Unified description of ground and excited states of finite systems: the self-consistent \textit{GW} approach

F. Caruso,\textsuperscript{1,2,*} P. Rinke,\textsuperscript{1,2} X. Ren,\textsuperscript{1,2} M. Scheffler,\textsuperscript{1,2} and A. Rubio\textsuperscript{1,2,3}

\textsuperscript{1}Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
\textsuperscript{2}European Theoretical Spectroscopy Facility
\textsuperscript{3}Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Universidad del País Vasco, CFM CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 Donostia, Spain

Abstract

\textit{GW} calculations with fully self-consistent \textit{G} and \textit{W} – based on the iterative solution of the Dyson equation – provide an approach for consistently describing ground and excited states on the same quantum mechanical level. We show that for the systems considered here self-consistent \textit{GW} reaches the same final Green function regardless of the initial reference state. Self-consistency systematically improves ionization energies and total energies of closed shell systems compared to \textit{G}_0\textit{W}_0 based on Hartree-Fock and (semi)local density-functional theory. These improvements also translate to the electron density as exemplified by an improved description of dipole moments and permit us to assess the quality of ground state properties such as bond lengths and vibrational frequencies.
Many-body perturbation theory (MBPT) \[1\] in the GW approximation of the electronic self-energy \[2, 3\], the state-of-the-art method for the spectral properties of solids \[4, 5\], has steadily gained popularity for molecules and nanosystems. In addition MBPT provides a prescription to extract total energies and structural properties from the GW approximation and therefore a consistent theoretical framework for single-particle spectra and total energies.

Due to their numerical cost, GW calculations are mostly performed perturbatively (one-shot \(G_0W_0\)) on a set of single particle orbitals and eigenvalues obtained from a preceding density functional theory \[6, 7\] (DFT) or Hartree-Fock (HF) calculation. This procedure introduces a considerable starting point dependence \[8–10\], which can be eliminated by iterating the Dyson equation to self-consistency. The resulting self-consistent GW (sc-GW) framework is a conserving approximation in the sense of Baym and Kadanoff \[11\] (i.e. it satisfies momentum, energy, and particle number conservation laws). sc-GW gives total energies \[12\] free from the ambiguities of the \(G_0W_0\) scheme, in which the results depend on the chosen total energy functional \[13\]. However, as in any self-consistent theory, the question remains, if the self-consistent solution of the Dyson equation is unique. This issue is fundamentally different from the initial-state dependence of \(G_0W_0\). For HF \[14\] and LDA/GGA+U \[15\] calculations, it is well known that the self-consistency cycle can reach local minima instead of the global minimum. Moreover, a previous sc-GW study for the Be atom showed that pseudopotential calculations do not produce the same final GW Green function (and corresponding ionization potential) as all-electron calculations \[16\].

In this letter, we demonstrate certain key aspects of the sc-GW approximation for closed shell molecules, that make sc-GW attractive as a general purpose electronic structure method. First, the iteration of the Dyson equation produces a self-consistent Green function that is independent of the starting point, and determines both the ground- and excited-state properties (quasiparticle spectra) of a given system on the same quantum mechanical level. This distinguishes sc-GW from other (partially) self-consistent GW schemes \[17, 18\], which do not lend themselves to total-energy calculations. Moreover the uniqueness of the sc-GW Green function facilitates an unprecedented and unbiased assessment of the GW approach, which previously was masked by the starting-point dependence of \(G_0W_0\). Second, self-consistency improves total and quasi-particle energies compared to \(G_0W_0\) based on HF or DFT in (semi)local approximations and yields good agreement with high level quantum-chemical calculations and photo-emission data. Third, unlike \(G_0W_0\), sc-GW yields
FIG. 1. (Color online) Total energy (a) and ionization energy (b) of \( \text{N}_2 \) at each iteration of the sc-GW loop for a HF (squares) and PBE (circles) input Green function, for the aug-cc-pVQZ \cite{19} basis set. The (absolute values of the) differences arising from HF and PBE initializations vanish exponentially for both total energy (c) and ionization energy (d).

