A Finite-field Approach for $GW$ Calculations

Beyond the Random Phase Approximation

He Ma,†‡ Marco Govoni,†¶ Francois Gygi,§ and Giulia Galli*,†‡¶

†Institute for Molecular Engineering, University of Chicago, Chicago, USA.
‡Department of Chemistry, University of Chicago, Chicago, USA.
¶Materials Science Division, Argonne National Laboratory, Chicago, USA.
§Department of Computer Science, University of California Davis, Davis, USA.

E-mail: gagalli@uchicago.edu

Abstract

We describe a finite-field approach to compute density response functions, which allows for efficient $G_0W_0$ and $G_0W_0\Gamma_0$ calculations beyond the random phase approximation. The method is easily applicable to density functional calculations performed with hybrid functionals. We present results for the electronic properties of molecules and solids and we discuss a general scheme to overcome slow convergence of quasiparticle energies obtained from $G_0W_0\Gamma_0$ calculations, as a function of the basis set used to represent the dielectric matrix.
1 Introduction

Accurate, first principles predictions of the electronic structure of molecules and materials are important goals in chemistry, condensed matter physics and materials science. In the past three decades, density functional theory (DFT) has been successfully adopted to predict numerous properties of molecules and materials. In principle, any ground or excited state properties can be formulated as functionals of the ground state charge density. In practical calculations, the ground state charge density is determined by solving the Kohn-Sham (KS) equations with approximate exchange-correlation functionals, and many important excited state properties are not directly accessible from the solution of the KS equations. The time-dependent formulation of DFT (TDDFT) provides a computationally tractable method to compute excitation energies and absorption spectra. However, using the common adiabatic approximation to the exchange-correlation functional, TDDFT is often not sufficiently accurate to describe certain types of excited states such as Rydberg and charge transfer states, especially when semi-local functionals are used.

A promising approach to predict excited state properties of molecules and materials is the many-body perturbation theory (MBPT). Within MBPT, the GW approximation can be used to compute quasiparticle energies that correspond to photoemission and inverse photoemission measurements; furthermore, by solving the Bethe-Salpeter equation (BSE), one can obtain neutral excitation energies corresponding to optical spectra. For many years since the first applications of MBPT, its use has been hindered by its high computational cost. In the last decade, several advances have been proposed to improve the efficiency of MBPT calculations, which are now applicable to simulations of relatively large and complex systems, including nanostructures and heterogeneous interfaces. In particular, GW and BSE calculations can be performed using a low rank representation of density response functions, whose spectral decomposition is obtained through iterative diagonalization using density functional perturbation theory (DFPT). This method does not
require the explicit calculation of empty electronic states and avoids the inversion or storage of large dielectric matrices. The resulting implementation in the WEST code has been successfully applied to investigate various systems including defects in semiconductors, nanoparticles, aqueous solutions, and solid/liquid interfaces.

In this work, we developed a finite-field (FF) approach to evaluate density response functions, which enters the definition of the screened Coulomb interaction $W$. The FF approach can be used as an alternative to DFPT, and presents the additional advantage of being applicable, in a straightforward manner, to both semilocal and hybrid functionals. In addition, FF calculations allow for the direct evaluation of density response functions beyond the random phase approximation (RPA).

Here we first benchmark the accuracy of the FF approach for the calculation of various density response functions, from which one can obtain the exchange correlation kernel ($f_{xc}$), defined as the functional derivative of the exchange-correlation potential with respect to the charge density. Then we discuss $G_0W_0$ calculations for various molecules and solids, carried out with either semi-local or hybrid functionals, and by adopting different approximations to include vertex corrections in the self-energy. In the last two decades a variety of methods have been proposed to carry out vertex-corrected $GW$ calculations, with different approximations to the vertex function $\Gamma$ and including various levels of self-consistency between $G$, $W$ and $\Gamma$. Here we focus on two formulations that are computationally tractable also for relatively large systems, denoted as $G_0W_0^{fxc}$ and $G_0W_0\Gamma_0$. In $G_0W_0^{fxc}$, $f_{xc}$ is included in the evaluation of the screened Coulomb interaction $W$; in $G_0W_0\Gamma_0$, $f_{xc}$ is included in the calculation of both $W$ and the self-energy $\Sigma$ through the definition of a local vertex function. Most previous $G_0W_0^{fxc}$ and $G_0W_0\Gamma_0$ calculations were restricted to the use of the LDA functional, for which an analytical expression of $f_{xc}$ is available. A work from Paier et al. reported $GW_0^{fxc}$ results for solids with HSE03 range-separated hybrid functional, with the exact exchange part of $f_{xc}$ defined through the nanoquanta kernel. In this work semilocal and hybrid functionals are treated in equal footing, and we present calculations...
using LDA, PBE, and PBE0 functional, as well as a dielectric-dependent hybrid (DDH) functional for solids.

A recent study of Thygesen and co-workers reported basis set convergence issues when performing $G_0W_0 \Gamma_0$@LDA calculations, which could be overcome by applying a proper renormalization to the short-range component of $f_{xc}$. In our work we generalized the renormalization scheme of Thygesen et al. to functionals other than LDA, and we show that the convergence of $G_0W_0 \Gamma_0$ quasiparticle energies is significantly improved using the renormalized $f_{xc}$.

The rest of the paper is organized as follows. In Sec. 2 we describe the finite-field approach and benchmark its accuracy. In Sec. 3 we describe the formalism used to perform $GW$ calculations beyond the RPA, including a renormalization scheme for $f_{xc}$, and we compare the quasiparticle energies obtained from different $GW$ approximations (RPA or vertex-corrected) for molecules in the GW100 test set and for several solids. Finally, we summarize our results in Sec. 4.
2 The finite field approach

We first describe the FF approach for iterative diagonalization of density response functions and we then benchmark its robustness and accuracy.

