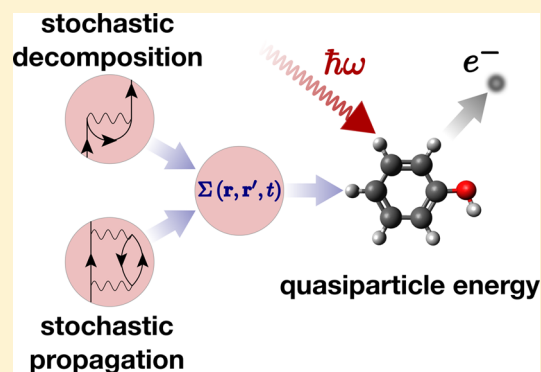


# Stochastic GW Calculations for Molecules

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**ABSTRACT:** Quasiparticle (QP) excitations are extremely important for understanding and predicting charge transfer and transport in molecules, nanostructures, and extended systems. Since density functional theory (DFT) within the Kohn–Sham (KS) formulation does not provide reliable QP energies, many-body perturbation techniques such as the GW approximation are essential. The main practical drawback of GW implementations is the high computational scaling with system size, prohibiting its use in extended, open boundary systems with many dozens of electrons or more. Recently, a stochastic formulation of GW (sGW) was presented (*Phys. Rev. Lett.* **2014**, *113*, 076402) with a near-linear-scaling complexity, illustrated for a series of silicon nanocrystals reaching systems of more than 3000 electrons. This advance provides a route for many-body calculations on very large systems that were impossible with previous approaches. While earlier we have shown the gentle scaling of sGW, its accuracy was not extensively demonstrated. Therefore, we show that this new sGW approach is very accurate by calculating the ionization energies of a group of sufficiently small molecules where a comparison to other GW codes is still possible. Using a set of 10 such molecules, we demonstrate that sGW provides reliable vertical ionization energies in close agreement with benchmark deterministic GW results (*J. Chem. Theory Comput.* **2015**, *11*, 5665), with mean (absolute) deviation of 0.05 and 0.09 eV. For completeness, we also provide a detailed review of the sGW theory and numerical implementation.



Using a set of 10 such molecules, we demonstrate that sGW provides reliable vertical ionization energies in close agreement with benchmark deterministic GW results (*J. Chem. Theory Comput.* **2015**, *11*, 5665), with mean (absolute) deviation of 0.05 and 0.09 eV. For completeness, we also provide a detailed review of the sGW theory and numerical implementation.

## 1. INTRODUCTION

First-principles electronic structure calculations play a central role in predicting and understanding the behavior of molecules, nanostructures, and materials. For the ground state, the methods of choice are density functional theory,<sup>1,2</sup> Hartree–Fock (HF), and to some extent post HF techniques such as the Möller–Plesset perturbation theory. Ground state calculations are routinely possible for extended, finite systems due to fast numerical electronic structure solvers and the increases in computational power (see ref 3 and refs therein).

For charge (quasiparticle) and neutral (optical) excitations, the calculations are computationally significantly more demanding.<sup>4–17</sup> While DFT is a theory for the ground state, recent developments using hybrid functionals<sup>18–20</sup> extend the use of DFT to describe QP excitations, even in system with thousands of electrons.<sup>21</sup> However, the description of the QP excitations within DFT hybrids lacks dynamical effects, such as screening and lifetime of the QPs. An alternative for describing electronic excitations is the many-body perturbation theory within the GW approximation for charged QPs<sup>4,22–26</sup> and BSE for QPs associated with neutral excitations.<sup>25,27–29</sup> Both approaches scale steeply with system size and therefore are very expensive for large systems.

Recently, we developed a stochastic approach for both flavors, stochastic GW (sGW)<sup>30</sup> and the stochastic Bethe–Salpeter equation (sBSE) approach.<sup>31</sup> The former scales near-linearly and the latter scales quadratically with system size. Both stochastic methods extend significantly the size of systems that can be studied within many-body perturbation techniques. Furthermore, of the two, sGW is fully ab initio and can be therefore compared to other GW formulations.

In this paper, we assess the accuracy and convergence of sGW versus other well-established codes. This is important since the GW literature contains widespread results for the same systems.<sup>32</sup> While the theoretical foundations of sGW are solid,<sup>30</sup> the approach has not been tested extensively for systems that are small enough so they can be studied by conventional deterministic programs. For this comparison, we selected a group of 10 small molecules containing first row atoms (for which experimental geometries and vertical ionization potentials are available) and compared the sGW results for vertical ionization energies to those of well-tested<sup>32</sup>

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state-of-the-art deterministic methods based on the GW implementation within TURBOMOLE<sup>14,33</sup> and FHI-aims.<sup>34,35</sup>

In section 2, we review the sGW formalism.<sup>30</sup> In section 3, we summarize the results for the subset of 10 molecules. Summary and conclusions follow in section 4.