In the \( GW \) approximation the self-energy \( \Sigma \) is defined in terms of the one-particle Green function \( G \) and the screened Coulomb interaction \( W \) as

\[
\Sigma(\mathbf{r}, \mathbf{r}', \omega) = i \int \frac{d\omega'}{2\pi} G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') e^{i\omega\eta},
\]

where \( \eta \) is a positive infinitesimal, and spin-variables are omitted throughout this paper for simplicity. The screened interaction is defined as \( W(\mathbf{r}, \mathbf{r}', \omega) = v(\mathbf{r}, \mathbf{r}')/[1 - v(\mathbf{r}, \mathbf{r}')\chi_0(\mathbf{r}, \mathbf{r'}\omega)] \), where \( v = 1/|\mathbf{r} - \mathbf{r}'| \) and the polarizability \( \chi_0 \) depends explicitly on the Green function through the equation \( \chi_0(\mathbf{r}, \mathbf{r'}, \tau) = -iG(\mathbf{r}, \mathbf{r'}, \tau)G(\mathbf{r}, \mathbf{r'}, -\tau) \). The Green function can in turn be expressed in terms of the self-energy through the Dyson equation

\[
G^{-1} = G_0^{-1} - [\Sigma - v_0 + \Delta v_H],
\]

where \( G_0 \) refers to the Green function of an independent particle system in an external potential \( v_{\text{ext}} \). \( \Delta v_H \) accounts for changes in the Hartree potential due to density differences.
between $G_0$ and $G$, and $v_0$ is the exact-exchange operator in HF or the Kohn-Sham exchange-correlation potential in DFT. The interdependence of Eq. 1 and Eq. 2 is the very origin of the self-consistent nature of the $GW$ approach.

It is common practice, however, to solve Eq. 1 and Eq. 2 just once, in the so-called $G_0W_0$ approximation. If Eq. 2 is not solved, the $G_0W_0$ quasi-particle energies are given in first-order perturbation theory as corrections to the reference eigenvalues ($\{\epsilon_n^0\}$) as

$$
\epsilon_n^{QP} = \epsilon_n^0 + \text{Re} \langle \psi_n^0 | \Sigma(\epsilon_n^{QP}) - v_0 | \psi_n^0 \rangle.
$$

In this work, Eqs. 1-2 were solved iteratively; moreover the screened interaction $W$ is also updated at each iteration taking into account the full frequency dependence of the polarizability $\chi_0$ on the imaginary axis. In sc-$GW$ the single particle excitation spectrum is given by the (integrated) spectral function:

$$
A(\omega) = -\frac{1}{\pi} \int dr \lim_{r' \to r} \text{Im} G(r, r', \omega).
$$

The ground-state density $n(r)$ also follows directly from the Green function [1]:

$$
n(r) = -2iG(r, r, \tau = 0^{-}).
$$

The situation is more complicated for the total energy. As alluded to above, for a given Green function different prescriptions exist to compute the associated total energy such as the Galitskii-Migdal formula [21], the Luttinger-Ward [22] or the Klein [23] functional. The latter two are variational in the sense that they are stationary at the self-consistent Green function, and therefore might provide better total energies than the Galitskii-Migdal formula when evaluated with non-self-consistent Green functions [24, 25]. However, at self-consistency all three approaches are equivalent. For this reason, we choose the Galitskii-Migdal formula

$$
E_{GM} = -i \int d\omega \frac{1}{2\pi} Tr \{[\omega + h_0] G(\omega) \} + E_{\text{ion}},
$$

because it is easier to implement. Equation 5 can be rewritten by using the equation of motion for the one particle Green function [26]

$$
E_{GM} = -i \sum_{i,j} G_{ij}(\tau = 0^{-})[t_{ij} + v_{ij}^e + v_{ij}^H + \Sigma_{ij}]
- \sum_{i,j} \int d\omega \frac{1}{2\pi} G_{ij}(\omega) \Sigma_{ij}(\omega) + E_{\text{ion}}.
$$
Here \( t \) is the kinetic-energy operator, \( v^H \) the Hartree potential and \( \Sigma^x \) and \( \Sigma^c \) are the exchange and correlation parts of the self-energy, respectively. The trace of Eq. 5 is expressed as sum over basis functions in Eq. 6 and the frequency integration can be conveniently performed along the imaginary axis \([26]\).