2.1 Formalism

Our $G_0W_0$ calculations are based on DFT single-particle energies and wavefunctions, obtained by solving the Kohn-Sham (KS) equations:

$$H_{KS}\psi_m(r) = \varepsilon_m \psi_m(r),$$

where the KS Hamiltonian $H_{KS} = T + V_{SCF} = T + V_{\text{ion}} + V_{H} + V_{xc}$. $T$ is the kinetic energy operator; $V_{SCF}$ is the KS potential that includes the ionic $V_{\text{ion}}$, the Hartree $V_{H}$ and the exchange-correlation potential $V_{xc}$. The charge density is given by $n(r) = \sum_m |\psi_m(r)|^2$. For simplicity we suppressed the spin index.

We consider the density response function (polarizability) of the KS system $\chi_0(r, r')$ and that of the physical system $\chi(r, r')$; the latter is denoted as $\chi_{\text{RPA}}(r, r')$ when the random phase approximation (RPA) is used. The variation of the charge density due to either a variation of the KS potential $\delta V_{\text{SCF}}$ or the external potential $\delta V_{\text{ext}}$ is given by:

$$\delta n(r) = \int K(r, r') \delta V(r') dr' ,$$

where $K = \chi_0(r, r')$ if $\delta V(r') = \delta V_{\text{SCF}}(r')$ and $K = \chi(r, r')$ if $\delta V(r') = \delta V_{\text{ext}}(r')$. The density response functions of the KS and physical system are related by a Dyson-like equation:

$$\chi(r, r') = \chi_0(r, r') + \int dr'' \int dr''' \chi_0(r, r'') [v_c(r'', r''') + f_{xc}(r'', r''')] \chi(r''', r')$$

where $v_c(r, r') = \frac{1}{|r-r'|}$ is the Coulomb kernel and $f_{xc}(r, r') = \frac{\delta V_{xc}(r)}{\delta n(r')}$ is the exchange-
correlation kernel.

Within the RPA, \( f_{xc} \) is neglected and \( \chi(r, r') \) is approximated by:

\[
\chi_{\text{RPA}}(r, r') = \chi_0(r, r') + \int dr'' \int dr''' \chi_0(r, r'') v_c(r'', r''') \chi(r'''', r').
\]  (4)

In the plane-wave representation (for simplicity we only focus on the \( \Gamma \) point of the Brillouin zone), \( v_c(G, G') = \frac{4\pi \delta(G, G')}{|G|^2} \) (abbreviated as \( v_c(G) = \frac{4\pi}{|G|^2} \)), and the dimensionless response function \( \tilde{K}(G, G') \), obtained by symmetrizing \( K(G, G') \) with respect to \( v_c \), is defined as:

\[
\tilde{K}(G, G') = v_c^\frac{1}{2}(G') K(G, G') v_c^\frac{1}{2}(G').
\]  (5)

In the formalism which we adopted to perform \( GW \) calculations without empty states, one needs to compute a low rank decomposition of \( \tilde{K} \):

\[
\tilde{K} = \sum_{i}^{N_{\text{PDEP}}} \lambda_i |\xi_i\rangle \langle \xi_i|
\]  (6)

where \( \lambda \) and \( |\xi\rangle \) denote eigenvalue and eigenvectors of \( \tilde{K} \), respectively. The set of \( \xi \) constitute the projective dielectric eigenpotential (PDEP) basis,\textsuperscript{17,19} and the accuracy of the low rank decomposition is controlled by \( N_{\text{PDEP}} \), the size of the PDEP basis. \( \lambda \) and \( |\xi\rangle \) are obtained through iterative diagonalization, e.g. with the Davidson algorithm,\textsuperscript{58} which requires to evaluate the action of \( \tilde{K} \) on an arbitrary function \( \xi \):

\[
(\tilde{K}\xi)(G') = \sum_{G''} v_c^\frac{1}{2}(G') K(G, G') v_c^\frac{1}{2}(G'') \xi(G'')
= v_c^\frac{1}{2}(G') \mathcal{F}^{-1} \left\{ \int K(r, r') \left( \mathcal{F}^{-1} \left[ v_c^\frac{1}{2}(G'') \xi(G'') \right] \right) (r') dr' \right\} (G)
\]  (7)

where \( \mathcal{F} \) and \( \mathcal{F}^{-1} \) denote forward and inverse Fourier transforms, respectively.

Defining \( \delta V(G') = v_c^\frac{1}{2}(G') \xi(G') \), the calculations of the real space integral in Eq. 7 is
equivalent to solving for the variation of the charge density $\delta n$ due to $\delta V$:

$$\int K(r, r') \left( F T^{-1} \left[ \frac{\mathcal{F}}{i} (G') \xi(G') \right] \right) (r') dr' = \int K(r, r') \delta V(r') dr' \equiv \delta n(r).$$  \hspace{1cm} (8)

In Ref. 19, $\delta n(r)$ is solved using DFPT for the case of $K = \chi_0$. In this work we solved Eq. 8 by a finite-field approach. In particular, two SCF calculations are performed under the action of the potentials $\pm \delta V$:

$$(H_{KS} \pm \delta V) \psi_m^\pm(r) = \varepsilon_m^\pm \psi_m^\pm(r),$$  \hspace{1cm} (9)

and $\delta n(r)$ is computed as:

$$\delta n(r) = \frac{1}{2} \left[ \sum_{m \text{occ.}} |\psi_m^+(r)|^2 - \sum_{m \text{occ.}} |\psi_m^-(r)|^2 \right]$$  \hspace{1cm} (10)

where a central difference instead of forward/backward difference is performed in Eq. 10 to increase the numerical accuracy of the computed $\delta n(r)$.