## 2. STOCHASTIC FORMULATION OF THE $G_0W_0$ APPROXIMATION

**2.1.  $G_0W_0$  in the Energy Domain.** It is possible to write a formal equation for the QP Dyson orbitals  $\psi_n^{\text{QP}}(\mathbf{r})$  and energies  $\varepsilon_n^{\text{QP}}$ :

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi_n^{\text{QP}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r})\psi_n^{\text{QP}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r})\psi_n^{\text{QP}}(\mathbf{r}) + \int \tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \varepsilon_n^{\text{QP}})\psi_n^{\text{QP}}(\mathbf{r}')d\mathbf{r}' = \varepsilon_n^{\text{QP}}\psi_n^{\text{QP}}(\mathbf{r}) \quad (1)$$

which is similar to a Schrödinger equation, containing kinetic energy and external potential energy [ $v_{\text{ext}}(\mathbf{r})$ ] operators as well as a mean electrostatic or Hartree potential

$$v_{\text{H}}(\mathbf{r}) = \int n(\mathbf{r}')u_{\text{C}}(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}' \quad (2)$$

where  $n(\mathbf{r})$  is the ground-state density of the  $N$ -electron system and  $u_{\text{C}}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0 r}$  is the bare Coulomb potential energy. This equation also contains a nonlocal energy-dependent self-energy term  $\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \omega)$  which incorporates the many-body exchange and correlation effects into the system. Eq 1 is exact but requires the knowledge of the self-energy which cannot be obtained without imposing approximations. One commonly used approach is based on the GW approximation.<sup>22</sup> However, even this theory is extremely expensive computationally and a further simplification is required, leading to the so-called  $G_0W_0$  approximation

$$\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \omega) = i \int_{-\infty}^{\infty} \tilde{G}_0(\mathbf{r}, \mathbf{r}', \omega + \omega')\tilde{W}_0(\mathbf{r}, \mathbf{r}', \omega')\frac{d\omega'}{2\pi} \quad (3)$$

$\tilde{G}_0(\mathbf{r}, \mathbf{r}', \omega)$  is a time-ordered Green's function given by

$$\tilde{G}_0(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \hbar \sum_n \phi_n^{\text{KS}}(\mathbf{r})\phi_n^{\text{KS}}(\mathbf{r}') \times \left[ \frac{f_n}{\hbar\omega - \varepsilon_n^{\text{KS}} - i\eta} + \frac{1 - f_n}{\hbar\omega - \varepsilon_n^{\text{KS}} + i\eta} \right] \quad (4)$$

within a Kohn–Sham (KS) DFT starting point.<sup>1,2</sup>  $\phi_n^{\text{KS}}(\mathbf{r})$  and  $\varepsilon_n^{\text{KS}}$  are the real KS eigenstates and eigenvalues, respectively, of the KS Hamiltonian (henceforth, we use atomic units where  $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ )

$$\hat{h}_{\text{KS}} = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \quad (5)$$

and  $v_{\text{xc}}(\mathbf{r})$  is the exchange-correlation potential that depends on the ground state density,  $n(\mathbf{r})$ . In eq 4,  $f_n$  is the occupation of the KS level  $n$ . In eq 3,  $\tilde{W}_0(\mathbf{r}, \mathbf{r}', \omega')$  is the time-ordered screened Coulomb potential defined as

$$\tilde{W}_0(\mathbf{r}, \mathbf{r}', \omega) = \int \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)u_{\text{C}}(|\mathbf{r}'' - \mathbf{r}'|)d\mathbf{r}'' \quad (6)$$

where  $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') + \int u_{\text{C}}(|\mathbf{r} - \mathbf{r}''|)\tilde{\chi}(\mathbf{r}'', \mathbf{r}', \omega)d\mathbf{r}''$  is the frequency dependent inverse dielectric function and  $\tilde{\chi}(\mathbf{r}, \mathbf{r}', \omega)$  is the reducible polarizability.

Once the self-energy is generated via eqs 3–6, the QP energies of eq 1 can be estimated perturbatively, as a correction to the KS orbital energies. To first order:<sup>4,23</sup>

$$\varepsilon_n^{\text{QP}} = \varepsilon_n^{\text{KS}} - V_{\text{xc},n} + \tilde{\Sigma}_n(\varepsilon_n^{\text{QP}}) \quad (7)$$

where  $V_{\text{xc},n} = \int v_{\text{xc}}(\mathbf{r})|\phi_n^{\text{KS}}(\mathbf{r})|^2d\mathbf{r}$  is the expectation value of the exchange-correlation potential, and  $\tilde{\Sigma}_n(\omega)$  is the self-energy expectation value at a frequency  $\omega$ :

$$\tilde{\Sigma}_n(\omega) = \iint \phi_n^{\text{KS}}(\mathbf{r})\tilde{\Sigma}(\mathbf{r}, \mathbf{r}', \omega)\phi_n^{\text{KS}}(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (8)$$

