basis functions and provide a convenient representation in which the non-interacting Green function is diagonal. In this basis, only diagonal matrix elements of the self-energy $\Sigma$ are needed to evaluate quasi-particle corrections at first-order. Thus, $G_0W_0$ grants a considerable simplification of the linear algebra operations which is decisive for applying the theory to large molecules and solids.

Although numerically more efficient than a non-perturbative approach, $G_0W_0$ suffers from several undesirable shortcomings such as the dependence on the starting point, the violation of conservation laws for momentum, total energy and particle number and – most importantly – the limited access to ground-state properties, which are kept unchanged from the preliminary density functional theory (DFT) or HF calculations.

It is known that the self-consistent $GW$ approach (sc-$GW$) – in which both the Green function $G$ and the screened Coulomb interaction $W$ are iterated to self-consistency – ameliorates most of the pathologies of perturbative $G_0W_0$. A particularly appealing feature of the sc-$GW$ method consists in the possibility of treating ground- and excited-states at the same level of theory. This property arises by virtue of the non-perturbative nature of the sc-$GW$ approach, whereby the Green function is updated and encompasses many-body effects introduced by the self-energy. In contrast, in perturbative theories (which generally do not introduce updates in the Green function) the electronic structure coincides with that of the corresponding starting point. Therefore, density and total energy – and derived quantities such as dipole moments, bond lengths, and binding energies – become accessible at self-consistency and reveal the quality of the $GW$ ground-state. Finally, at self-consistency excited- and ground-state properties are independent of the starting point, at least for closed shell systems and provide an unbiased assessment of the $GW$ approach.

A previous study on the homogeneous electron gas (HEG) reported a deterioration of the sc-$GW$ spectral properties, as compared to $G_0W_0$. This has been attributed to a poor description of the satellite peaks
at self-consistency. For extended systems, the performance of sc-GW remains controversial due to the scarce number of calculations for real solids. Part of this controversy can be traced back to basis set problems in early all-electron calculations and to the large influence that pseudo-potentials may have on GW band gaps. More recently, sc-GW calculations for atoms and molecules have shown improvements in the description of the first ionization energies and for transport properties of finite systems.

The price to pay in sc-GW is the demanding iterative procedure. The higher complexity of sc-GW arises for the following reasons. i) The Green function obtained from the solution of the Dyson equation is in general non-diagonal. This considerably increases the computational cost of the evaluation of the dielectric matrix. ii) The non-diagonal matrix elements of $\Sigma$ are needed to solve the Dyson equation. iii) Fourier transforms of dynamical quantities are needed that introduce their own computational difficulties.

In the first part of this paper, we present an all-electron implementation of the sc-GW method in the localized basis-set code FHI-aims and propose a recipe to efficiently address points i)-iii). An optimized set of localized basis functions was used to represent the Green function and the self-energy operator. Non-local two-particle operators, such as the screened Coulomb interaction, were computed by means of the resolution of the identity technique (also known as density fitting method) in a general framework previously introduced by some of us. Finally, an auxiliary basis of Lorentzian functions was introduced for an efficient analytical evaluation of Fourier transforms between imaginary time and frequency.

The second part of the paper, focuses on the assessment of ground- and excited-state properties as obtained from sc-GW for molecules. The quality of the sc-GW ground state was investigated by computing binding energies, bond lengths, vibrational frequencies, densities, and dipole moments for a small set of hetero- and homoatomic dimers. The full valence excitation spectra were evaluated for a set of molecules relevant for organic photovoltaic applications (thiophene, benzoithiazole, 1,2,5-thiadiazole, naphthalene, and tetrathiafulvalene). From this study we conclude that sc-GW systematically improves the spectral properties of finite systems over the entire excitation spectrum (that is, not only for the first ionization energy) as compared to standard perturbative $G_0W_0$ calculations based on semi-local DFT and HF. Nonetheless, for certain starting points exemplified by the PBE0 hybrid functional – $G_0W_0$ slightly outperforms sc-GW, providing ionization energies in better agreement with experimental reference data, as also previously demonstrated for benzene and the azabenzenes in Ref. 12. For structural properties the sc-GW method yields a less satisfactory agreement with experiment. For dimers, bond lengths and binding energies are slightly underestimated, and in this case there is no substantial improvement over perturbative approaches such as $G_0W_0$ or the random-phase approximation (RPA). Finally, self-consistency gives an accurate description of the electron density as manifested by the accurate dipole moments of diatomic molecules. These results suggest that sc-GW is a promising method for charge transfer compounds and interfaces. However, our study also indicates the importance of including higher order exchange and correlation diagrams beyond GW to accurately describe the structural properties of molecules.

The paper is organized as follows: Section II gives a brief introduction to the GW approximation recalling the basic equations needed for the computation of the Green function $G$ and the self-energy $\Sigma$. An optimal representation of Hedin’s equations in terms of localized basis functions and of the resolution of the identity is presented in Sec. III. In Sec. IV we present the scheme employed in the computation of the Fourier integrals of the Green function and other dynamical quantities. We report in Sec. V an assessment of sc-GW for the excitation spectra of molecules and, in Sec. VI, for the ground-state properties of diatomic molecules. Our conclusions and final remarks are reported in Sec. VII.

## I. THEORETICAL FRAMEWORK

In MBPT the complexity of the many-body problem is recast into the calculation of the single-particle Green function. Knowledge of the Green function grants immediate access to the (charged) single-particle excitation energies of the system, to the total energy and, more generally, expectation values of any single-particle operator. Green function theory is well documented in the literature and we recall here only the basic equations relevant for the GW approach, adhering to Hartree atomic units $\hbar = m_e = e^2 = 1$.

For a system of non-interacting electrons described through a time-independent Hamiltonian, the Green function can be written explicitly in terms of the single-particle eigenstates $\psi^\sigma_n(r)$ and eigenvalues $\epsilon^\sigma_n$:

\[
G_0^\sigma(r, r', \omega) = \sum_n \frac{\psi^\sigma_n(r)\psi^{\ast\sigma_n}(r')}{\omega - (\epsilon^\sigma_n - \mu) - i\eta \text{sgn}(\mu - \epsilon^\sigma_n)},
\]  

(1)

where $n$ and $\sigma$ refer to orbital and spin quantum numbers, respectively. $\mu$ is the electron chemical potential, and $\eta$ a positive infinitesimal. In practice, $\psi^\sigma_n(r)$ and $\epsilon^\sigma_n$ are generally obtained from the self-consistent solution of the Hartree-Fock or (generalized) KS equations.

For interacting electrons, the Green function has to be evaluated by solving the Dyson equation:

\[
G^\sigma(r, r', \omega) = G_0^\sigma(r, r', \omega) + \int dr_1 dr_2 G_0^\sigma(r, r_1, \omega) \times \\
\times [\Sigma^\sigma(r_1, r_2, \omega) + \Delta \psi^\sigma_{\text{xc}}(r_1) \delta(r_1 - r_2) - \\
- \psi^\sigma_{\text{xc}}(r_1, r_2)] G^\sigma(r_2, r', \omega),
\]  

(2)
Here $\Delta v_n^0$ is the change in the Hartree potential accounting for density differences between $G_n^0$ and $G^0$, and $v_n^{xc}$ is the exchange-correlation part of the single-particle Hamiltonian corresponding to the non-interacting Green function $G_0$. For example, if $G_0$ is the Hartree-Fock Green function, then $v_n^{xc}$ corresponds to the non-local exchange operator $\Sigma_x$. Alternatively, for a KS Green function, $v_n^{xc}$ is the local exchange-correlation potential. The electron self-energy $\Sigma^\sigma$ encompasses all many-body exchange-correlation effects and therefore its practical evaluation requires approximations. Following Hedin,\textsuperscript{26} the self-energy can be expanded in a perturbative series of the screened Coulomb interaction $W$, with the first-order term given by the $GW$ approximation:

$$\Sigma^\sigma(r, r', \tau) = iG^\sigma(r, r', \tau)W(r, r', \tau) \quad (3)$$

By virtue of the time translation invariance it suffices to express $\Sigma$ in terms of time differences ($\tau = t - t'$). The screened interaction $W(r, r', \omega)$ is in turn defined through another Dyson equation:

$$W(r, r', \omega) = v(r, r') + \int dr_1dr_2v(r, r_1)\chi(r_1, r_2, \omega)W(r_2, r', \omega) \quad (4)$$