Self-consistent solutions of Eq. 8-10 correspond to considering $K = \chi$ in Eq. 12. If $V_{xc}$ is kept fixed during the SCF iterations, the solution of Eq. 10 corresponds to $K = \chi_{RPA}$. If both $V_{xc}$ and $V_H$ are kept fixed during the SCF iterations, the solution of Eq. 10 corresponds to $K = \chi_0$.

The response functions $\tilde{\chi}_{RPA}$ and $\tilde{\chi}_0$ (see Eq. 4) have the same eigenvectors, and their eigenvalues are related by:

$$\lambda_{\chi_{RPA}}^i = \frac{\lambda_0^i}{1 - \lambda_0^i},$$  \hspace{1cm} (11)

where $\lambda_{\chi_{RPA}}^i$'s and $\lambda_0^i$'s are eigenvalues of $\tilde{\chi}_{RPA}$ and $\tilde{\chi}_0$, respectively. In general the eigenvalues and eigenvectors of $\tilde{\chi}_{RPA}$ are different from those of $\tilde{\chi}$ due to the presence of $f_{xc}$ in Eq. 3.

In comparison to DFPT, the finite-field approach adopted here allows for the straightforward calculation of response functions beyond the RPA (i.e. for the calculation of $\chi$ instead
of $\chi_0$ or $\chi_{\text{RPA}}$, and it can be readily applied to hybrid functionals for which analytical expressions of $f_{\text{xc}}$ are not available. We note that finite-field calculations with hybrid functionals can easily benefit from any methodological development that reduces the computational complexity of evaluating exact exchange potentials.\[40]-[61]

Once the PDEP basis is obtained by iterative diagonalization of $\tilde{\chi}_0$, the projection of $\tilde{\chi}$ on the PDEP basis can be performed using the finite field approach as well. Then the symmetrized exchange-correlation kernel $\tilde{f}_{\text{xc}} = \frac{1}{2} f_{\text{xc}} \frac{1}{v_c} - \frac{1}{2} f_{\text{xc}} \frac{1}{v_c}$ can be computed by inverting the Dyson-like equation (Eq. 3):

$$\tilde{f}_{\text{xc}} = \tilde{\chi}_0^{-1} - \tilde{\chi}^{-1} - 1.$$ (12)

On the right hand side of Eq. 12 all matrices are $N_{\text{PDEP}} \times N_{\text{PDEP}}$ and therefore the resulting $\tilde{f}_{\text{xc}}$ is also defined on the PDEP basis.

When using orbital-dependent functionals such as meta-GGA and hybrid functionals, the $\tilde{f}_{\text{xc}}$ computed from Eq. 12 needs to be interpreted with caution. In this case, DFT calculations for $H_{\text{KS}} \pm \delta V$ can be performed using either the optimized effective potential (OEP) or the generalized Kohn-Sham (GKS) scheme. In the OEP scheme, $v_{\text{xc}}$ is local in space and $f_{\text{xc}}(r, r') = \frac{\delta V_{\text{xc}}(r)}{\delta n(r')} \frac{1}{\delta n(r')}$ depends on $r$ and $r'$, as in the case of semi-local functionals. In the GKS scheme, $V_{\text{xc}}$ is non-local and $f_{\text{xc}}(r, r'; r''; r''') = \frac{\delta V_{\text{xc}}(r, r')}{\delta n(r''')} \frac{1}{\delta n(r''')}$ depends on three position vectors. We expect $\delta n$ to be almost independent of the chosen scheme, whether GKS or OEP, since both methods yield the same result within first order in the charge density.\[63]

We conducted hybrid functional calculations within the GKS scheme, assuming that for every GKS calculation an OEP can be defined yielding the same charge density; with this assumption the $f_{\text{xc}}$ from Eq. 12 is well defined within the OEP formalism.

### 2.2 Implementation and Verification

We implemented the finite-field algorithm described above by coupling the WEST\[19] and Qbox\[64] codes in client-server mode, using the workflow summarized in Fig 1. In particular,
in our implementation the WEST code performs an iterative diagonalization of $\tilde{K}$ by outsourcing the evaluation of the action of $\tilde{K}$ on an arbitrary function to Qbox, which performs DFT calculations in finite field. The two codes communicate through the filesystem.

Figure 1: Workflow of finite-field calculations. The WEST code performs an iterative diagonalization of $\tilde{K}$ ($\tilde{\chi}_0$, $\tilde{\chi}_{\text{RPA}}$, $\tilde{\chi}$). In GW calculations beyond the RPA, $f_{xc}$ is computed from Eq. 12 which requires computing the spectral decomposition of $\tilde{\chi}_0$ and evaluating $\tilde{\chi}$ in the space of $\tilde{\chi}_0$ eigenvectors. Finite-field calculations are carried out by the Qbox code, and the communications of $\delta n$ and $\delta V$ between WEST and Qbox is carried through the filesystem.