For comparison, we also computed \( G_0 W_0 \) total energies with different starting points. However, as indicated above, \( G_0 W_0 \) total energies are not uniquely defined, because the Green function and the self-energy are never on the same level. If, for example, the Dyson equation is not solved, \( G_0 \) and \( \Sigma_0 = G_0 W_0 \) enter Eq. 6. If the Dyson equation is solved, the resulting \( G_1 \) is still inconsistent with \( \Sigma_0 \). In the following we refer to the combination of \( G_0 \) and \( \Sigma_0 \) in Eq. 6 as \( G_0 W_0 \) total energy and denote the corresponding starting point with \( @ \) starting point.

We have implemented sc-GW in the all-electron electronic structure code FHI-aims \([27, 28]\). Equation 1-4 and Eq. 6 are solved in a numerical atomic orbital (NAO) basis using the resolution of identity technique to treat all two-particle operators efficiently \([28]\). All calculations are performed on the imaginary frequency axis and the spectral function is obtained by analytic continuation to the real frequency axis \([28]\). The analytic continuation constitutes the only approximation of our implementation of the sc-GW method. More information on the computation of the screened Coulomb interaction in sc-GW is given in the Supplemental Material \([29]\). Further details of the implementation will be given elsewhere \([30]\).

In Fig. 1 we demonstrate for \( N_2 \) that the sc-GW Green function provides total energies

\( E_{\text{tot}} - E_{\text{CI}} \) [eV]

\( \text{LiH H}_2 \text{ H He Li Be B C N O F Ne} \)

FIG. 2. (Color online) Difference between Galitskii-Migdal total energies \( (E_{\text{GM}}) \) and full configuration interaction values \( (E_{\text{CI}}) \), with \( E_{\text{GM}} \) evaluated from sc-GW (diamonds), \( G_0 W_0 \)@HF (squares) and \( G_0 W_0 \)@PBE (circles). PBE total energy differences with full-CI are reported as crosses. The calculations were performed using the aug-cc-pV5Z basis set \([19]\).
(a) and vertical ionization energies (b) that are independent of the starting point. Figure 1 explicitly illustrates this for initializing the self-consistency cycle with HF and DFT in the Perdew, Burke, and Ernzerhof (PBE) [34] generalized gradient approximation, but other initializations like the local-density approximation (LDA) or the simple Hartree approximation produce the same final sc-GW Green function (not shown). The deviation in the Green function exemplified by the (absolute value of the) total energy difference (Fig. 1(c)) and the ionization energy difference (Fig. 1(d)) converges exponentially fast with the number of iterations, canceling the starting point dependence. Further tests performed on a set of 30 closed shell molecules (see Fig. 4) confirm this fact and demonstrate that sc-GW provides a recipe for linking different reference systems of independent electrons (or non-interacting Kohn-Sham particles) to a unified interacting many-body state.

Having established that the sc-GW solution is independent of the starting point we now turn to an assessment of the performance of the GW approach for ionization potentials, electron densities and total energies. For elements in the first two rows of the periodic table (i.e. $Z = 1 - 10$) and small molecules like $H_2$ and LiH accurate reference data from configuration interaction (CI) calculations are available [31–33]. Figure 2 reports the difference to these CI values for basis set converged sc-GW, $G_0W_0@PBE$ and $G_0W_0@HF$ calculations. A subset of these has previously been calculated using sc-GW [13] and our results are in excellent agreement with the published results (with a maximum deviation of $\approx 0.4\%$). In line with previous calculation for the electron gas [24, 26, 35], atoms and small molecules [13], $G_0W_0$ total energies (in various flavors) tend to be too negative. The self-consistent treatment largely (but not fully) corrects this overestimation and provides total energies in more satisfying agreement with full CI. The remaining overestimation provides a clear and unbiased quantification of the required vertex corrections in a beyond GW treatment.