Here, $v$ is the bare Coulomb interaction $1/|r - r'|$ and $\chi$ the irreducible polarizability, which in $GW$ is approximated by the product of two Green functions:

$$\chi(r, r', \tau) = -i\sum_\sigma G^\sigma(r, r', \tau)G^\sigma(r', r, -\tau) \quad (5)$$

The self-consistent nature of Eqs. 2,5\textsuperscript{15} arises from the interdependence of the self-energy and the Green function. In the $G_0W_0$ approach, the self-energy is evaluated non-self-consistently, and the Dyson equation is solved approximately in a perturbative fashion. The quasi-particle excitation energies are then obtained from the quasi-particle equation:

$$\epsilon_{n,\sigma}^{QP} = \epsilon_n + \text{Re}\langle \psi_n^\sigma|\Sigma^\sigma(\epsilon_{n,\sigma}^{QP}) - v_{xc}^\sigma|\psi_n^\sigma\rangle \quad (6)$$

In this work, Eqs. 2,6\textsuperscript{14} are solved fully self-consistently. In practice, an iterative procedure requires the following steps:

1. Construction of an initial non-interacting Green function $G_0$ from a preliminary SCF calculation through Eq. 4.
2. Evaluation of the polarizability $\chi$ from Eq. 5 and Fourier transformation of $\chi$ to the frequency domain.
3. Calculation of the screened Coulomb interaction $W$ from Eq. 4 and Fourier transformation of $W$ to the time domain.
4. Evaluation of the self-energy $\Sigma$ from the Eq. 3 and Fourier transformation of $\Sigma$ to the frequency domain.

5. Update of the Green function from the Dyson equation (Eq. 2) and Fourier transformation of $G$ to the time domain.
6. Mixing of the Green function to accelerate the convergence of the self-consistent loop.
7. Iteration of steps 2.-5. until a convergence criterion is satisfied.

In a numerical implementation, a choice for the basis set expansion of the quantities in Eqs. 2,5\textsuperscript{14} has to be made. Our choice will be discussed in the next Section.

II. SELF-CONSISTENT GW WITHIN A LOCALIZED BASIS

Previous implementations of sc-GW were based on Gaussians or Slater orbitals,\textsuperscript{18,25} full potential linear augmented plane-waves,\textsuperscript{20,21} real-space grids,\textsuperscript{22} and numeric atom-centered orbitals (NAO)\textsuperscript{9}. In the present work, the Green function $G$, the self-energy $\Sigma$, and all single-particle operators, are expanded in a numeric atom-centered orbital basis \{\varphi_i(r)\}, with basis functions of the form:

$$\varphi_i(r) = \frac{u_i(r)}{r}Y_{lm}(\Omega) \quad (7)$$

where $u_i(r)$ are numerically tabulated radial functions and $Y_{lm}(\Omega)$ spherical harmonics. For numerical convenience, we work with real-valued basis functions by requiring – without loss of generality – that $Y_{lm}(\Omega)$ denotes the real part (for $m = 0, \ldots, l$) and the imaginary part (for $m = -l, \ldots, -1$) of complex spherical harmonics. In FHI-aims the choice of the radial functions $u_i(r)$ is not limited. In this work we will show results for numerically tabulated Gaussian orbital basis sets and the Tier hierarchy of FHI-aims for NAOs.\textsuperscript{27} We refer to Ref.\textsuperscript{27} for details on the construction and optimization as well as the properties of the NAO basis sets in FHI-aims.

In terms of the $\varphi_i$ basis functions, the Green function can be expanded as:

$$G^\sigma(r, r', i\omega) = \sum_{ijlm} N_{basis} \varphi_i(r) s_{ij}^{-1} G_{ij}^\sigma(i\omega) s_{im}^{-1} \varphi_m(r') \quad (8)$$

where $s_{ij} = \int dr_1 \varphi_i(r) \varphi_j(r)$ is the overlap matrix taking into account the non-orthonormality of the basis set and $N_{basis}$ is the total number of basis functions. In the following, sums over latin indexes $i, j, l, m$ are implicitly assumed to run from $1$ to $N_{basis}$, whereas sums over $n$ run over the total number of states. The coefficients $G_{ij}^\sigma(i\omega)$ of the expansion are given by:

$$G_{ij}^\sigma(i\omega) = \int dr dr' \varphi_i(r) G^\sigma(r, r', i\omega) \varphi_j(r') \quad (9)$$
The representation in Eq. [9] can be easily applied to the non-interacting Green function in Eq. [1] yielding
\[ G^\sigma_{0,ij}(i\omega) = \sum_n \sum_{lm} s_{il} c_{ln}^\sigma c_{jm}^\sigma s_{mj}, \]
where we introduced the expansion of the HF/KS orbitals in the NAO basis \( \psi_\sigma^n(r) = \sum_i c_i^n \varphi_i(r) \) and the Green function was continued to the imaginary frequency axis. The matrix representation in Eq. [9] is also adopted for the Hartree potential \( v^H_\sigma \), the self-energy \( \Sigma^\sigma \), and the exchange-correlation potential \( v^xc \). We emphasize that in our implementation the summation over empty states – which is at the origin of the basis-set convergence problem of GW calculations – enters only through Eq. [10].

The expansion coefficients, as:
\[ (ij|kl) = \int \frac{\varphi_i(r)\varphi_j(r)\varphi_k(r')\varphi_l(r')}{|r-r'|} dr dr' . \]

The computation of the Coulomb repulsion integrals in Eq. [11] is a problem extensively discussed in the literature and efficient techniques have been developed over the years to make this calculation affordable. Numerically, the difficulty arises from the large number of NAO pairs and from the memory requirements of storing the 4-index matrix \( (ij|kl) \). In the NAO framework, the integrals in Eq. [11] are often evaluated by introducing an auxiliary basis set \( \{ P_\mu(r) \} \), with basis functions \( P_\mu(r) \) defined to span the Hilbert space of NAO pairs
\[ \varphi_i(r)\varphi_j(r) \simeq \sum_{\mu=1} C_{ij}^\mu P_\mu(r) \],
where \( C_{ij}^\mu \) are the coefficients of the expansion. Due to the high linear dependence of the NAO products, the number of product basis functions \( N_{aux} \) is much smaller than the number of NAO pairs \( O(N^2) \), making the numerical evaluation of Eq. [11] affordable. This technique, known as the resolution of the identity (RI) – or also density-fitting technique – was implemented in the FHI-aims code and we refer to Ref. [31] for a detailed account of the variational approach employed in the determination of the RI coefficients \( C_{ij}^\mu \) and for a review of the overall accuracy of the RI approach for correlated calculations.