To verify the correctness of our implementation, we computed $\tilde{\chi}_0$, $\tilde{\chi}_{\text{RPA}}$, $\tilde{\chi}$ for selected molecules in the GW100 set and we compared the results to those obtained with DFPT. Sec. 1 of the SI summarizes the parameters used ($E_{\text{cut}}$, $N_{\text{PDEP}}$, etc.). In finite-field calculations we optimized the ground state wavefunction using a preconditioned steepest descent algorithm with Anderson acceleration. The magnitude of $\delta V$ was chosen to insure that calculations were performed within the linear response regime (see Sec. 2 of the SI). All calculations presented in this section were performed with the PBE functional unless otherwise specified.

Fig 2a shows the eigenvalues of $\tilde{\chi}_{\text{RPA}}$ for a few molecules obtained with three approaches: iterative diagonalization of $\tilde{\chi}_{\text{RPA}}$ with the finite-field approach; iterative diagonalization of $\tilde{\chi}_0$ with either the finite-field approach or with DFPT, followed by a transformation of
The three approaches yield almost identical eigenvalues. Figure 2: Comparison of the eigenvalues(a) and eigenfunctions(b) of $\tilde{\chi}_{\text{RPA}}$ obtained from DFPT and finite-field (FF) calculations. Three approaches are used: diagonalization of $\tilde{\chi}_0$ by DFPT, diagonalization of $\tilde{\chi}_0$ by FF (denoted by FF(0)) and diagonalization of $\tilde{\chi}_{\text{RPA}}$ by FF (denoted by FF(RPA)). In the case of DFPT and FF(0), Eq. [11] was used to obtain the eigenvalues of $\tilde{\chi}_{\text{RPA}}$ from those of $\tilde{\chi}_0$. In (b) we show the first $32 \times 32$ elements of the $\langle \xi_{i}^{\text{DFPT}} | \xi_{j}^{\text{FF}(0)} \rangle$ and $\langle \xi_{i}^{\text{DFPT}} | \xi_{j}^{\text{FF}(RPA)} \rangle$ matrices (see Eq. [6]).

The eigenvectors of the response functions are shown in Fig. 2, where we report elements of the matrices defined by the overlap between finite-field and DFPT eigenvectors. The inner product matrices are block-diagonal, with blocks corresponding to the presence of degenerate
eigenvalues. The agreement between eigenvalues and eigenvectors shown in Fig. 2 verifies the accuracy and robustness of finite-field calculations.

Fig. 3 shows the eigendecomposition of $\tilde{\chi}$ compared to that of $\tilde{\chi}_{\text{RPA}}$.

![Figure 3: Comparison of eigenvalues(a) and eigenfunctions(b) of $\tilde{\chi}$ and $\tilde{\chi}_{\text{RPA}}$ obtained from finite-field calculations. In (b), the first 32 x 32 elements of the $\langle \xi_{\text{RPA}} | \xi_{\text{full}} \rangle$ matrices are presented.](image)

As indicated by Fig. 3a, including $f_{xc}$ in $\chi$ results in a stronger screening. The eigenvalues of $\tilde{\chi}$ are systematically more negative than those of $\tilde{\chi}_{\text{RPA}}$, though they asymptotically converge to zero in the same manner. While the eigenvalues are different, the eigenvectors (eigenspaces in the case of degenerate eigenvalues) are almost identical, as indicated by the block-diagonal form of the eigenvector overlap matrices (see Fig. 3b).

Finally, $\tilde{f}_{xc}$ can be computed from $\tilde{\chi}$ and $\tilde{\chi}_0$ according to Eq. 12. Due to the similarity of the eigenvectors of $\tilde{\chi}$ and $\tilde{\chi}_{\text{RPA}}$ (identical to that of $\tilde{\chi}_0$), the $\tilde{f}_{xc}$ matrix is almost diagonal. In Sec. 3 of the SI we show the $\tilde{f}_{xc}$ matrix in the PDEP basis for a few systems. To verify the accuracy of $\tilde{f}_{xc}$ obtained by the finite-field approach, we performed calculations with
the LDA functional, for which \( f_{xc} \) can be computed analytically. In Fig 4 we present for a number of systems the average relative difference of the diagonal terms of the \( \tilde{f}_{xc} \) matrices obtained analytically and through finite-field (FF) calculations. We define \( \Delta f_{xc} \) as

\[
\Delta f_{xc} = \frac{1}{N_{PDEP}} \sum_{i} \frac{\left| \langle \xi_{i} | \tilde{f}_{xc}^{FF} | \xi_{i} \rangle - \langle \xi_{i} | \tilde{f}_{xc}^{\text{analytical}} | \xi_{i} \rangle \right|}{\langle \xi_{i} | \tilde{f}_{xc}^{\text{analytical}} | \xi_{i} \rangle}.
\]  

(13)

As shown in Fig 4, \( \Delta f_{xc} \) is smaller than a few percent for all systems studied here. To further quantify the effect of the small difference found for the \( \tilde{f}_{xc} \) matrices on \( GW \) quasiparticle energies, we performed \( G_{0}W_{0}^{f_{xc}} \) @LDA calculations (\( f_{xc} \) is included in \( W \), see Sec. 3) for all the systems shown in Fig 4 using the analytical \( f_{xc} \) and \( f_{xc} \) computed from finite-field calculations. The two approaches yielded almost identical quasiparticle energies, with mean absolute deviations of 0.04 and 0.004 eV for HOMO and LUMO levels, respectively.