**2.2.  $G_0W_0$  in the Time Domain.** The computational challenge of  $G_0W_0$  is to estimate the frequency-dependent function  $\tilde{\Sigma}_n(\omega)$  involving integration over 6-dimensional quantities. A simplification is achieved when we Fourier transform to the time-domain

$$\Sigma_n(t) \equiv \int_{-\infty}^{\infty} \tilde{\Sigma}_n(\omega)e^{-i\omega t}\frac{d\omega}{2\pi} \quad (9)$$

since the self-energy in the time domain is a simple product of the time domain Green's function and screened potential

$$\Sigma(\mathbf{r}, \mathbf{r}', t) = iG_0(\mathbf{r}, \mathbf{r}', t)W_0(\mathbf{r}, \mathbf{r}', t^+) \quad (10)$$

instead of the convolution in eq 3. In eq 10,  $t^+$  is a time infinitesimally later than  $t$  and  $G_0(\mathbf{r}, \mathbf{r}', t)$  is the Fourier transform of  $\tilde{G}_0(\mathbf{r}, \mathbf{r}', \omega)$ , given by

$$iG_0(\mathbf{r}, \mathbf{r}', t) = \sum_n \phi_n^{\text{KS}}(\mathbf{r})\phi_n^{\text{KS}}(\mathbf{r}')e^{-ie_n^{\text{KS}}t/\hbar} \times [(1 - f_n)\theta(t) - f_n\theta(-t)] \quad (11)$$

The time domain screened potential  $W_0(\mathbf{r}, \mathbf{r}', t)$  is the potential at point  $\mathbf{r}$  and time  $t$  due to a QP introduced at time  $t = 0$  at point  $\mathbf{r}'$ . Hence it is composed of an instantaneous Coulomb term and a time-dependent polarization contribution:

$$W_0(\mathbf{r}, \mathbf{r}', t) = u_{\text{C}}(|\mathbf{r} - \mathbf{r}'|)\delta(t) + W_{\text{p}}(\mathbf{r}, \mathbf{r}', t) \quad (12)$$

$W_{\text{p}}(\mathbf{r}, \mathbf{r}', t)$  is the polarization potential of the density perturbation due to the QP:

$$W_{\text{p}}(\mathbf{r}, \mathbf{r}', t) = \iint u_{\text{C}}(|\mathbf{r} - \mathbf{r}''|)\chi(\mathbf{r}'', \mathbf{r}', t) \times u_{\text{C}}(|\mathbf{r}'' - \mathbf{r}'|)d\mathbf{r}''d\mathbf{r}'' \quad (13)$$

which is given in terms of the time-ordered reducible polarization function  $\chi(\mathbf{r}, \mathbf{r}', t)$ . Using these definitions, we write the self-energy expectation value as a sum of instantaneous and time-dependent contributions:

$$\Sigma_n(t) = \Sigma_n^{\text{X}}\delta(t) + \Sigma_n^{\text{P}}(t) \quad (14)$$

Here, the instantaneous contribution is

$$\Sigma_n^{\text{X}} = -\iint \phi_n^{\text{KS}}(\mathbf{r})u_{\text{C}}(|\mathbf{r} - \mathbf{r}'|)\rho^{\text{KS}}(\mathbf{r}, \mathbf{r}')\phi_n^{\text{KS}}(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (15)$$

(i.e., the expectation value of the exact exchange operator), where

$$\rho^{\text{KS}}(\mathbf{r}, \mathbf{r}') = -iG_0(\mathbf{r}, \mathbf{r}', 0^-) = \sum_n f_n \phi_n^{\text{KS}}(\mathbf{r})\phi_n^{\text{KS}}(\mathbf{r}') \quad (16)$$

is the KS density matrix. Finally, the polarization self-energy is given by the integral

$$\Sigma_n^P(t) = \iint \phi_n^{\text{KS}}(\mathbf{r}) iG_0(\mathbf{r}, \mathbf{r}', t) W_p(\mathbf{r}, \mathbf{r}', t) \phi_n^{\text{KS}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (17)$$

Despite the fact that the time-dependent formalism circumvents the convolution appearing in the frequency-dependent domain, the numerical evaluation of  $\Sigma_n^P(t)$  is a significant challenge with numerical effort typically scaling proportionally to  $N_e^4$  or  $N_e^{5,11,15,36}$ . This is due to the fact that  $G_0(\mathbf{r}, \mathbf{r}', t)$  involves all (occupied and unoccupied) KS orbitals and  $W_p(\mathbf{r}, \mathbf{r}', t)$  involves 6-dimensional integrals (eq 13) depending on the reducible polarization function  $\chi(\mathbf{r}'', \mathbf{r}''', t)$ .

**2.3. Stochastic  $G_0W_0$ .** We now explain how stochastic orbitals enable an efficient near-linear-scaling calculation of  $\Sigma_n(t)$ .<sup>30</sup> The calculation uses a real space 3D Cartesian grid with equally spaced points  $\mathbf{r}_{ijk} = (i\hat{x} + j\hat{y} + k\hat{z})h$ , where  $i, j$ , and  $k$  are integers and  $h$  is the grid spacing, assumed for simplicity to be equal in the  $x, y$ , and  $z$  directions. The application of the Kohn–Sham Hamiltonian  $\hat{h}_{\text{KS}}$  onto any function on the grid can be performed using Fast Fourier Transforms in  $N_g \log N_g$  scaling, where  $N_g$  is the size of the grid.