In short, we used the “RI-V” variant of the RI scheme, in which the expansion coefficients are given by:
\[ C_{ij}^\mu = \sum_{\nu} (ij|\nu) V_{\nu\mu}^{-1} . \]

where \( (ij|\nu) \equiv \int dr \varphi_i(r)\varphi_j(r)P_\nu(r')/|r-r'| \) and \( V_{\nu\mu} \) denotes matrix elements of the Coulomb matrix in the auxiliary basis, i.e., \( V_{\nu\mu} = \int dr dr' P_\nu(r)P_\mu(r')/|r-r'| \). For numerical efficiency, it is convenient to work with the generalized coefficients:
\[ M_{ij}^\mu = \sum_{\nu} C_{ij}^\nu V_{\nu\mu}^{1/2} . \]

Following Ref. [31], one can write the RI version of the Dyson equation for the screened Coulomb interaction (Eq. [9]) as:
\[ \bar{W}_{\mu\nu}(i\omega) \equiv [v^{-1} W(i\omega)]_{\mu\nu} = [1 - \Pi(i\omega)]_{\mu\nu}^{-1} , \]
where we defined \([\Pi(i\omega)]_{\mu\nu} \equiv [\chi(i\omega)v]_{\mu\nu} \). In contrast to the RI-based implementation of the \( G_0W_0 \) method, the operator \( \Pi \) has to be expressed as an explicit functional of \( G \). Moreover, all non-diagonal matrix elements in the Green function have to be included. These two criteria are satisfied by evaluating \( \Pi \) in terms of the \( M_{ij}^\mu \) coefficients, as:
\[ [\Pi(i\tau)]_{\mu\nu} = -i \sum_{ijlm} M_{ij}^\mu M_{jm}^\nu \sigma G_{ij}(i\tau)G_{lm}^\sigma(-i\tau) . \]

Here we defined
\[ \sigma_{ij}(i\tau) \equiv \sum_{lm} s_{il}^{-1} G_{lm}(i\tau)s_{mj}^{-1} . \]

The quadruple sum in Eq. [16] may be reduced to double sums – with a considerable reduction of computational cost – by introducing the intermediate quantity \( A_{ij,\sigma}^\mu(i\tau) \equiv \sum_{lm} M_{ij}^\mu \sigma G_{lm}(i\tau) \bar{W}_{\mu\nu}(i\tau) \). In terms of these coefficients Eq. [16] becomes:
\[ [\Pi(i\tau)]_{\mu\nu} = -i \sum_{ij} A_{ij,\sigma}^\mu(i\tau)A_{ji,\sigma}^\mu(-i\tau) . \]

The self-energy can be evaluated in terms of Eq. [15] providing the following matrix representation of Eq. [9]
\[ \Sigma^\sigma_{ij}(i\tau) = \frac{i}{2\pi} \sum_{lm} \sum_{\mu\nu} M_{ij}^\mu M_{jm}^\nu \sigma G_{lm}(i\tau)\bar{W}_{\mu\nu}(i\tau) \].

By introducing the auxiliary quantity \( B_{jm,\sigma}^\mu(i\tau) = \sum_{lm} M_{jm}^\nu \bar{W}_{\mu\nu}(i\tau) \), the self-energy can again be cast into a double-sum form:
\[ \Sigma^\sigma_{ij}(i\tau) = \frac{i}{2\pi} \sum_{lm} \sum_{\mu} A_{im,\sigma}^\mu(i\tau)B_{jm,\sigma}^\mu(i\tau) \]

The correlation (exchange) contribution to the self-energy can be derived straightforwardly from Eq. [19] by substituting \( \bar{W} \) with \( \bar{W}_{\mu\nu} \equiv \bar{W}_{\mu\nu} - \delta_{\mu\nu} (\bar{W}_{\mu\nu} \equiv \delta_{\mu\nu}) \). The Hartree potential \( v^H_\sigma \) is also evaluated as an explicit functional of \( G \) as:
\[ v^H_{\mu,ij} = \sum_{lm} \sum_{\mu} M_{ij}^\mu M_{lm}^\nu \sigma G_{lm}(i\tau = 0^-) . \]
Finally, the matrix representation of the Dyson equation for the Green function completes the set of Hedin’s equations:

$$\overline{G}^\sigma_{ij}(i\omega) = \left[\overline{G}^\sigma_{ij}(i\omega)^{-1} - \Sigma^\sigma_{ij}(i\omega) + v^\sigma_{xc} - \Delta v^\sigma_{ij}\right]^{-1} \quad (22)$$

Here $\Delta v^\sigma_{ij}$ is the difference between the Hartree potential of the interacting and the non-interacting Green function.

To facilitate the convergence of the sc-GW loop, the input Green function $\overline{G}^{\text{input}}_{ij}$ of the $(N+1)$-th iteration is obtained from a linear mixing scheme:

$$\overline{G}^{\text{input}}_{ij}(i\tau) = \alpha \overline{G}^N_{ij}(i\tau) + (1-\alpha)\overline{G}^{N-1}_{ij}(i\tau) \quad (23)$$

where $\overline{G}^N$ denotes the Green function obtained from the $N$-th solution of the Dyson equation, and $\alpha$ is the mixing parameter. As illustrated in panel (b) of Fig. 1, we find that $\alpha = 0.2$ is typically a good choice. The convergence of the self-consistent loop is monitored looking at the average deviation of the Green function at each iteration $\Delta$, defined as:

$$\Delta = \frac{1}{N_{\text{basis}}^2} \sum_{i,j} |\overline{G}^N_{ij}(i\tau = 0^-) - \overline{G}^{N-1}_{ij}(i\tau = 0^-)|$$

$$\Delta_{\text{th}}$$

The sc-GW loop is considered converged when $\Delta$ drops below a chosen threshold $\Delta_{\text{th}}$. Default settings used in most calculations are $\Delta_{\text{th}} = 10^{-5}$, which suffices to converge both total and quasi-particle energies. The convergence of sc-GW is illustrated in Fig. 1, where $\Delta$ is reported as a function of the number of iterations for $\text{H}_2$, $\text{H}_2\text{O}$ and $\text{C}_6\text{H}_6$.

Equations 15-22 constitute a matrix representation of Hedin’s equations in the $\text{GW}$ approach (Eqs. 4-5). We emphasize again that in Eqs. 15-22, i) all electrons are treated on the same quantum mechanical level, i.e. fully self-consistently; ii) no model screening was used in the calculation of $W$; iii) all non-diagonal matrix elements of $G$ and $\Sigma$ are correctly accounted for.

The evaluation of Eqs. 10 and 11 is the most computationally demanding operation of our implementation. The scaling of the computational time as a function of the basis set size equals that of $G_0W_0$ calculations but with a larger prefactor. To illustrate this aspect, we report in Fig. 2 the total computational time spent for a single iteration of Eqs. 15-22 as function of the length of a linear hydrogen chain in a minimal basis set (i.e., with one NAO per atom). As compared to conventional $G_0W_0$ implementations, the additional computational cost arises from the necessity of accounting for non-diagonal matrix elements in the calculation of $G$ and $\Sigma$.

The only approximation introduced up to this point is the resolution of the identity for the expansion of the product of NAO pairs (Eq. 12). As discussed in Ref. 31, the accuracy of the RI can be monitored systematically by means of two control parameters: $\varepsilon_{\text{orth}}$ and $\varepsilon_{\text{SVD}}$. $\varepsilon_{\text{orth}}$ sets the accuracy threshold for the Gram-Schmidt orthonormalization employed for the reduction of the linear dependence of on-site (i.e. on the same atom) product basis functions $P_\mu$. In practice, by choosing smaller values of $\varepsilon_{\text{orth}}$ one may increase the number of product basis functions used in the expansion in Eq. 12. Similarly, the parameter $\varepsilon_{\text{SVD}}$ controls the singular value decomposition (SVD) for the orthonormalization of product basis functions on different atoms. A more detailed description of the effects of these parameters can be found in Ref. 31. To show the effect of the RI scheme on the self-consistent Green function, we report in Fig. 3 the sc-GW total energy – evaluated from Eq. 31, introduced in Sec. 5 – of the water molecule as a function of $\varepsilon_{\text{orth}}$ (left panel), and $\varepsilon_{\text{SVD}}$ (right panel). For a wide range of values of the control parameters $\varepsilon_{\text{orth}}$ and $\varepsilon_{\text{SVD}}$, the changes of the total energy are of the order of $10^{-4}$ eV or less. In all following calculations we therefore used $\varepsilon_{\text{orth}} = 10^{-5}$ and $\varepsilon_{\text{SVD}} = 10^{-4}$. 