Figure 4: Average relative differences \( \Delta f_{xc} \) (see Eq. 13) between diagonal elements of the \( \tilde{f}_{xc} \) matrices computed analytically and numerically with the finite-field approach. Calculations were performed with the LDA functional.
3 $GW$ calculations

3.1 Formalism

In this section we discuss $GW$ calculations within and beyond the RPA, utilizing $f_{xc}$ computed with the finite-field approach. In the following equations we use 1, 2, ... as shorthand notations for $(r_1, t_1)$, $(r_2, t_2)$, ... Indices with bars are integrated over. When no indices are shown, the equation is a matrix equation in reciprocal space or in the PDEP basis. The following discussion focuses on finite systems; for periodic systems a special treatment of the long-range limit of $\chi$ is required and relevant formulae are presented in Sec. 4 of the SI.

Based on a KS reference system, the Hedin equations\cite{Hedin65} relate the exchange-correlation self-energy $\Sigma_{xc}$ (abbreviated as $\Sigma$), Green’s function $G$, the screened Coulomb interaction $W$, the vertex $\Gamma$ and the irreducible polarizability $P$:

$$\Sigma(1,2) = iG(1,\bar{4})W(1^+,\bar{3})\Gamma(\bar{4},2;\bar{3}),$$

$$W(1,2) = v_c(1,2) + v_c(1,\bar{3})P(\bar{3},\bar{4})W(\bar{4},2),$$

$$P(1,2) = -iG(1,\bar{3})G(\bar{4},1)\Gamma(\bar{3},\bar{4},2),$$

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \frac{\delta\Sigma(1,2)}{\delta G(\bar{4},5)}G(\bar{4},6)G(7,\bar{5})\Gamma(\bar{6},\bar{7},3),$$

$$G(1,2) = G^0(1,2) + G^0(1,\bar{3})\Sigma(\bar{3},\bar{4})G(\bar{4},2).$$

We consider three different $G_0W_0$ approximations: the first is the common $G_0W_0$ formulation within the RPA, here denoted as $G_0W_0^{\text{RPA}}$, where $\Gamma(1,2;3) = \delta(1,2)\delta(1,3)$ and $\Sigma$ is given by:

$$\Sigma(1,2) = iG(1,2)W_{\text{RPA}}(1^+,2),$$

where

$$W_{\text{RPA}}(1,2) = v_c(1,2) + v_c(1,\bar{3})\chi_{\text{RPA}}(\bar{3},\bar{4})v_c(\bar{4},2),$$

$$\chi_{\text{RPA}}(\bar{3},\bar{4}) = \chi_{\text{RPA}}(\bar{4},\bar{3}) = -\chi_{\text{RPA}}(\bar{3},\bar{4}) = -\chi_{\text{RPA}}(\bar{4},\bar{3}) = \chi_{\text{RPA}}(\bar{4},\bar{3}) = \chi_{\text{RPA}}(\bar{3},\bar{4}) = -\chi_{\text{RPA}}(\bar{3},\bar{4}) = -\chi_{\text{RPA}}(\bar{4},\bar{3}).$$
and
\[ \chi_{\text{RPA}} = (1 - \chi_0 v_c)^{-1} \chi_0. \]  \hfill (21)

The second approximation, denoted as \( G_0 W_{fxc}^0 \), includes \( f_{xc} \) in the definition of \( W \). Specifically, \( \chi \) is computed from \( \chi_0 \) and \( f_{xc} \) with Eq. 3:

\[ \chi = (1 - \chi_0 (v_c + f_{xc}))^{-1} \chi_0, \]  \hfill (22)

and is used to construct screened the Coulomb interaction beyond the RPA:

\[ W_{fxc} = v_c (1, 2) + v_c (1, 3) \chi (3, 4) v_c (4, 2). \]  \hfill (23)

The third approximation, denoted \( G_0 W_0 \Gamma_0 \), includes \( f_{xc} \) in both \( W \) and \( \Sigma \). In particular, an initial guess for \( \Sigma \) is constructed from \( V_{xc} \):

\[ \Sigma_0 (1, 2) = \delta (1, 2) V_{xc} (1) \]  \hfill (24)

from which one can obtain a zeroth order vertex function by iterating Hedin’s equations once:\textsuperscript{20}

\[ \Gamma_0 (1, 2; 3) = \delta (1, 2) (1 - f_{xc} \chi_0)^{-1} (1, 3). \]  \hfill (25)

Then the self-energy \( \Sigma \) is constructed using \( G \), \( W_{fxc} \) and \( \Gamma_0 \):

\[ \Sigma (1, 2) = i G (1, 4) W_{fxc} (1^+, 3) \Gamma_0 (4, 2; 3) \]
\[ = i G (1, 2) W_\Gamma (1^+, 3) \]  \hfill (26)

where we defined an effective screened Coulomb interaction:\textsuperscript{21}

\[ W_\Gamma = v_c (1, 2) + v_c (1, 3) \chi_\Gamma (3, 4) v_c (4, 2), \]  \hfill (27)
\[ \chi_R = \left[ v_c - v_c \chi_0 (v_c + \tilde{f}_{xc}) \right]^{-1} - v_c^{-1}. \] (28)

The symmetrized forms of the three different density response functions (reducible polarizabilities) defined in Eq. 21, 22, 28 are:

\[ \tilde{\chi}_{RPA} = [1 - \tilde{\chi}_0]^{-1} \tilde{\chi}_0 \] (29)
\[ \tilde{\chi} = [1 - \tilde{\chi}_0 (1 + \tilde{\tilde{f}}_{xc})]^{-1} \tilde{\chi}_0 \] (30)
\[ \tilde{\chi}_\Gamma = [1 - \tilde{\chi}_0 (1 + \tilde{\tilde{f}}_{xc})]^{-1} - 1 \] (31)

Eqs. 29, 31 have been implemented in the WEST code.\(^{19}\)

We note that finite-field calculations yield \( \tilde{\tilde{f}}_{xc} \) matrices at zero frequency. Hence the results presented here correspond to calculations performed within the adiabatic approximation, as they neglect the frequency dependence of \( \tilde{\tilde{f}}_{xc} \). An interesting future direction would be to compute frequency-dependent \( \tilde{\tilde{f}}_{xc} \) by performing finite-field calculations using real-time time-dependent DFT (RT-TDDFT).