To assess other ground state properties, like the equilibrium atomic structure, would require atomic forces (i.e. derivatives of the total energy with respect to atomic coordinates), which are presently not available for sc-GW. For diatomic molecules, however, structural properties such as vibrational frequencies, bond lengths and binding energies can be determined directly from the potential energy curve. Other ground state properties, e.g. dipole moments, can be inferred directly from the electron density also for more complex systems. For brevity, we only present the case of CO here and refer to a future publication for a more detailed discussion of ground state properties in sc-GW [30].
|     | d   | $\nu_{vib}$ | $\mu$ | $E_b$  |
|-----|------|-------------|-------|-------|
| CO  | 1.128 | 2169       | 0.11  | 11.11 |
| Exp. [36] |      |             |       |       |
| sc-GW | 1.118 | 2322       | 0.07  | 10.19 |
| $G_0W_0@HF$ | 1.119 | 2647       | -     | 11.88 |
| $G_0W_0@PBE$ | 1.143 | 2322       | -     | 12.16 |
| (EX+cRPA)$@HF$ | 1.116 | 2321       | -     | 10.19 |
| (EX+cRPA)$@PBE$ | 1.135 | 2115       | -     | 10.45 |
| PBE | 1.137 | 2128       | 0.20  | 11.67 |
| HF  | 1.102 | 2448       | -0.13 | 7.63  |

**TABLE I.** Equilibrium bond length $d$, vibrational frequency $\nu_{vib}$, dipole moment $\mu$ and binding energy $E_b$ of the CO dimer. Units are respectively Å, cm$^{-1}$, Debye and eV. All calculations were performed with a Tier 4 basis set.

In Table I we report the experimental values for the bond length $d$, vibrational frequency $\nu_{vib}$, dipole moment $\mu$ and binding energy $E_b$ of CO [36] together with the theoretical values obtained from several perturbative and non-perturbative approaches. DFT in the exact-exchange plus correlation in the random-phase approximation (EX+cRPA) is currently regarded as one of the most advanced DFT functionals. Based on PBE, it is remarkably accurate for the bond length and vibrational frequency of CO [37]. However, like $G_0W_0$, EX+cRPA exhibits a considerable starting point dependence and gives no direct access to dipole moments. In sc-GW, the quality of the new density, obtained through Eq. 4, is manifested in the improved dipole moment, which is in much better agreement with the experimental value than PBE and HF. Additional information on the quality of the sc-GW electron density are reported in the Supplemental Material [29]. The vibrational frequency, on the other hand, is overestimated and not substantially different from the perturbative $G_0W_0$ values. Self-consistency over-corrects the overestimation of the $G_0W_0$ binding energy, resulting in an underestimation of about 1 eV for $E_b$ compared to experiment. Similarly, the sc-GW bond length is slightly too small and is close to $G_0W_0@HF$. This assessment of the GW approach for ground state properties, facilitated by sc-GW, clearly indicates where future challenges in going beyond GW lie.

Finally, we turn to the description of spectral properties. For the electron gas Holm and
von Barth first reported a deterioration of the spectral properties [39] in sc-GW compared to $G_0 W_0$@LDA calculations. For the spectra of simple solids like silicon and sodium, controversy then arose with some authors advocating self-consistency [40] and others dismissing it [35, 41]. Part of this controversy can be traced back to convergence difficulties in the early all-electron calculations [42], while the influence of the pseudopotential approximation in GW turned out to be larger than initially anticipated [43].