### Figures

**FIG. 1. (Color online) Panel (a): values of $\Delta$ – defined in Eq. 24 – as a function of the number of iterations of the sc-GW loop for $\text{H}_2$, $\text{H}_2\text{O}$ and $\text{C}_6\text{H}_6$ in their equilibrium geometry in a Tier 2 basis set. A linear mixing parameter $\alpha = 0.2$ was used for all molecules. $\Delta_{\text{th}}$ indicates the default value of the convergence threshold. Panel (b): values of $\Delta$ for $\text{H}_2\text{O}$ as a function of the number of iterations for different values of $\alpha$.**

**FIG. 2. (Color online) Total time (in seconds, on a single CPU) per iteration of the sc-GW loop, for linear hydrogen chains of different lengths. The total time required for the evaluation of the self-energy in $G_0W_0$ is included for comparison.**
III. DISCRETIZATION OF THE FOURIER INTEGRALS

In this implementation, we solve Eqs. 19-22 in imaginary time and frequency, taking advantage of the reduced number of frequency points required to describe $G^\sigma(i\omega)$ and other dynamical quantities, as compared to real frequency implementations. In a mixed time-frequency formalism convolutions on the frequency axis can be expressed, by virtue of the convolution theorem, as products on the time axis after a Fourier transform. Due to the slow decay of $G^\sigma(i\omega)$ at large frequencies, the computation of Fourier transforms may require extended and dense frequency grids. We obviate this problem by introducing a basis for the frequency/time dependence of all dynamical quantities. This permits an analytic evaluation of the Fourier integrals – as one can choose basis functions with a Fourier transform known analytically – and substantially reduces the number of frequency points needed to converge the calculation.

Following the approach introduced in Ref. 45, we expand the Green function in a set of Lorentzian functions of the form $f_n(i\omega) = 1/(b_n + i\omega)$, with Fourier transform $f(\tau) = 1/(2\pi)e^{-b_n\tau}$. The parameters $b_n$ are fixed at the beginning of the calculation and are distributed logarithmically in the energy range covered by the Kohn-Sham or Hartree-Fock eigenvalues $\epsilon_n$. Although in principle other functions could be used, the functions $f_n(i\omega)$ constitute a natural choice for the expansion of the Green function, as the frequency dependence of $f_n(i\omega)$ closely resembles the analytic structure of $G$ and captures the $1/i\omega$ behaviour at large frequency. This is illustrated in Fig. 4 where the real and imaginary parts of $f_n(i\omega)$ – with different values of $b_n$ – are compared to a Green function matrix element for the Ne atom. The Green function can be expanded in the basis of Lorentzian functions as:

$$G_{ij}^\sigma(i\omega) = \sum_{n=1}^{N_{\text{poles}}} [\alpha_{ij} f_{n}^{\text{Re}}(i\omega) + \beta_{ij} f_{n}^{\text{Im}}(i\omega)],$$

where $N_{\text{poles}}$ denotes the number of functions $f_n$, and $f_{n}^{\text{Re}}(i\omega)$ and $f_{n}^{\text{Im}}(i\omega)$ the real (imaginary) part of $f_n(i\omega)$. The real and imaginary part of the Green function have been treated separately to maintain a real-valued linear-least square problem, leading in turn to real-valued coefficients $\alpha_n$ and $\beta_n$. Since the Fourier transform of the $f_n(i\omega)$ is known, the coefficients $\alpha_n$ and $\beta_n$ also determine the expansion of the Green function in imaginary time. Expansions similar to Eq. 25 were employed also for the Fourier transform of $\chi$, $W$ and $\Sigma$.

The imaginary time and frequency axes are then discretized on exponentially spaced grids composed of $N_\omega$ points in the range $\{0, \omega_{\text{max}}\}$, and by $2N_\tau + 1$ points in the range $\{-\tau_{\text{max}}, \tau_{\text{max}}\}$. The grid points $\omega_n$ and integration weights $w(\omega_n)$ are defined as:

$$\omega_k = \omega_0 \left[ e^{(k-1)h} - 1 \right], \quad w(\omega_k) = h \omega_0 e^{(k-1)h}$$

and similarly for $\tau_k$ and $w(\tau_k)$. The constant $h$ is obtained by imposing the maximum frequency $\omega_{\text{max}}$ from
the constraint $\omega_{\text{max}} = \omega_0 \left[ e^{\eta \tau} - 1 \right]$ and the parameter $\omega_0$ sets the initial spacing of the grid. Typical values adopted in our calculations are $\omega_{\text{max}} = 5000 \text{ Ha}$, $\tau_{\text{max}} = 1000 \text{ Ha}^{-1}$ and $\omega_0 = \tau_0 = 0.001$.

The error introduced by the Fourier transform can be quantified for functions known analytically on both the (imaginary) frequency and time axes such as, for instance, the non-interacting Green function given in Eq. (1). In Fig. 5 we report the mean absolute error (MAE) in the Fourier transform of the non-interacting Green function $G_0^r(i\omega)$ of the nitrogen dimer $\text{N}_2$, averaged over all matrix elements. The MAE drops exponentially when increasing the number of functions $f_n$, and few tens of frequency points suffice to converge the Fourier integrals with an accuracy of the order of $10^{-8}$. In our calculations we used $N_\omega = N_\tau = 60$ as default parameters.

IV. SPECTRAL PROPERTIES OF MOLECULES

We turn now to the spectral properties in sc-GW. At self-consistency, the excitation spectrum is given by the spectral function:

$$A(\omega) = -1/\pi \int d\mathbf{r} \lim_{\mathbf{r} \to \mathbf{r}'} \text{Im} \ G(\mathbf{r}, \mathbf{r}', \omega)$$

$$= -1/\pi \text{Tr} \left[ \text{Im} \ G(\omega) \right]$$, \hspace{1cm} (27)

where the Green function has to be evaluated on the real frequency axis. To evaluate Eq. (27) we first obtain the real frequency self-energy by means of the analytic continuation based on a two-pole fitting scheme. In this approach, the matrix elements of the self-energy in the imaginary frequency domain (i.e., the Fourier transform of Eq. (20)) are fit by polynomials of the form:

$$\Sigma(i\omega) \simeq \sum_{n=1}^{2} \frac{a_n}{i\omega + b_n}$$, \hspace{1cm} (28)

Here the matrix element indices were suppressed for notational simplicity and the coefficients $a_n$ and $b_n$ are determined by means of a non-linear least-square fit, solved with a Levenberg-Marquardt algorithm. By replacing $i\omega$ by $\omega$ in Eq. (28) the self-energy can then be evaluated on the real frequency axis. Once the real-frequency self-energy is obtained, the Dyson equation is solved directly in real frequency on a fine, equally spaced grid. The resulting Green function is used to determine the sc-GW spectral function $A(\omega)$.

Previous works have indicated that the two-pole model presented in Eq. (28) reliably reproduce quasiparticle energies with an average relative error of the 0.2% for solids. The parameter $\eta$ in the denominator of Eq. (1) necessary to avoid the numerical divergence of $G_0$ is set to $\eta = 10^{-4}$. This parameter contributes negligibly to the broadening of the spectral function and has no effect on the position of the quasiparticle peaks.

As an example, we report the sc-GW spectral functions of $\text{H}_2\text{O}$, NH$_3$ and N$_2$ in Fig. 6 calculated using basis sets of increasing size. The sc-GW spectral function shows sharp $\delta$-function-like peaks at the quasi-particle energies. The absence of broadening in the quasi-particle peaks in Fig. 6 may be associated with a infinite lifetime of the corresponding quasi-particle states, as expected for states close to the Fermi energy. As discussed in Sec. IV A, higher energy excitations may decay through the formation of electron-hole pairs, leading to a finite lifetime and thus to a more pronounced broadening of the quasi-particle peaks. In panels a), b) and c) of Fig. 6 we report the spectral function corresponding to the highest occupied quasi-particle states evaluated with a Tier 1, Tier 2 and Tier 3 basis; panels d), e) and f) show the peaks corresponding to the lowest unoccupied quasi-particle states. The $G_0W_0$ ionization energies are reported in panels g), h) and i) of Fig. 6 as a function of the basis set size. The $G_0W_0$ ionization energy is calculated from the linearized quasi-particle equation (Eq. 9), whereas in sc-GW it is extracted from the highest (valence) peak of the spectra shown in panels a), b) and c).