When using the \( G_0W_0\Gamma_0 \) formalism, the convergence of quasiparticle energies with respect to \( N_{\text{PDEP}} \) turned out to be extremely challenging. As discussed in Ref. 53 the convergence problem originates from the incorrect short-range behavior of \( \tilde{\tilde{f}}_{xc} \). In Sec. 3.2 below we describe a renormalization scheme of \( \tilde{\tilde{f}}_{xc} \) that improves the convergence of \( G_0W_0\Gamma_0 \) results.

### 3.2 Renormalization of \( f_{xc} \)

Thygesen and co-workers\(^{53}\) showed that \( G_0W_0\Gamma_0 \)@LDA calculations with \( f_{xc} \) computed at the LDA level exhibit poor convergence with respect to the number of unoccupied states and plane wave cutoff. We observed related convergence problems of \( G_0W_0\Gamma_0 \) quasiparticle energies as a function of \( N_{\text{PDEP}} \), the size of the basis set used here to represent response functions, see Sec. 5 of the SI. In this section we describe a generalization of the \( f_{xc} \) renormalization scheme proposed by Thygesen and co-workers\(^{52,56}\) to overcome the convergence...
The approach of Ref. 53 is based on the properties of the homogeneous electron gas (HEG). For an HEG with density \( n \), \( f_{xc}^{\text{HEG}}[n](\mathbf{r}, \mathbf{r}') \) depends only on \( (\mathbf{r} - \mathbf{r}') \) due to translational invariance, and therefore \( f_{xc}^{\text{HEG}}[n](\mathbf{q}) \) is diagonal in reciprocal space. We denote the diagonal elements of \( f_{xc}^{\text{HEG}}[n](\mathbf{q}) \) as \( f_{xc}^{\text{HEG}}[n](\mathbf{k}) \) where \( \mathbf{k} = \mathbf{q} + \mathbf{G} \). When using the LDA functional, the exchange kernel \( f_{x} \) exactly cancels the Coulomb interaction \( v_{c} \) at wavevector \( k = 2k_{F} \) (the correlation kernel \( f_{c} \) is small compared to \( f_{x} \) for \( k \geq 2k_{F} \) ), where \( k_{F} \) is the Fermi wavevector. For \( k \geq 2k_{F} \), \( f_{xc}^{\text{HEG-LDA}} \) shows an incorrect asymptotic behavior, leading to an unphysical correlation hole. Hence Thygesen and co-workers introduced a renormalized LDA kernel \( f_{xc}^{\text{HEG-rLDA}}(k) \) by setting \( f_{xc}^{\text{HEG-rLDA}}(k) = f_{xc}^{\text{HEG-LDA}}(k) \) for \( k \leq 2k_{F} \) and \( f_{xc}^{\text{HEG-rLDA}}(k) = -v_{c}(k) \) for \( k > 2k_{F} \). They demonstrated that the renormalized \( f_{xc} \) improves the description of the short-range correlation hole as well as the correlation energy, and when applied to GW calculations substantially accelerates the basis set convergence of \( G_{0}W_{0}\Gamma_{0} \) quasiparticle energies.

While within LDA \( f_{xc} \) can be computed analytically and \( v_{c} + f_{x} = 0 \) at exactly \( k = 2k_{F} \), for a general functional it is not known \textit{a priori} at which \( k \) this condition is satisfied. In addition, for inhomogenous systems such as molecules and solids the \( f_{xc} \) matrix is not diagonal in reciprocal space. Ref. 53 used a wavevector symmetrization approach to evaluate \( f_{xc}^{\text{HEG-rLDA}} \) for inhomogenous systems, which is not easily generalizable to the formalism in this work where \( f_{xc} \) is represented in the PDEP basis.

To overcome these difficulties, here we first diagonalize the \( \tilde{f}_{xc} \) matrix in the PDEP basis:

\[
\tilde{f}_{xc} = \sum_{i}^{N_{\text{PDEP}}} f_{i} \langle \zeta_{i} \rangle \langle \zeta_{i} | ,
\]

where \( f \) and \( \zeta \) are eigenvalues and eigenvectors of \( \tilde{f}_{xc} \). Then we define a renormalized \( \tilde{f}_{xc} \) as:

\[
\tilde{f}_{xc}^{r} = \sum_{i}^{N_{\text{PDEP}}} \max(f_{i}, -1) \langle \zeta_{i} \rangle \langle \zeta_{i} | .
\]
Note that for $f_{xc} = -1$, $f_{xc} = -\nu_c$, therefore $f_{xc}'$ is strictly greater or equal to $-\nu_c$. When applied to the HEG, the $f_{xc}'@\text{LDA}$ is equivalent to $f_{xc}^{\text{HEG-rLDA}}$ in the limit $N_{\text{PDEP}} \to \infty$, where the PDEP and plane-wave basis are related by a unitary transformation. Thus, Eq. 33 represents a generalization of the scheme of Thygesen et al. to any functional and to inhomogeneous electron gases. When using $f_{xc}'$, we observed a faster basis set convergence of $G_0W_0\Gamma_0$ results than $G_0W_0^{\text{RPA}}$ results, consistent with Ref. 53. In Sec. 5 of the SI we discuss in detail the effect of the $f_{xc}$ renormalization on the description of the density response functions $\chi$ and $\chi_\Gamma$, and we rationalize why the renormalization improves the convergence of $G_0W_0\Gamma_0$ results. Here we only mention that the response function $\tilde{\chi}_\Gamma$ may possess positive eigenvalues for large PDEP indices. When the renormalized $f_{xc}$ is used, the eigenvalues of $\tilde{\chi}_\Gamma$ are guaranteed to be nonpositive and decay rapidly toward zero as the PDEP index increase, which explains the improved convergence of $G_0W_0\Gamma_0$ quasiparticle energies.