We now introduce a real stochastic orbital  $\zeta(\mathbf{r})$  on the grid assigning randomly  $+h^{-3/2}$  or  $-h^{-3/2}$  with equal probability to  $\zeta(\mathbf{r})$  at each grid point  $\mathbf{r}$ .<sup>37,38</sup> The average of the expectation value (expressed by  $\langle \dots \rangle_\zeta$ ) of the projection  $\langle l\zeta | \langle \zeta | \rangle_\zeta$  is equal to the unit matrix,  $\langle l\zeta | \langle \zeta | \rangle_\zeta = \hat{I}$ , resulting in a “stochastic resolution of identity”.<sup>39</sup> In practical calculations the expectation values (i.e., averages over  $\zeta$ ) are estimated using a finite sample of  $N_\zeta$  random states. In accordance with the central limit theorem, this average converges to the expectation value as  $N_\zeta \rightarrow \infty$  (for a discussion of the convergence of the stochastic estimates see section 3).

With the use of the stochastic resolution of the identity, any operator can be represented as an average over a product of stochastic orbitals. For example, for the KS Green’s function:

$$iG_0(\mathbf{r}, \mathbf{r}', t) = \langle \zeta(\mathbf{r}) \zeta(\mathbf{r}', t) \rangle_\zeta \quad (18)$$

where  $\zeta(\mathbf{r}) = \langle r | \zeta \rangle$  is the real random orbital and

$$\begin{aligned} \zeta(\mathbf{r}, t) &= \langle r | i\hat{G}_0(t) | \zeta \rangle \\ &= \langle r | e^{-i\hat{h}_{\text{KS}}t/h} [\theta(t) - \theta_\beta(\mu - \hat{h}_{\text{KS}})] | \zeta \rangle \end{aligned} \quad (19)$$

is the  $G$ -operated random orbital. Here,  $\mu$  is the chemical potential,  $\theta(t)$  is the Heaviside function, and  $\theta_\beta(\epsilon) = \frac{1}{2}[1 + \text{erf}(\beta\epsilon)]$  [in the limit  $\beta \rightarrow \infty$ ,  $\theta_\beta(\epsilon) \rightarrow \theta(\beta\epsilon)$ ]. The application of  $i\hat{G}_0(t)$  on  $\zeta$  in eq 18 is performed using a Chebyshev expansion [for applying  $\theta_\beta(\mu - \hat{h}_{\text{KS}})$ ] and a split operator propagator for the time evolution, both taking advantage of the sparsity of the KS Hamiltonian in the real-space grid representation. The Chebyshev series includes a finite number of terms  $N_C \approx 2\beta\Delta E$  where  $\Delta E$  is the eigenvalue range of the KS Hamiltonian  $\hat{h}_{\text{KS}}$  and where  $\beta$  is large enough so that  $\beta E_g \gg 1$  where  $E_g$  is the occupied–unoccupied eigenvalue gap (see, e.g., refs 40 and 41).

The representation used in eq 18 decouples the position-dependence on  $\mathbf{r}$  and  $\mathbf{r}'$  and eliminates the need to represent  $iG_0(\mathbf{r}, \mathbf{r}', t)$  by all occupied and unoccupied orbitals. The polarization part of the self-energy is recast as

$$\Sigma_n^P(t) = \langle \Sigma_{n\zeta}^P(t) \rangle_\zeta$$

$$\Sigma_{n\zeta}^P(t) = \iint \phi_n^{\text{KS}}(\mathbf{r}) \zeta(\mathbf{r}, t) W_p(\mathbf{r}, \mathbf{r}', t) \phi_n^{\text{KS}}(\mathbf{r}') \zeta(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (20)$$

where  $\zeta$  is the stochastic orbital used to characterize  $G_0$ . Further simplifications are obtained by inserting yet another, independent, real stochastic orbital  $\xi(\mathbf{r})$  using the identity

$$\begin{aligned} &\phi_n^{\text{KS}}(\mathbf{r}) \zeta(\mathbf{r}, t) W_p(\mathbf{r}, \mathbf{r}', t) \\ &= \langle \int d\mathbf{r}'' \phi_n^{\text{KS}}(\mathbf{r}'') \zeta(\mathbf{r}'', t) \xi(\mathbf{r}'') \xi(\mathbf{r}) W_p(\mathbf{r}, \mathbf{r}', t) \rangle_\xi \end{aligned}$$

decoupling the two  $t$ -dependent functions. Therefore, the polarization part of the self-energy becomes an average over a product of two time-dependent stochastic functions  $A_{n\zeta\xi}(t)$  and  $B_{n\zeta\xi}(t)$ :

$$\Sigma_{n\zeta}^P(t) = \langle A_{n\zeta\xi}(t) B_{n\zeta\xi}(t) \rangle_\xi \quad (21)$$

where

$$A_{n\zeta\xi}(t) = \int \phi_n^{\text{KS}}(\mathbf{r}) \zeta(\mathbf{r}, t) \xi(\mathbf{r}) d\mathbf{r} \quad (22)$$

and

$$B_{n\zeta\xi}(t) = \iint \xi(\mathbf{r}) W_p(\mathbf{r}, \mathbf{r}', t) \phi_n^{\text{KS}}(\mathbf{r}') \zeta(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (23)$$