For the quasi-particle energies corresponding to occupied states, the largest change is observed going from Tier 1 to Tier 2. For N$_2$ for example, we observe a change in the HOMO of approximately 0.2 eV going from Tier 1 (which consists of 14 NAO basis functions per atom) to Tier 2 (39 NAO per atom). A further increase of the basis set from Tier 2 to Tier 3 (55 NAO per atom) leads to changes of the order of 5 meV in the HOMO – as illustrated in the right panels of Fig. 6. Lower lying quasi-particle peaks show a similar convergence behavior as the HOMO. H$_2$O, and NH$_3$ exhibit a qualitatively similar behavior. Surprisingly, for all systems considered here, sc-GW data converge faster with the basis set size than perturbative $G_0W_0$ calculations. In the following, we will focus on closed shell molecules, which in many instances do not have a stable anionic state. Therefore, we will focus on the spectral function of occupied states only.

To investigate the performance of the GW approximation at self-consistency, we have performed sc-GW calculations for a set of molecules relevant for organic photovoltaic applications. We report in Fig. 7 the comparison between experimental and theoretical ionization energies evaluated from sc-GW and $G_0W_0$ based on the HF, PBE, and PBE0 starting points, for thiophene, benzothiazole, 1, 2, 5-thiadiazole, naphthalene, and tetraphiafulvalene. For an unbiased assessment, it would be desirable to benchmark sc-GW against higher level theories, since in experiment the distinction between vertical and adiabatic ionization energies is difficult and vibrational effects are always present. For naphthalene the coupled cluster singles doubles with perturbative triples (CCSD(T)) method, that is currently considered as the gold standard in quantum chemistry, gives a vertical ionization potential of 8.241 eV, which sc-GW underes-
estimates (-7.48 eV). For this molecule, the difference between the vertical and the adiabatic ionization potential is only 0.1 eV in CCSD(T). For thiophene, CCSD(T) calculations of the adiabatic ionization energy obtain 8.888 eV, in good agreement with experiment, whereas sc-GW yields 8.45 eV. Zero-point vibration effects are small and cancel with core-correlation and relativistic effects. However, the authors of this study indicate that the geometry of the cation differs considerably from that of the molecule, but did not give values for the vertical ionization energy. It therefore remains an open question, by how much vertical and adiabatic ionization potentials differ for thiophene. For benzothiazole, 1,2,5-thiadiazole, and tetrafluorinated benzene we were not able to find CCSD(T) calculations for the vertical ionization potential.

Despite the tendency to underestimate the first ionization energy, for these systems sc-GW ionization energies are in good agreement with experiment, and give a good overall description of the excitation spectrum: full self-consistency leads to an average error of 0.4 eV (with a maximum error of 1.5 eV for \( G_0 W_0 \)@HF, and 1.6 eV for \( G_0 W_0 \)@PBE). Interestingly, \( G_0 W_0 \)@PBE0 ionization energies are close to the sc-GW ones. Moreover, the \( G_0 W_0 \)@PBE0 spectrum is in slightly better agreement with experiments with an average deviation of 0.3 eV (with a maximum error of 1.2 eV) – as recently also reported for benzene and the azabenzenes in Ref. 12.

For small molecules, the improvements of the spectral properties at self-consistency can partially be traced back to corrections of the over- or under-screening in \( G_0 W_0 \). In PBE based \( G_0 W_0 \) calculations, the small HOMO-LUMO gap induces an overestimation of the screening in the Coulomb interaction. This is the origin of a systematic error in the \( G_0 W_0 \)@PBE quasi-particle energies. Similar considerations are easily generalized to the HF starting point, where HOMO-LUMO gaps are generally too large due to the missing correlation energy. PBE0, on the other hand, often gives a good compromise. Therefore, the over- and under-screening is reduced in \( G_0 W_0 \)@PBE0 and the resulting excitation spectrum is similar to sc-GW, where – because of the self-consistent calculation of \( W \) – this problem is mitigated. Based on these results, PBE0 emerges as an optimal starting point for the perturbative calculation of the spectral properties. It was
argued that the screened Coulomb interaction obtained from sc-GW may also be underscreened due to the lack of electron-hole interactions – typically accounted for by vertex corrections. This would in principle lead to a systematic overestimation of the quasi-particle energies, as reported in Ref. 55 for semiconductors. Figure 7 on the other hand, indicates a slight underestimation of the sc-GW quasi-particle energies, confirming the expectation that effects of the electron-hole attraction on the screened Coulomb interaction are small in molecules with large HOMO-LUMO gaps.

As alluded to in the introduction, previous sc-GW studies have reported conflicting conclusions on the accuracy of the spectral properties. Consequently, no consensus has so far been reached in this respect. sc-GW calculations for the homogeneous electron gas (HEG) indicated a deterioration of the spectra as compared to perturbative $G_0W_0$ based on the local-density approximation (LDA). For the HEG, Holm and von Barth observed a transfer of spectral weight from the plasmon satellite to the quasi-particle peak in self-consistent calculations. This results in a weaker plasmon peak and a broader valence band, that worsens the agreement with photo-emission experiments for metallic sodium.

The first self-consistent calculation for real systems – performed for potassium and silicon in the pseudopotential approximation – confirmed the picture outlined by Holm and von Barth, indicating a deterioration of the band width and band gap at self-consistency. In a later work, Ku and Eguiluz attributed the origin of this failure to the pseudo-potential approximation, emphasizing the importance of accounting for core-valence coupling in the determination of the screening. However, several groups have questioned the convergence of these calculations with respect to the number of bands. Nevertheless, these earlier studies gave the impression that full self-consistency deteriorates the spectral properties compared to perturbative $G_0W_0$, and that it is not recommended to perform sc-GW calculations. However, in our opinion, the scarce numerical evidence for realistic systems is not enough to corroborate this notion.

It was argued that the deterioration of spectra in sc-GW might arise due to the iterative construction of the polarizability $\chi$ as the product of two Green functions. This would systematically weaken the incoherent part of the Green function, and reduce the intensity of the plasmon satellites. For molecules however, this mechanism does not apply since quasi-particle peaks carry integer spectral weight, and no plasmon satellites are observed. For extended systems, this mechanism might effectively deteriorate the sc-GW spectral function, as for the homogeneous electron gas. Nonetheless, more investigations are needed to provide a general and systematic assessment of sc-GW for real solids.

A. Lifetimes of quasi-particle peaks

To facilitate the comparison between $G_0W_0$ and sc-GW, we report in Fig. 8 the full sc-GW and $G_0W_0$ spectral function of thiophene and 1,2,5-thiadiazole. Figure 8 illustrates that even if the peak positions in sc-GW and $G_0W_0$ are very similar, there are qualitative differences.
We observe that quasi-particle peaks corresponding to high-energy excitations are accompanied by a finite broadening. The broadening in turn, being inversely proportional to the lifetime of the corresponding quasi-particle state, yields important information on the dynamics and damping of excitations. In finite systems, finite lifetimes of electronic excitations are a well known aspect that has been extensively discussed in the literature. For single atoms, for which vibrational decay channels are not available, electronic lifetimes of holes have been measured with photo-emission techniques and pump-probe techniques. The most likely process that leads to the decay of holes is Auger recombination.