All $G_0W_0\Gamma_0$ results shown in Sec. 3.3 were obtained with renormalized $f_{xc}$ matrices, while $G_0W_0^{f_{xc}}$ calculations were conducted without renormalizing $f_{xc}$, since we found that the renormalization had a negligible effect on $G_0W_0^{f_{xc}}$ quasiparticle energies (see SI Sec. 5).

### 3.3 Results

In this section we report $GW$ quasiparticle energies for molecules in the GW100 set and for several solids. Calculations are performed at $G_0W_0^{\text{RPA}}$, $G_0W_0^{f_{xc}}$ and $G_0W_0\Gamma_0$ levels of theory and with semi-local and hybrid functionals. Computational parameters ($E_{\text{cut}}$, $N_{\text{PDEP}}$, etc.) for all calculations are summarized in Sec. 1 of the SI. A discussion of the convergence of $G_0W_0^{\text{RPA}}$ quasiparticle energies with respect to these parameters can be found in Ref. 20.

We computed the vertical ionization energy (VIP), vertical electron affinity (VEA) and fundamental gaps for molecules with LDA, PBE and PBE0 functionals. VIP and VEA are defined as $\text{VIP} = \varepsilon^{\text{vac}} - \varepsilon^{\text{HOMO}}$ and $\text{VEA} = \varepsilon^{\text{vac}} - \varepsilon^{\text{LUMO}}$ respectively, where $\varepsilon^{\text{vac}}$ is the vacuum level estimated with the Makov-Payne method; $\varepsilon^{\text{HOMO}}$ and $\varepsilon^{\text{LUMO}}$ are HOMO and LUMO $GW$ quasiparticle energies, respectively. The results are summarized in Fig. 5 and...
compared with experimental values.\textsuperscript{65} VIP values are also compared with existing results from quantum chemistry CCSD(T) calculations.\textsuperscript{69}

Figure 5: Vertical ionization energy (VIP), vertical electron affinity (VEA) and electronic gap of molecules in the GW100 set computed at $G_0W_0^{RPA}$, $G_0W_0^{fxc}$ and $G_0W_0\Gamma_0$ levels of theory, compared to experimental and CCSD(T) results (black dashed lines).\textsuperscript{71}

The VIP values computed at $G_0W_0^{fxc}$ ($G_0W_0\Gamma_0$) level are systematically higher (lower) than the corresponding $G_0W_0^{RPA}$ results. Compared to experiments and CCSD(T) results, $G_0W_0^{fxc}$ results show an improvement over $G_0W_0^{RPA}$ ones, when semilocal functionals (LDA, PBE) are used as starting points; instead, when using the PBE0 functional $G_0W_0^{fxc}$ leads to a slight overestimation of VIP. $G_0W_0\Gamma_0$ results underestimate VIP with all functionals tested here, compared to experiments. At the LDA level, the comparison between different GW approximations is consistent with the observation by Morris \textit{et al} for He, Be and Ne
In general, vertex corrections have larger effects on quasiparticle energies computed with hybrid functionals, as the difference between the results obtained with different \(GW\) approximations are more prominent when starting from PBE0 calculations than starting from semi-local ones.

Different \(GW\) approximations yielded very similar results for the VEA, with \(G_0W_0^{fxc}\) (\(G_0W_0\Gamma_0\)) results marginally higher (lower) than \(G_0W_0^{RPA}\) ones.

Finally we report \(G_0W_0^{RPA}\), \(G_0W_0^{fxc}\) and \(G_0W_0\Gamma_0\) results for several solids: Si, SiC (4H), C (diamond), AlN, WO\(_3\) (monoclinic), Si\(_3\)N\(_4\) (amorphous). We performed calculations starting with LDA and PBE functionals for all solids, and for Si we also performed calculations with the dielectric-dependent hybrid (DDH) functional. All solids are represented by supercells with 64-96 atoms (see Sec. 1 of the SI) and only the \(\Gamma\)-point is used to sample the Brillouin zone. In Table 1 we present the band gaps computed with different \(GW\) approximations and functionals. Note that the supercells used here do not yield fully converged results as a function of supercell size (or k-point sampling); however the comparisons between different \(GW\) calculations are sound and represent the main result we are discussing in this section.