Calculating  $B_{n\zeta\xi}(t)$  is done efficiently using the time-dependent Hartree (TDH) method equivalent to the popular random phase approximation (RPA).<sup>42</sup> There is an important caveat, however. The real-time formulation based on TDH provides a description of the retarded  $W^r(\mathbf{r}, \mathbf{r}', t)$  rather than the time-ordered  $W_p(\mathbf{r}, \mathbf{r}', t)$  needed in eq 23. Fortunately, in linear-response, the two functions are simply related through the corresponding Fourier transforms:<sup>43</sup>

$$\tilde{B}_{n\zeta\xi}(\omega) = \text{Re}\tilde{B}_{n\zeta\xi}^r(\omega) + i \text{sign}(\omega) \text{Im}\tilde{B}_{n\zeta\xi}^r(\omega) \quad (24)$$

where  $\tilde{B}_{n\zeta\xi}^r$  is obtained with  $W^r(\mathbf{r}, \mathbf{r}', t)$ . Consequently, we first provide a formulation for  $B_{n\zeta\xi}^r(t)$  and then, as mentioned, use eq 24 to obtain the corresponding time-ordered function  $B_{n\zeta\xi}(t)$ .

$B_{n\zeta\xi}^r(t)$  are obtained by combining the linear response relation eq 13 (with  $\chi^r$  replacing  $\chi$ ) with the definition eq 23, yielding

$$B_{n\zeta\xi}^r(t) = \iint \xi(\mathbf{r}) u_C(|\mathbf{r} - \mathbf{r}'|) \Delta n_{n\zeta}^r(\mathbf{r}', t) d\mathbf{r} d\mathbf{r}' \quad (25)$$

which is calculated in near linear-scaling (rather than quadratic-scaling) using Fast Fourier Transforms for the convolutions. Here,  $\Delta n_{n\zeta}^r(\mathbf{r}, t)$  is formally given by

$$\Delta n_{n\zeta}^r(\mathbf{r}, t) = \int \chi^r(\mathbf{r}, \mathbf{r}', t) v_{n\zeta}(\mathbf{r}') d\mathbf{r}' \quad (26)$$

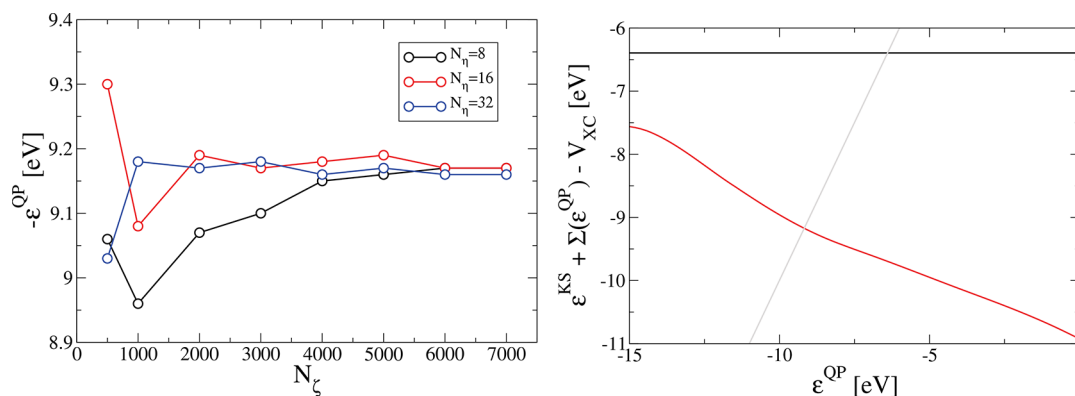
with

$$v_{n\zeta}(\mathbf{r}') = \int u_C(|\mathbf{r}' - \mathbf{r}''|) \phi_n^{\text{KS}}(\mathbf{r}'') \zeta(\mathbf{r}'') d\mathbf{r}'' \quad (27)$$

In practice, we calculate the density perturbation by taking  $N_\eta$  stochastic orbitals  $\bar{\eta}(\mathbf{r})$  which are projected on the occupied space using the Chebyshev expansion of the operator  $\theta_\beta(\mu - \hat{h}_{\text{KS}})$ ,

$$\eta = \theta_\beta(\mu - \hat{h}_{\text{KS}}) \bar{\eta} \quad (28)$$

Each orbital is then perturbed at time zero:



**Figure 1.** (Left) Convergence of the sGW estimate of the QP hole energy for a benzene molecule as a function of  $N_\zeta$  for different values of  $N_\eta$ . (Right) A graphic representation of the self-consistent solution of eq 7 for  $-IP = \epsilon_n^{\text{QP}}$  of benzene. The solid red line represents the right-hand side of eq 7. The intersect with the solid grey line represents the self-consistent solution. For reference, we also depict  $\epsilon_n^{\text{KS}}$  (solid black line).

$$\eta_\tau(\mathbf{r}, 0) = e^{-i\nu_{\zeta}(\mathbf{r})\tau} \eta(\mathbf{r}) \quad (29)$$

where  $\tau$  is a small-time parameter. In the RPA, the orbital is now propagated in time by a TDH equation similar to the stochastic time-dependent DFT:<sup>44</sup>

$$i \frac{\partial}{\partial t} \eta_\tau(\mathbf{r}, t) = \hat{h}_{\text{KS}}^r \eta_\tau(\mathbf{r}, t) + \left( \int \frac{\Delta n_{n\zeta}^r(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \eta_\tau(\mathbf{r}, t) \quad (30)$$

where

$$\Delta n_{n\zeta}^r(\mathbf{r}, t) = \frac{1}{\tau} \langle |\eta_\tau(\mathbf{r}, t)|^2 - |\eta_{\tau=0}(\mathbf{r}, t)|^2 \rangle_\eta \quad (31)$$

From  $\Delta n_{n\zeta}^r(\mathbf{r}, t)$ , we then evaluate  $B_{n\zeta\xi}^r(t)$  via eq 28, and then Fourier transform the coefficients from time to frequency and back via eq 24 to yield the required  $B_{n\zeta\xi}(t)$ .