Green’s function theory is in principle exact, and is therefore expected to correctly account for the lifetime (i.e., the broadening) of quasi-particle excitations, if the exact self-energy were used. The origin of peak broadening can easily be understood from the structure of the Lehmann representation:

\[ G^\sigma(\mathbf{r}, \mathbf{r}', \omega) = \sum_s \frac{f_s^\sigma(\mathbf{r}) f_{s'}^{*\sigma}(\mathbf{r}')}{\omega - \varepsilon_s - i\eta}, \]

where we considered only holes for simplicity. We defined \( \varepsilon_s \equiv E_{s}^{N-1} - E_0 \), and \( f_s \) are the Lehmann amplitudes. Here \( E_0 \) denotes the ground-state energy of the \( N \)-particle system, and \( E_{s}^{N-1} \) the \( s \)-th excited state of the \( N-1 \) particle system. If the hole left behind by the photo-emission process is close to the Fermi energy, the energies \( E_{s}^{N-1} \) (and subsequently also \( \varepsilon_s \)) are discrete. The spectral function therefore exhibits a series of \( \delta \)-functions. However, if the holes are low enough in energy, \( E_{s}^{N-1} \) lies in the continuum of the \( N-1 \) particle systems. Correspondingly, \( \varepsilon_s \) varies continuously and gives rise to a series of delta peaks that are infinitely closely spaced and merge into a single quasiparticle peak with a finite broadening.

For a quantitative assessment of lifetimes in molecules we would have to consider effects beyond \( GW \), such as the coupling to vibrations and the satisfaction of selection rules in the decay process. However, this goes beyond the purpose of the present work. We will therefore limit the following discussion to the origin of lifetimes in molecules and briefly characterize their starting point dependence.

For all molecules considered in this work, the quasi-particle peaks close to the Fermi energy have a \( \delta \)-function-like character. This structure reflects the infinite lifetime of the quasi-particle excitation, and is due to absence of allowed electronic transitions that could annihilate the hole created in the photo-emission process. The excitations of lower valence and core electrons, on the other hand, may have a finite lifetime, and therefore the quasi-particle peak gets broadened. The physical origin of the lifetime is simple. The hole created in a lower valence (or core) state by the photoemission process can in principle recombine with electrons close to the Fermi energy. The energy released in this process has to be converted into an internal excitation of the system, since isolated molecules cannot dissipate energy. If the energy released is larger than the HOMO-LUMO gap, a particle-hole pair can be created. This opens up a scattering or decay channel for the hole, which therefore acquires a lifetime. The energy threshold for electron-hole formation is then given by \( \Delta \equiv E_{\text{HOMO}}^{GS} - E_{\text{gap}}^{GS} \), with \( E_{\text{HOMO}}^{GS} \) and \( E_{\text{gap}}^{GS} \) the HOMO level and the HOMO-LUMO gap of the starting point, respectively. In other words, only quasi-particle states with an energy below \( \Delta \) may decay, and acquire a finite broadening. This argument is general and
does not only apply to \( GW \). What is particular to \( G_0W_0 \) is that the relevant gap for this process is determined by the starting point; in this case the DFT functional for the ground state.

To illustrate this effect on the broadening of the quasi-particle peaks, we report in Fig. 9 the spectrum of benzene evaluated from \( G_0W_0 \) based on different starting points and at self-consistency. Values of \( \Delta \) for the different exchange-correlation functionals are reported as vertical dashed lines (in green). PBE has the smallest HOMO-LUMO gap (\( \sim 5.2 \text{ eV} \)) and we observe a noticeable peak broadening (i.e., short lifetime) at \( \sim 14 \text{ eV} \) in the \( G_0W_0\@\text{PBE}0 \) spectrum. A systematic increase of the broadening is then observed the further a state lies below \( \Delta \). Adding exact exchange to the DFT functional and increasing its admixture opens the HOMO-LUMO gap. The onset of the finite lifetime subsequently moves to lower energies.

In sc-\( GW \), the broadening of the quasi-particle peaks is consistent with the HOMO-LUMO gap at the GW level, and the ambiguity of the starting point dependence is lifted. Consequently, for benzene only peaks below \(-19 \text{ eV} \) acquire a small finite broadening. Based on the sc-\( GW \) results, the large broadening observed in the \( G_0W_0\@\text{PBE}0 \) spectrum can be attributed to the small HOMO-LUMO gap of the underlying \text{PBE}0 calculation. The inclusion of a fraction of exact exchange partially ameliorates this problem, but not fully. This indicates that the calculation of lifetimes presents an additional situation in which – due to the severe dependence on the starting point – resorting to full self-consistency is essential.

### B. Independence of the starting point

Previous work showed that partially self-consistent approaches such as eigenvalue self-consistent \( GW \) or quasi-particle self-consistency, reduce the starting point dependence but they do not eliminate it. Only full self-consistency successfully removes any dependence on the starting point, as we discussed in Ref. 17. This is a major advantage of the sc-\( GW \) scheme, as it allows a systematic assessment of the GW approximation unbiased by spurious dependence on the input Green function.

To illustrate the independence of the starting point of the sc-\( GW \) Green function, we report in Fig. 10 the spectral function of the carbon monoxide molecule as a function of the number of iterations of the Dyson equation initialized with HF, \text{PBE}, and \text{PBE}0. After just a few iterations of the sc-\( GW \) loop, the quasi-particle peaks in the spectral function are located at the same energies demonstrating the independence of the starting point in sc-\( GW \).
accounts for the repulsive nuclear energy. As discussed in Ref. 32, Eq. 30 can be computed directly in imaginary frequency taking advantage of the reduced size of the integration grid needed to describe the one-body density matrix of the DFT/HF or PBE, and hybrid PBE0 starting points. The first iteration corresponds to the $G_0W_0$ approximation.

In the following, we provide an assessment of the $G_0W_0$ method for bond lengths, binding energies, and vibrational frequencies based on the calculations of the potential energy curve of LiH, LiF, HF, CO, H$_2$, and N$_2$. To illustrate the convergence with the basis set, we report in Fig. 11 the binding energy of the carbon monoxide dimer evaluated with sc-GW, RPA@PBE, $G_0W_0$@PBE, and PBE-based renormalized second-order perturbation theory (rPT2) using increasingly larger NAO basis sets (Tier 1-4).

The mean absolute errors of theoretical bond lengths, binding energies, and vibrational frequencies as compared to experiment are reported in Fig. 12. The corresponding numerical values are reported in Appendix C. Since our calculations are performed in the Born-Oppenheimer approximation with clamped nuclei, we compared our calculations with zero-point motion corrected experimental binding energies from Ref. 69. PBE, HF, and several perturbative approaches based on MBPT, namely $G_0W_0$, EX+cRPA, and rPT2 are included for comparison.

Self-consistency provides better bond lengths than perturbative $G_0W_0$ calculations. However, the accuracy achieved by sc-GW for the bond lengths is still comparable to perturbative RPA and not as good as rPT2@PBE, which includes higher order exchange and correlation diagrams.

The binding energies obtained from $G_0W_0$ based on HF and PBE, reported in Table 11, are systematically overestimated. Self-consistent GW over-corrects this trend and yields binding energies that slightly underestimate experiment. RPA@HF and sc-GW give a very similar

FIG. 10. (Color online) Spectral function of the CO dimer evaluated for the first five iterations of the Dyson equation from the HF, PBE, and hybrid PBE0 starting points. The first iteration corresponds to the $G_0W_0$ approximation.

FIG. 11. (Color online) BSSE corrected binding energy of CO evaluated with Tier 1, 2, 3 and 4. Each curve is aligned at their respective Tier 4 value. All data are in eV.
FIG. 12. (Color online) Mean absolute error (MAE) of bond lengths (upper panel), binding energies (central panel), and vibrational frequencies (lower panel) of LiH, LiF, HF, CO, H$_2$, and N$_2$ evaluated at different levels of theory. The estimated zero-point motion correction has been subtracted from the experimental binding energies (reported from Ref. 69). Calculations were done with a Tier 3 basis set (the largest basis set available) for H$_2$, LiH, and HF, whereas a Tier 4 basis was used for N$_2$ and CO. Numerical values are reported in Tables III, II, and IV in the Appendix.