To test the quality of the sc-GW spectral function we chose the benzene molecule as a benchmark, for which the sc-GW spectral function in Fig. 3 is compared to the $G_0 W_0$@HF and $G_0 W_0$@PBE ones calculated using Eq. 3. The vertical ionization energies (VIEs) shown in the right panel of Fig. 3 correspond to the peak positions in the corresponding spectra. All the peaks reported in the left panel of Fig. 3 correspond to occupied quasi-particle states and the associated energy can be directly related to ionization energies from photoemission spectroscopy. No evidence of collective excitations was observed for the systems considered in the present work. sc-GW and $G_0 W_0$@HF show the same qualitative spectral features being characterized by sharp $\delta$-function like quasi-particle peaks. The $G_0 W_0$ spectra in Fig. 3 depend strongly on the starting point: HF-(PBE-)based $G_0 W_0$ has a tendency to overestimate (underestimate) VIEs. The deviation between $G_0 W_0$@HF and $G_0 W_0$@PBE is $\simeq 0.5$ eV for the first ionization energy and can be as large as $\simeq 3$ eV for lower lying quasi-particle states (Fig. 3 right panel). Furthermore, due to overscreening $G_0 W_0$@PBE
yields a large broadening (i.e. short quasi-particle lifetimes) for states below \(-10\ \text{eV}\). At self-consistency, the quasi-particle energies and lifetimes are uniquely defined, the systematic (over)underestimation of $G_0W_0$ calculations is considerably reduced and the resulting quasi-particle energies are in better agreements with photoemission data \[38\].

We further assessed the quality of sc-$GW$ quasi-particle energies for the set of 30 molecules proposed by Rostgaard et al. \[44\]. For brevity our results are summarized in Fig. 4 and we refer to the Supplemental Material for the actual numerical values \[29\]. In Ref. \[44\] sc-$GW$ was based on the frozen-core approximation, whereas our work fully accounts for the importance of core electrons in the solution of Hedin’s equations \[43\]. Core-valence coupling is therefore correctly included in our implementation, and we tentatively attribute the deviation of 0.1-0.5 \text{eV} in the first VIEs between our and Rostgaard et al.’s sc-$GW$ calculations to the frozen core approximation made in their work. As for benzene, $G_0W_0@HF$ tends to overestimate VIEs, while $G_0W_0@PBE$ underestimates. sc-$GW$ also slightly underestimates the VIEs, but gives an average deviation of only 2\% compared to 6\% in $G_0W_0@PBE$ and 4\% in $G_0W_0@HF$. PBE and HF present two extreme starting points. In PBE the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is severely underestimated, while in HF it is considerably overestimated. This in part explains the behavior of $G_0W_0@PBE$ and $G_0W_0@HF$. Since the screening strength is inversely proportional to the HOMO-LUMO gap, $G_0W_0@PBE$ overscreens and $G_0W_0@HF$ underscreens. By tuning the fraction of exact exchange in the ground states, as e.g. in hybrid functionals, the deviation between $G_0W_0$ and experiment could be further reduced for this data set. However, this procedure is neither predictive, nor universal or transferable, because different systems will require a different amount of exact exchange. To really assess the quality of the $GW$ approximation, self-consistency is therefore indispensable.

In summary, we have demonstrated that sc-$GW$ is independent of the starting point for closed shell molecules. Self-consistency improves the total energy and the spectral properties of the test sets compared to $G_0W_0$ based on HF or PBE, whereas structural properties worsen compared to EX+cRPA. Moreover, electron densities become accessible in sc-$GW$, whose quality is demonstrated by the improved description of the dipole moment of CO. The sc-$GW$ approach therefore provides a unified theory for the electronic ground- and excited-state properties of many-body systems. Most importantly, sc-$GW$ gives unambiguous reference data that is essential for developing vertex corrections for (bio)molecules, nanostructures and
FIG. 4. (Color online) First vertical ionization energy (VIE) for 30 closed-shell molecules composed of 2 to 8 atoms. Experimental values are taken from Ref. [36]. All calculations were performed using a Tier 2 basis set.

extended systems, in particular for the challenging class of “strongly correlated” materials.

AR acknowledges financial support from MEC (FIS2011-65702-C02-01), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT-319-07), and the European Research Council (ERC-2010-AdG -No. 267374).