Finally, the exchange part of the self-energy is simplified, by replacing the 6-dimensional integral in eq 15 by two 3-dimensional integrals involving projected occupied orbitals

$$\Sigma_n^X = -\langle \int \phi_n^{\text{KS}}(\mathbf{r}) \eta(\mathbf{r}) v_\eta^{\text{aux}}(\mathbf{r}) d\mathbf{r} \rangle_\eta \quad (32)$$

where the auxiliary potential is

$$v_\eta^{\text{aux}}(\mathbf{r}) = \int u_C(|\mathbf{r} - \mathbf{r}'|) \eta(\mathbf{r}) \phi(\mathbf{r}') d\mathbf{r}' \quad (33)$$

Note that we are allowed to use the same projected states  $\eta$  obtained from eq 28 also for calculating the exchange part, which is therefore obtained automatically as a byproduct of the polarization self-energy with essentially no extra cost.

**2.4. Algorithm.** We summarize the procedure above by the following algorithm for computing the sGW QP energies:

- (1) Generate a stochastic orbital  $\zeta(\mathbf{r})$  and  $N_\xi$  stochastic orbitals  $\xi(\mathbf{r})$ . Use eq 19 to generate the projected time-dependent orbital  $\zeta(\mathbf{r}, t)$ .
- (2) Generate the set of  $N_\xi$  time-dependent functions  $A_{n\zeta\xi}(t)$  from eq 22 using  $\xi(\mathbf{r})$  and  $\zeta(\mathbf{r}, t)$ .
- (3) Generate  $N_\eta$  independent stochastic orbitals, project each of them to the occupied subspace according eq 28, obtaining the projected  $N_\eta$  functions  $\eta(\mathbf{r})$  from which  $\Sigma_n^X$  is computed using eqs 32 and 33.
- (4) Then use the same  $N_\eta$  projected stochastic functions  $\eta(\mathbf{r})$  together with  $\zeta(\mathbf{r})$  and the set of  $\xi(\mathbf{r})$  to generate  $B_{n\zeta\xi}^r(t)$  using eqs 23–31, where  $n_{n\zeta}^r(\mathbf{r}, t)$  is obtained as an average over  $\eta$ .

- (5) Fourier transform  $B_{n\zeta\xi}^r(t) \rightarrow \tilde{B}_{n\zeta\xi}^r(\omega)$  and converts to the time-ordered quantity  $\tilde{B}_{n\zeta\xi}^r(\omega)$  using eq 24. Fourier transform back  $\tilde{B}_{n\zeta\xi}^r(\omega) \rightarrow B_{n\zeta\xi}^r(t)$  and calculate, by averaging on  $\xi$ , the polarization self-energy  $\Sigma_{n\zeta}^P(t)$  using eq 23.

- (6) Repeat steps 1–5  $N_\zeta$  times, averaging

$$\Sigma_n^P(t) = \frac{1}{N_\zeta} \sum_\zeta [\Sigma_{n\zeta}^P(t)] \text{ and similarly averaging } \Sigma_n^X.$$

- (7) Fourier transform  $\Sigma_n^P(t) \rightarrow \tilde{\Sigma}_n^P(\omega)$  and using this function estimate the QP energy  $\epsilon_n^{\text{QP}}$  by solving eq 7 self-consistently.

In practice, the stochastic error is then estimated by dividing the set of  $N_\zeta$  calculations to e.g., 100 subsets (in each of which we use  $\frac{N_\zeta}{100}$  stochastic orbitals) and then estimating the error based on the values of  $\epsilon_n^{\text{QP}}$  from each of the 100 subsets.

### 3. RESULTS

We now evaluate the performance of sGW by application to a set of 10 small enough molecules for which reliable deterministic calculations and experimental vertical ionization energies are available. The sGW calculation is based on the local density approximation, denoted henceforth as  $\epsilon_n^{\text{sGW}}_{\text{@LDA}}$  and implemented on a Fourier real-space grid using Troullier-Martins pseudopotentials<sup>45</sup> and the technique for screening periodic charge images of ref 46. For all molecules, experimental geometries were used, taken from the NIST database.<sup>47</sup>

The sGW estimate of  $\epsilon_n^{\text{sGW}}_{\text{@LDA}}$  is governed by convergence of multiple parameters. The grid spacing was determined in the preparatory DFT step by requiring convergence of the LDA eigenvalues to better than 1 meV (our LDA eigenvalues deviate by 0.03 eV or less from those obtained by the QuantumE-spresso program using the same pseudopotentials). For all molecules, we chose the inverse temperature parameter as  $\beta = 200E_h^{-1}$  from which the Chebyshev expansion length  $N_C$  was derived to be between 18000 and 19000 (see discussion appearing below eq 19). The time propagation is performed using a discretized time-step of  $\Delta t = 0.05E_h^{-1}\hbar$  for both the Green's function calculation as well as the RPA screening; we checked that this leads to QP energies converged to within less than 0.02 eV.