Table 1: Band gaps (eV) for solids computed by different \(GW\) approximations and exchange-correlation (XC) functionals (see text). All calculations are performed at the \(\Gamma\)-point of supercells with 64-96 atoms (see Sec. 1 of the SI for details).

| System         | XC   | DFT | \(G_0W_0^{RPA}\) | \(G_0W_0^{fxc}\) | \(G_0W_0\Gamma_0\) |
|----------------|------|-----|-----------------|-----------------|-----------------|
| Si             | LDA  | 0.55| 1.35            | 1.33            | 1.24            |
|                | PBE  | 0.73| 1.39            | 1.37            | 1.28            |
|                | DDH  | 1.19| 1.57            | 1.50            | 1.48            |
| C (diamond)    | LDA  | 4.28| 5.99            | 6.00            | 5.89            |
|                | PBE  | 4.46| 6.05            | 6.06            | 5.95            |
| SiC (4H)       | LDA  | 2.03| 3.27            | 3.23            | 3.26            |
|                | PBE  | 2.21| 3.28            | 3.23            | 3.28            |
| AlN            | LDA  | 3.85| 5.67            | 5.72            | 5.66            |
|                | PBE  | 4.04| 5.67            | 5.74            | 5.68            |
| WO\(_3\) (monoclinic) | LDA  | 1.68| 3.10            | 3.07            | 3.15            |
|                | PBE  | 1.78| 2.97            | 2.87            | 3.03            |
| Si\(_3\)N\(_4\) (amorphous) | LDA  | 3.04| 4.84            | 4.92            | 4.81            |
|                | PBE  | 3.19| 4.86            | 4.96            | 4.83            |
Overall, band gaps obtained with different $GW$ approximations are very similar, with differences much smaller than those observed for molecules. To further investigate the positions of the band edges obtained from different $GW$ approximations, we plotted in Fig 6 the $GW$ quasiparticle corrections to VBM and CBM, defined as $\Delta_{VBM/CBM} = \varepsilon^{GW}_{VBM/CBM} - \varepsilon^{DFT}_{VBM/CBM}$ where $\varepsilon^{GW}_{VBM/CBM}$ and $\varepsilon^{DFT}_{VBM/CBM}$ are the $GW$ quasiparticle energy and the Kohn-Sham eigenvalue of VBM/CBM, respectively.
Figure 6: GW quasiparticle corrections to the valance band maximum (VBM) and the conduction band minimum (CBM). Circles, squares and triangles are $G_0W_{RPA}^0$, $G_0W_{fxc}^0$ and $G_0W_{0}\Gamma_0$ results respectively; red, blue, green markers correspond to calculations with LDA, PBE and DDH functionals.

Compared to $G_0W_{0}^{RPA}$, VBM and CBM computed at the $G_0W_{0}^{fxc}$ level are slightly lower, while VBM and CBM computed at the $G_0W_{0}\Gamma_0$ level are significantly higher. For Si, $\Delta_{VBM/CBM}$ obtained with LDA starting point are $-0.75/0.06$ ($G_0W_{0}^{RPA}$), $-0.86/-0.08$
$(G_0W_0^{fsc})$, -0.21/0.49 eV $(G_0W_0\Gamma_0)$ respectively, showing a trend in agreement with the results reported by Del Sole et al (-0.36/0.27, -0.44/0.14, 0.01/0.67 eV), but with an overall overestimate of the band gap due to a lack of convergence in our Brillouin zone sampling. The deviation of band edges computed by different $GW$ approximations is larger with the DDH functional compared to that of semi-local functionals. Overall the trends observed for solids are consistent with those found for molecules, except that for solids the shift of the CBM resembles those of the VBM when vertex corrections are included, while for molecules VEA is insensitive to vertex corrections.
4 Conclusions

In summary, we developed a finite-field approach to compute density response functions \( \chi_0 \), \( \chi_{\text{RPA}} \) and \( \chi \) for molecules and materials. The approach is non-perturbative and can be used in a straightforward manner with both semilocal and orbital-dependent functionals. Using this approach, we computed the exchange-correlation kernel \( f_{xc} \) and performed GW calculations using dielectric responses evaluated beyond the RPA.

We evaluated quasiparticle energies for molecules and solids and compared results obtained within and beyond the RPA, and using DFT calculations with semi-local and hybrid functionals as input. We found that the effect of vertex corrections on quasiparticle energies is more notable when using input wavefunctions and single-particle energies from hybrid functionals calculations. For the small molecules in the GW100 set, \( G_0W_0f_{xc} \) calculations yielded higher VIP compared to \( G_0W_0^{\text{RPA}} \) results, leading to a better agreement with experimental and high-level quantum chemistry results when using LDA and PBE starting points, and to a slight overestimate of VIP when using PBE0 as the starting point. \( G_0W_0\Gamma_0 \) calculations instead yielded a systematic underestimate of VIP of molecules. VEA of molecules were found to be insensitive to vertex corrections. In the case of solids, the energy of the VBM and CBM shifts in the same direction, relative to RPA results, when vertex corrections are included, and overall the band gaps were found to be rather insensitive to the choice of the GW approximation.

In addition, we reported a scheme to renormalize \( f_{xc} \), which is built on previous work\textsuperscript{53} using the LDA functional. The scheme is general and applicable to any exchange-correlation functional and to inhomogeneous systems including molecules and solids. Using the renormalized \( \tilde{f}_{xc} \), the basis set convergence of \( G_0W_0\Gamma_0 \) results was significantly improved.

Overall, the method introduced in our work represents a substantial progress towards efficient computations of dielectric screening and large-scale \( G_0W_0 \) calculations for molecules and materials beyond the random phase approximation.
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Supporting Information Available

The following files are available free of charge. The Supporting Information contains parameters used for calculations, convergence tests, detailed discussion of $f_{xc}$ matrix and its renormalization, extension of beyond-RPA GW formalism to solids, and an analysis of the spectral function of KH molecule.
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(71) For KH molecule, $G_0W_0^{fsc}@PBE$ calculation for the HOMO converged to a satellite instead of the quasiparticle peak. The spectral function of KH is plotted and discussed in SI Sec. 6 and the correct quasiparticle energy is used here.