C. Density and dipole moments at self-consistency

In perturbative approaches, such as $G_0W_0$, EX+cRPA, and rPT2, the electron density of a system is defined by the eigenstates of the unperturbed reference Hamiltonian – although in principle perturbative corrections to the eigenstates of the unperturbed Hamiltonian could be calculated. This constitutes a major drawback, as it is in part responsible for the well-known starting point dependence of perturbative schemes. Self-consistency, on the other hand, permits us to incorporate exact exchange and dynamical correlation effects into the electron density. To illustrate this aspect in sc-GW, we discuss in the following the effects of self-consistency on the density and the dipole moment of diatomic molecules.

FIG. 13. (Color online) Difference between the sc-GW and Hartree-Fock densities for the hydrogen fluoride dimer at its experimental equilibrium geometry ($d = 0.917$ Å). At self-consistency, electron density is shifted from negative (dark) to positive regions (light). Units are Å$^{-3}$ and the calculation were performed using a Tier 3 basis set.

Description of the binding energy, the deviation between the two methods being approximately 10 – 20 meV. This similarity is expected for two reasons: First, in diatomic molecules screening is small, thus the sc-GW Green function resembles the Hartree-Fock one (since in absence of polarization $W$ reduces to the bare Coulomb interaction). Second, the RPA total energy is a variational functional of the Green function, and therefore RPA total energies are close to sc-GW ones, if the input Green function is close enough to the sc-GW Green function. Larger discrepancies between perturbative RPA and sc-GW are to be expected for the structural properties of systems for which the sc-GW density is substantially different as compared to HF or semi-local DFT. Example of these material are molecular interfaces and charge transfer compounds, where the ground-state density (and the charge transfer) depends strongly on the level alignment between the individual components of the system. This will be addressed in future works. Also, for binding energies and bond lengths, sc-GW is outperformed by rPT2@PBE, which illustrates the importance of including exchange and correlation diagrams beyond the GW approximation for a systematic improvement of the ground-state properties of finite systems.

For vibrational frequencies, the dependence on the starting point is larger than for binding energies or bond lengths. In this case, the best agreement with experiment is achieved with the PBE functional, whereas for HF the errors are substantially larger. Similarly, PBE-based $G_0W_0$ and EX+cRPA deviate less from experiment than HF-based schemes. For instance, the mean absolute error of EX+cRPA@HF is approximately a factor of two larger that EX+cRPA@PBE, and the same is observed for $G_0W_0$. Consequently, sc-GW gives smaller MAEs compared to HF-based schemes, but does not improve over PBE-based perturbative schemes.
angular correlation. Moreover, density is shifted from the two lobes perpendicular to the molecular axis to the bond region, leading to a reduction of the dipole moment as compared to HF, which is in better agreement with experiment (see Table I).

The dipole moment provides a systematic way to quantify the quality of the electron density of a system, as it is directly comparable with experimental data. We report in Table I the dipole moment of LiH, LiF, HF and CO evaluated from sc-GW, PBE, and HF. sc-GW dipole moments are in good agreement with experiments and reduce the deviation from experiment by approximately a factor of two compared to HF and PBE, that tend to under and overestimate, respectively. The quality of the dipole moment for the small set of molecules presented here, indicates that sc-GW is a promising method for the description of charge-transfer compounds, such as molecular interfaces and hetero-structures.

### VI. CONCLUSIONS

We have presented an all-electron implementation of the fully self-consistent GW method based on a numeric atom-centered orbital basis in the FHI-aims code.25 Self-consistent GW is based on the iterative solution of Hedin’s equations with the GW self-energy and polarizability, and therefore it is significantly different from partially self-consistent approaches based on perturbation theory, such as the quasi-particle self-consistent GW scheme32 and self-consistency in the eigenvalues.19,71

In our implementation, the two-particle operators are treated efficiently by means of the resolution of identity technique.22 The introduction of an auxiliary basis for the representation of the frequency and time dependence of dynamic operators, facilitates an accurate evaluation of Fourier integrals that require just few tens of grid points. These ingredients allow us to reformulate Hedin’s equations in a matrix form, that can be solved with standard linear algebra packages.

We presented an assessment of the spectral properties of five molecules of interest for organic photo-voltaic applications: thiophene, benzothiazole, 1,2,5-thiadiazole, naphthalene, and tetrathiafulvalene. For these systems, the quasi-particle energies extracted from the sc-GW spectral function are found to be in good agreement with experimental photo-emission data for all valence states. The sc-GW excitation spectrum systematically improves over perturbative $G_0W_0$ based on semi-local DFT and Hartree-Fock. This is interpreted as a consequence of the mitigation of over- and under-screening errors characteristic of $G_0W_0$@PBE and $G_0W_0$@HF, respectively. $G_0W_0$ based on PBE0, on the other hand, provides results in slightly better agreement with experimental data than sc-GW. Thus, the PBE0 functional appears to be close to an optimal starting point for perturbative calculations.

Self-consistent GW total energies based on the Galitskii-Migdal formula permit an assessment of ground-state and structural properties of molecules. For a small set of diatomic molecules we evaluated binding energies, bond lengths and vibrational frequencies. The bond lengths improve at self-consistency, but still have an accuracy comparable to other perturbative methods such as exact-exchange with correlation from the random-phase approximation. Binding energies are typically underestimated compared to experimental reference data and do not substantially improve over perturbative $G_0W_0$ calculations. Our results indicate and quantify the importance of including vertex corrections – or alternatively, higher order correlation and exchange diagrams – in order to achieve an accurate description of the structural properties of molecules.

Finally, the dipole moments of a set of hetero-atomic dimers were studied to investigate the accuracy of the sc-GW density. Compared to Hartree-Fock and PBE, the sc-GW dipole moments are found in better agreement with experiment. These results indicate that sc-GW is a promising approach for the description of charge-transfer compounds and hetero-junctions, where the relative ordering of the frontier orbitals influences the charge transfer at the interface.

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### Appendix A: Rewriting the Galitskii-Migdal formula

In Hartree atomic units ($\hbar = e = m = 1$), the electronic contribution of the Galitskii-Migdal total energy

|          | LiH | HF | LiF | CO | MAE |
|----------|-----|----|-----|----|-----|
| Exp.     | 5.88 | 1.82 | 6.28 | 0.11 | -   |
| sc-GW    | 5.90 | 1.85 | 6.48 | 0.07 | 0.07|
| PBE      | 5.63 | 1.77 | 6.12 | 0.20 | 0.14|
| PBE0     | 5.77 | 1.81 | 6.20 | 0.09 | 0.06|
| HF       | 6.04 | 1.89 | 6.46 | -0.13 | 0.17|
is:

\[ E_{GM} = -i \sum_\sigma \int dr \, dt \lim_{t' \to t} \left[ i \frac{\partial}{\partial t} + h_0 \right] G^\sigma (r, r') \]. \quad (A1)

Here, \( h_0 \) is the single-particle term of the many-body Hamiltonian, i.e., the sum of the kinetic energy operator and the external potential due to the nuclei. Introducing the equation of motion for the interacting Green’s function (see e.g. Ref. 72)

\[
\left[ \frac{\partial}{\partial t} + \frac{\nabla^2}{2} - v_H(r) - v_{\text{ext}}(r) \right] G^\sigma (r, r') - \\
\int d\omega d\omega' \Sigma^\sigma (r, r'' \omega') G^\sigma (r'' \omega', r') = \\
\delta (r - r') \delta (t - t'),
\]

\quad (A2)

Eq. (A1) can be simplified by eliminating the partial derivative with respect to time, obtaining:

\[ E_{GM} = -i \sum_\sigma \int dr \, dr' \, dt \, dt' \lim_{t' \to t} \left[ \left(-\frac{\nabla^2}{2} + 2v_{\text{ext}}(r) + v_H(r) \right) \delta (r - r') \delta (t - t') \right] \\
+ \Sigma^\sigma (r, r') \right] G^\sigma (r', r'). \quad (A3)