Other parameters only negligibly influence the result. Specifically, the strength of the perturbation was controlled by the parameter  $\tau$  (see eq 29); changing its value between 0.01



Table 1. Vertical Ionization Energies (eV) for the Indicated Molecules<sup>a</sup>

| system            | exp.  | $-\epsilon_{@PBE}^{EXTRA}$ | $-(\epsilon_{@LDA}^{RI} - \epsilon_{@PBE}^{RI})$ | $-\epsilon_{@LDA}^{EXTRA}$ | $-\epsilon_{@LDA}^{sGW}$ | diff  | $h/a_0$ | $N_\zeta$ |
|-------------------|-------|----------------------------|--|----------------------------|--------------------------|-------|---------|-----------|
| benzene           | 9.23  | 9.10(0.01)                 | 0.03   | 9.13                       | 9.17(0.03)               | 0.04  | 0.30    | 6000      |
| cyclooctatetraene | 8.43  | 8.18(0.02)                 | 0.02   | 8.20                       | 8.33(0.03)               | 0.13  | 0.35    | 6000      |
| acetaldehyde      | 10.20 | 9.66(0.03)                 | 0.08   | 9.74                       | 9.90(0.06)               | 0.16  | 0.30    | 8000      |
| water             | 12.60 | 12.05(0.03)                | 0.08   | 12.13                      | 12.10(0.07)              | -0.04 | 0.25    | 14000     |
| phenol            | 8.75  | 8.51(0.01)                 | 0.05   | 8.56                       | 8.61(0.03)               | 0.05  | 0.35    | 9000      |
| urea              | 10.15 | 9.46(0.02)                 | 0.12   | 9.58                       | 9.65(0.05)               | 0.07  | 0.30    | 11000     |
| methane           | 14.40 | 14.00(0.06)                | 0.03   | 14.03                      | 14.09(0.01)              | 0.06  | 0.40    | 10000     |
| nitrogen          | 15.60 | 15.05(0.04)                | 0.11   | 15.16                      | 15.05(0.06)              | -0.11 | 0.35    | 7000      |
| ethylene          | 10.70 | 10.40(0.03)                | 0.03   | 10.43                      | 10.40(0.06)              | -0.03 | 0.35    | 12000     |
| pyridine          | 9.50  | 9.17(0.01)                 | 0.06   | 9.23                       | 9.42(0.04)               | 0.19  | 0.35    | 7000      |
|                   |       |                            |  |                            | mean:                    | 0.05  |         |           |
|                   |       |                            |  |                            | mean Abs:                | 0.09  |         |           |

<sup>a</sup>The complete-basis-set-limit-extrapolated GW@PBE result,  $\epsilon_{@PBE}^{EXTRA}$  (with extrapolation uncertainties in parentheses) is taken from ref 32.  $\epsilon_{@LDA}^{RI} - \epsilon_{@PBE}^{RI}$  is the estimated GW@LDA to GW@PBE difference, calculated using GW-TURBOMOLE<sup>14</sup> within the RI approximation and the def2-QZVP basis-set. The extrapolated GW@LDA results  $\epsilon_{@LDA}^{EXTRA}$  represent our estimate of the fully converged GW@LDA energies (given in eq 34) which are used to benchmark the sGW@LDA energies  $\epsilon_{@LDA}^{sGW}$  (with statistical uncertainties given in parentheses). For each molecule, the grid spacing  $h$  and the number of stochastic orbitals  $N_\zeta$  required for producing converged sGW to the indicated accuracy are given in the table.

to  $0.0001 E_h^{-1} \hbar$  influences the QP energy by less than 0.001 eV. In practice, we employ  $\tau = 0.001 E_h^{-1} \hbar$ . Furthermore, we used  $N_\xi = 100$  and ascertained that increasing this value to 200 causes changes in the QP energies smaller than 0.01 eV.

The most influential parameters are  $N_\eta$ , the number of stochastic states  $\eta$  used for the RPA screening calculation, and  $N_\zeta$  used for representing the Green's function. In the left panel of Figure 1, the convergence of the QP energy for a benzene molecule is illustrated as a function of  $N_\zeta$  for several values of  $N_\eta$ . Evidently, for this molecule,  $N_\zeta = 6000$  and  $N_\eta = 8$  are sufficient to converge the QP energy with a statistical error of  $\pm 0.03$  eV. Note that as  $N_\eta$  increases, the convergence toward the final QP value is reached after a smaller number of  $N_\zeta$  stochastic orbitals.