* caruso@fhi-berlin.mpg.de

[1] A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems (Dover Publications, 2003).

[2] L. Hedin, Phys. Rev. 139, A796 (1965).

[3] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. 61, 237 (1998).

[4] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. 54, 1 (2000).

[5] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).

[6] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[7] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[8] P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt, and M. Scheffler, New J. Phys. 7, 126 (2005).

[9] F. Fuchs, J. Furthmüller, F. Bechstedt, M. Shishkin, and G. Kresse, Phys. Rev. B 76, 115109 (2007).
[10] P. Rinke, A. Qteish, J. Neugebauer, and M. Scheffler, Phys. Stat. Sol. B 245, 929 (2008).
[11] G. Baym and L. P. Kadanoff, Phys. Rev. 124, 287 (1961).
[12] C.-O. Almbladh, U. V. Barth, and R. V. Leeuwen, Int. J. Mod. Phys. B 13, 535 (1999).
[13] A. Stan, N. E. Dahlen, and R. van Leeuwen, J. Chem. Phys. 130, 114105 (2009).
[14] A. J. W. Thom and M. Head-Gordon, Phys. Rev. Lett. 101, 193001 (2008).
[15] B. Meredig, A. Thompson, H. A. Hansen, Wolverton, and A. van de Walle, Phys. Rev. B 82, 195128 (2010).
[16] K. Delaney, P. García-González, A. Rubio, P. Rinke, and R. W. Godby, Phys. Rev. Lett. 93, 249701 (2004).
[17] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. 93, 126406 (2004).
[18] M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007).
[19] T. H. Dunning, J. Chem. Phys. 90, 1007 (1989).
[20] M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986).
[21] V. Galitskii and M. A, Sov. Phys. JETP 7, 96 (1958).
[22] J. M. Luttinger and J. C. Ward, Phys. Rev. 118, 1417 (1960).
[23] A. Klein, Phys. Rev. 121, 950 (1961).
[24] B. Holm, Phys. Rev. Lett. 83, 788 (1999).
[25] N. E. Dahlen and R. van Leeuwen, J. Chem. Phys. 122, 164102 (2005).
[26] P. García-González and R. W. Godby, Phys. Rev. B 63, 075112 (2001).
[27] V. Blum et al., Comp. Phys. Comm. 180, 2175 (2009).
[28] X. Ren et al., submitted.
[29] See Supplemental Material at tobeaddedbypublisher.
[30] F. Caruso, X. Ren, P. Rinke, A. Rubio, and M. Scheffler, in preparation.
[31] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. p Fischer, Phys. Rev. A 47, 3649 (1993).
[32] X. Li and J. Paldus, J. Chem. Phys. 118, 2470 (2003).
[33] L. Wolniewicz, J. Chem. Phys. 99, 1851 (1993).
[34] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[35] A. Kutepov, S. Y. Savrasov, and G. Kotliar, Phys. Rev. B 80, 041103 (2009).
[36] http://cccbdb.nist.gov/
[37] X. Ren, P. Rinke, and M. Scheffler, Phys. Rev. B 80, 045402 (2009).
[38] C. Fridh, L. Asbrink, and E. Lindholm, Chem. Phys. Lett. 15, 282 (1972).

[39] B. Holm and U. von Barth, Phys. Rev. B 57, 2108 (1998).

[40] W. Ku and A. G. Eguiluz, Phys. Rev. Lett. 89, 126401 (2002).

[41] W.-D. Schöne and A. G. Eguiluz, Phys. Rev. Lett. 81, 1662 (1998).

[42] C. Friedrich, A. Schindlmayr, S. Blügel, and T. Kotani, Phys. Rev. B 74, 045104 (2006).

[43] R. Gomez-Abal, X. Li, M. Scheffler, and C. Ambrosch-Draxl, Phys. Rev. Lett. 101, 106404 (2008).

[44] C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, Phys. Rev. B 81, 085103 (2010).