Making use of the matrix representation of the Green function \( G^\sigma (r, r', \tau) = \sum_{ij} \varphi_i(r) \overline{G}_{ij} (\tau) \varphi_j(r') \) – with \( \overline{G} \equiv s^{-1} G^s s^{-1} \) – the first three terms in Eq. (A3) can be rewritten as:

\[ -i \sum_\sigma \int dr \lim_{r' \to r} \left[ -\nabla^2 \right] + 2v_{\text{ext}}(r) + v_H(r) \right] \times \\
\sum_{ij} \varphi_i(r) \overline{G}_{ij} (\tau = 0^-) \varphi_j(r') = \\
- \sum_\sigma \sum_{ij} \overline{G}_{ij} (\tau = 0^-) \left[ 2t_{ij} + 2v_{\text{ext}} + v_H \right]. \quad (A4)

For time independent Hamiltonians, the Green function depends only on time differences \( \tau \equiv t - t' \). In the last step of Eq. (A4) we defined the matrix representation of the kinetic energy operator as \( t_{ij} = \int dr \varphi_i(r) \left[ -\nabla^2 \right] \varphi_j(r) \), and use a similar representation for \( v_{\text{ext}}^{ij} \) and \( v_H^{ij} \). Finally, the last term in Eq. (A3) can be rearranged by using the Fourier transform of the Green function and the self-energy \( G(t, t') = \int_{-\infty}^{t'} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} G(\omega) \), and substituting the matrix representation of \( G \):

\[ -i \sum_\sigma \int dr \, dr' \, dt \, dt' \lim_{t' \to t} \Sigma^\sigma (r, r'' t'' \omega') G^\sigma (r'' t'', r') = \\
- i \sum_\sigma \sum_{ij} \int \frac{d\omega}{2\pi} \Sigma_{ij} (\omega) G_{ij} (\omega) e^{i\omega}. \quad (A5)

Summing Eqs. (A4) and (A5) and separating the self-energy in its exchange and correlation components \( \Sigma_{ij} (\omega) = \Sigma_{ij}^e (\omega) + \Sigma_{ij}^c (\omega) \), one finally arrives at the expression reported in Eq. (31). We refer to Ref. 73 for a discussion on the evaluation of the Galitskii-Migdal formula on the imaginary frequency axis.

Appendix B: Binding energies, bond lengths, and vibrational frequencies of diatomic molecules

In Tables I and II we report counterpoise corrected74 binding energies and bond lengths for H\(_2\), Li\(_2\), LiF, HF, N\(_2\), and CO. The corresponding vibrational frequency are reported in Table IV. The sc-GW results are compared with experimental values,69,70 and several perturbative approaches based on MBPT, namely \( G_0 \), EX+cRPA, and rPT2@PBE. HF and PBE are included for comparison.
TABLE II. sc-GW, and perturbative $G_0W_0$ binding energies (evaluated from the Galitskii-Migdal formula) of diatomic molecules compared to (zero point motion corrected) experimental reference data taken from Ref. [69]. We report perturbative RPA, HF, PBE, and renormalized second-order perturbation theory (rPT2) for comparison. Calculations were done with a Tier 3 basis set (the largest basis set available) for H$_2$, LiH, and HF, whereas a Tier 4 basis was used for N$_2$ and CO. The mean absolute errors (MAE) are reported in panel (b) of Fig. 12. All values are in eV.

|       | H$_2$ | LiH | HF | LiF | N$_2$ | CO | MAE |
|-------|-------|-----|----|-----|-------|----|-----|
| Exp   | -4.75 | -2.52 | -6.12 | -6.02 | -9.91 | -11.24 | 0.72 |
| sc-GW | -4.41 | -2.16 | -5.55 | -5.50 | -8.42 | -10.19 | 0.46 |
| $G_0W_0$@HF  | -5.05 | -2.72 | -6.45 | -6.60 | -10.61 | -11.88 | 0.77 |
| $G_0W_0$@PBE  | -5.32 | -2.90 | -6.49 | -6.67 | -11.50 | -12.34 | 0.78 |
| $G_0W_0$@PBE0  | -4.41 | -2.17 | -5.54 | -5.52 | -8.51 | -10.19 | 0.70 |
| RPA@HF  | -4.68 | -2.32 | -5.60 | -5.43 | -9.54 | -10.48 | 0.42 |
| RPA@PBE  | -5.32 | -2.90 | -6.49 | -6.67 | -11.50 | -12.34 | 0.78 |
| rPT2@PBE  | -5.32 | -2.90 | -6.49 | -6.67 | -11.50 | -12.34 | 0.78 |
| HF      | -3.64 | -1.49 | -4.22 | -3.95 | -5.10 | -7.62 | 2.42 |
| PBE     | -4.54 | -2.32 | -6.17 | -6.03 | -10.58 | -11.67 | 0.26 |

TABLE III. sc-GW and perturbative $G_0W_0$ bond lengths of diatomic molecules compared to experimental reference data taken from Ref. [70]. RPA, HF, PBE, and renormalized second-order perturbation theory (rPT2) are included for comparison. Mean absolute errors (MAE) are reported in panel (a) of Fig. 12. All values are in Å.

|       | H$_2$ | LiH | HF | LiF | N$_2$ | CO | MAE |
|-------|-------|-----|----|-----|-------|----|-----|
| Exp   | 0.741 | 1.595 | 0.917 | 1.564 | 1.098 | 1.128 | 0.011 |
| sc-GW | 0.735 | 1.579 | 0.919 | 1.586 | 1.085 | 1.118 | 0.012 |
| $G_0W_0$@HF | 0.733 | 1.560 | 0.919 | 1.579 | 1.093 | 1.119 | 0.017 |
| $G_0W_0$@PBE | 0.746 | 1.582 | 0.938 | 1.593 | 1.116 | 1.143 | 0.014 |
| $G_0W_0$@PBE0 | 0.741 | 1.564 | 0.932 | 1.590 | 1.100 | 1.136 | 0.009 |
| RPA@HF | 0.734 | 1.587 | 0.914 | 1.576 | 1.087 | 1.117 | 0.009 |
| RPA@PBE | 0.745 | 1.597 | 0.927 | 1.589 | 1.107 | 1.137 | 0.010 |
| rPT2@PBE | 0.739 | 1.597 | 0.914 | 1.578 | 1.091 | 1.225 | 0.005 |
| HF | 0.734 | 1.606 | 0.898 | 1.560 | 1.066 | 1.102 | 0.017 |
| PBE | 0.751 | 1.605 | 0.930 | 1.575 | 1.104 | 1.136 | 0.010 |

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TABLE IV. sc-GW, and perturbative $G_0W_0$ vibrational frequencies of diatomic molecules compared to experimental reference data taken from Ref. 74. RPA, HF, PBE, and renormalized second-order perturbation theory (rPT2) are included for comparison. The mean absolute errors (MAE) are reported in panel (c) of Fig. 12. All values are in cm$^{-1}$.

|          | H$_2$ | LiH | HF | LiF | N$_2$ | CO | MAE |
|----------|-------|-----|----|-----|-------|----|-----|
| Exp.     | 4401  | 1405| 4138| 911 | 2359  | 2170|     |
| sc-GW    | 4533  | 1743| 4266| 971 | 2543  | 2322| 166 |
| $G_0W_0@$HF | 4585  | 1827| 4341| 1010| 2490  | 2647| 252 |
| $G_0W_0@$PBE | 4341  | 1743| 4589| 971 | 2346  | 2322| 105 |
| $G_0W_0@$PBE0 | 4425  | 1813| 4273| 922 | 2386  | 2222| 109 |
| RPA@HF   | 4533  | 1685| 5512| 952 | 2544  | 2321| 360 |
| RPA@PBE  | 4357  | 1691| 4757| 933 | 2354  | 2115| 172 |
| HF       | 4567  | 1473| 4569| 949 | 2736  | 2448| 226 |
| PBE      | 4320  | 1364| 3991| 899 | 2328  | 2128| 59  |
| rPT2@PBE | 4460  | 1605| 4620| 922 | 2507  | 2251| 163 |

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