When transforming from the time to the frequency domain, we use a Gaussian damping factor,  $\tilde{B}_{n\zeta}^r(\omega) = \int_0^T dt e^{i\omega t} B_{n\zeta}^r(t) \times e^{-(\gamma t)^2/2}$ , where  $\gamma = 0.04 E_h \hbar^{-1}$  and  $T \approx 4/\gamma = 100 \hbar E_h^{-1}$  are enough to yield QP energies converged to within 0.01 eV. Note that a value of  $N_\eta = 8$  is sufficient for a stable and accurate time propagation up to  $T = 100 \hbar E_h^{-1}$  but when longer times  $T$  are used,  $N_\eta$  must be increased accordingly due to an instability in stochastic TDDFT time propagation.<sup>31</sup>

The right panel of Figure 1 provides a graphic representation of the self-consistent solution of eq 7 as the intersect between  $\epsilon^{QP}$  and  $\epsilon^{KS} + \Sigma(\epsilon^{QP}) - V_{XC}$ . Note that even though the stochastic calculation has by its nature fluctuations, the energy dependence of  $\Sigma(\epsilon^{QP})$  is smooth.

The sGW estimated vertical ionization energies  $\epsilon_{@LDA}^{sGW}$  were converged with respect to all parameters described above and especially, grid-size and number of stochastic orbitals  $N_\zeta$ . Hence, they should be compared to deterministic GW results, which are of a complete basis set quality at the GW@LDA level, denoted  $\epsilon_{@LDA}^{EXTRA}$ , extrapolated to the complete basis set limit. These results were based on the GW@PBE extrapolated results  $\epsilon_{@PBE}^{EXTRA}$  calculated under the FHI-aims code<sup>34,35</sup> as given in ref 32, which were then augmented for LDA-based energies using the relation:

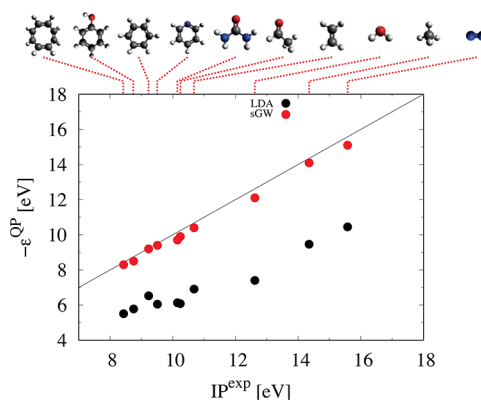
$$\epsilon_{@LDA}^{EXTRA} \equiv \epsilon_{@PBE}^{EXTRA} + (\epsilon_{@LDA}^{RI} - \epsilon_{@PBE}^{RI}) \quad (34)$$

where  $\epsilon_{@LDA}^{RI} - \epsilon_{@PBE}^{RI}$  is an estimate of the difference between PBE- and LDA-based GW results (typically a very small energy in the range of 0.01–0.08 eV).  $\epsilon_{@LDA}^{RI}$  and  $\epsilon_{@PBE}^{RI}$  are the GW-

TURBOMOLE<sup>14</sup> energies calculated using the def2-QZVP basis-set and the resolution-of-identity (RI) approximation. The switch between FHI-aims code and GW-TURBOMOLE codes is not expected to pose a problem since both give almost identical excitation energies.<sup>32</sup> We have also ascertained, using several tests on small molecules, that  $\epsilon_{@LDA}^{RI} - \epsilon_{@PBE}^{RI}$  is quite independent of the RI approximation (even though RI does affect the separate values of each energy).

In Table 1, we compare the GW and sGW LDA-based vertical ionization energies, showing a high level of agreement, with mean and absolute deviations of 0.05 and 0.09 eV, respectively, typically on the order of the given uncertainties in the deterministic and the stochastic calculations.

We also note that both these values are also in good overall agreement with experimental values, as seen in Figure 2, although both results (stochastic or deterministic) generally



**Figure 2.** Ionization potentials as predicted by various calculations for the set of molecules listed in Table 1 are plotted against experimental values (note that the sGW statistical error bars are smaller than the corresponding symbol sizes). Each molecule is depicted above the graph and dotted red line points to its experimental ionization potential on the horizontal axis. The sketches of the individual molecules use black, white, blue, and red spheres to indicate positions of C, H, N, and O atoms, respectively. LDA results that served as a starting point for the calculations are shown by black circles.  $G_0W_0$  results are given by filled red circles. The black line represents the one-to-one correspondence to experimental values.

underestimate the experiment by 0.1–0.5 eV. This is primarily due to the known limitations of the  $G_0W_0$  approach, which can be improved using self-consistent-GW.<sup>6,13,17,48</sup>

#### 4. CONCLUSIONS

In conclusion, we reviewed in detail the sGW method and its algorithmic implementation. The sGW exhibits a near-linear scaling with system size complexity<sup>30</sup> and hence for large systems, it is expected to be much faster relative to the deterministic basis-set implementations having quartic or quintic<sup>14</sup> asymptotic scaling. Therefore, comparison of sGW estimations with those of deterministic GW can only be made on relatively small molecules, and here we selected a set of 10 such molecules having  $N_e = 10$ –50 electrons. For this set, sGW and deterministic GW predicted vertical ionization energies which were very close, with maximal deviation smaller than 0.2 eV and average and absolute deviations of 0.05 and 0.1 eV.

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##### Notes

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