We calculate the interacting bandgap energy of a solid within the random-phase approximation (RPA) to density functional theory (DFT). The interacting bandgap energy is defined as $E_g = E_{\text{RPA}}^{\text{d}}(N+1) + E_{\text{RPA}}^{\text{s}}(N-1) − 2E_{\text{RPA}}^0(N)$, where $E_{\text{RPA}}^0(N)$ is the total DFT-RPA energy of the $N$-electron system. We compare the interacting bandgap energy with the Kohn-Sham bandgap energy, which is the difference between the conduction and valence band edges in the Kohn-Sham band structure. We show that they differ by an unrenormalized “$G_0W_0$” self-energy correction (i.e., a GW self-energy correction computed using Kohn-Sham orbitals and energies as input). This provides a well-defined and meaningful interpretation to $G_0W_0$ quasiparticle bandgap calculations, but questions the physics behind the renormalization factors in the expression of the bandgap energy. We also separate the kinetic from the Coulomb contributions to the DFT-RPA bandgap energy, and discuss the related problem of the derivative discontinuity in the DFT-RPA functional. Last we discuss the applicability of our results to other functionals based on many-body perturbation theory.

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I. INTRODUCTION

The density functional theory (DFT) is widely used today to calculate the ground-state properties of solids and molecules. The local density approximation (LDA) and the generalized gradient approximation (GGA) have notably proved very successful in predicting the structural and vibrational properties of many materials. The LDA and GGA, however, miss long-range correlations; they thus fail to reproduce the ground-state energy surfaces of Van der Waals bonded systems or of layered materials such as graphite. These shortcomings have stimulated the need for fully non-local approximations able to account for long-range effects.

There are many ways to design nonlocal approximations for the exchange-correlation energy, including many-body perturbation theory, Kohn-Sham perturbation theory, and the adiabatic-connection fluctuation-dissipation (ACFD) theorem within time-dependent DFT. The prototype of the ACFD functionals is based on the so-called random-phase approximation for the density-density response function (DFT-RPA functional). It will be reviewed in Sec. II. At variance with the LDA and GGA, the DFT-RPA is an explicit functional of the Kohn-Sham (KS) orbitals and energies, and thus only an implicit functional of the density. It has been applied to the homogeneous electron gas more than three decades ago, then to jellium slabs and surfaces; the calculation of the ground-state energy surface of simple diatomic molecules and solids (Si, Na, …) is much more demanding than the LDA and GGA (by a factor $10^2$ to $10^3$), has been achieved only recently. The DFT-RPA properly describes Van der Waals interactions, but misses important short-range correlations. This deficiency can, however, be cured with LDA-like corrections or using refined time-dependent DFT kernels. The DFT-RPA exchange-correlation potential $v_{xc}^{\text{RPA}}(r)$ satisfies a complex integral equation known as the linear-response Sham-Schlüter equation. In Refs. 35–37, we have investigated the asymptotic behavior of the DFT-RPA potential, and we have notably shown that $v_{xc}^{\text{RPA}}(r) \sim -1/r + Q/r^3 - \alpha/(2r^4)$ (in finite, closed shell systems with spherical symmetry), where $Q$ is a screened quadrupole moment and $\alpha$ is the RPA polarizability of the system. This is in much better agreement with the expected behavior than the LDA and GGA (and to a lesser extent, exact exchange). As for (semi)extended systems, the linear-response Sham-Schlüter equation has been solved by Enguita et al. for a jellium surface and by Godby et al. in bulk silicon, where the potential was found to be close to the LDA. Approximate DFT-RPA potentials have also been calculated in some bulk metals and silicon by Kotani.

One of the main limitations of DFT in solids is the well-known “bandgap problem.” Indeed, the Kohn-Sham (KS) bandgap energy $E_g^{\text{KS}}$ is usually found much lower than the experimental bandgap. As a matter of fact, the KS bandgap energy might differ from the interacting bandgap energy $E_g = E(N+1) + E(N-1) − 2E(N)$, where $E(N)$ is the total energy of the $N$-electron system, due to the existence of a derivative discontinuity in the exchange-correlation functional. In practice, the bandgap energy and quasiparticle band structure are thus computed with many-body Green function techniques such as the GW method. In principle, the Green function $G$ should be updated with Dyson equation until self-consistency is achieved. This “$G_0W_0$” approach has been successfully applied to a wide variety of materials. There has been, however, recent controversy about the effects of self-consistency on the quasiparticle band structure and about the rationale behind $G_0W_0$ calculations.
factors. This definitely provides a clear rationale behind $G_0 W_0$ quasiparticle bandgap calculations, but questions the physics behind these renormalization factors. We then further split the DFT-RPA bandgap energy into kinetic and Coulomb contributions, that we calculate in silicon and diamond. Last, we discuss the related problem of the derivative discontinuity in the DFT-RPA functional, as well as the applicability of our results to other functionals based on many-body perturbation theory.

This paper is organized as follows. We briefly review the basics of the DFT-RPA functional in Sec. II, then calculate the DFT-RPA interacting bandgap energy in Sec. III. We discuss the links with the $G_0 W_0$ approach in Sec. IV, the kinetic and Coulomb contributions to the bandgap energy in Sec. V; last the derivative discontinuity in the DFT-RPA functional and the applicability to other functionals in Sec. VI.

II. THE DFT-RPA CORRELATION FUNCTIONAL

The DFT-RPA is the prototype of a large class of functionals based on the adiabatic-connection and fluctuation-dissipation (ACFD) theorems.\textsuperscript{10,11} The adiabatic connection formula indeed yields the sum of the Hartree ($E_{\text{H}}$), KS exchange ($E_{\text{x}}$), and correlation ($E_{\text{c}}$) energies of a $N$-electron system:

$$E_{\text{xc}} = \int_0^1 d\lambda \langle \Psi_\lambda | V_{\text{xc}} | \Psi_\lambda \rangle.$$  \hspace{1cm} (1)

$V_{\text{xc}}$ is the Coulomb interaction operator and $|\Psi_\lambda\rangle$ is the many-body ground-state wave function of a system with a scaled Coulomb repulsion $\lambda V_{\text{xc}}$ between electrons and with a one-body potential $v_{\text{xc}}(\mathbf{r})$ such that the ground-state density $n_{\text{g}}(\mathbf{r})$ equals the physical density $n_{\lambda}(\mathbf{r})$ [hence $v_{\text{1}}(\mathbf{r})=v_{\text{xc}}(\mathbf{r})$] is the external (ionic) potential, while $v_{\text{0}}(\mathbf{r})=v_{\text{KS}}(\mathbf{r})$ is the KS potential]. The ground-state expectation value of the Coulomb interaction operator can then be calculated with the fluctuation-dissipation theorem:

$$\langle \Psi_\lambda | V_{\text{xc}} | \Psi_\lambda \rangle = E_{\text{h}} + E_{\text{x}} - \frac{1}{2} \int \frac{d\mu}{2\pi} \text{Tr} \{ \nu [\chi_{\lambda}(\mu) - \chi_{\lambda}(\mu)] \}.$$ \hspace{1cm} (2)

The symbol $\text{Tr}$ stands for the trace over spatial coordinates $\text{Tr}[A(\mathbf{r}) B(\mathbf{r})]=\int d\mathbf{r} d\mathbf{r}' A(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'') B(\mathbf{r}'', \mathbf{r}, \mathbf{r}'').$ $\nu(\mathbf{r}, \mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$ is the bare Coulomb interaction, and $\chi_{\lambda}(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'')$ is the imaginary-frequency density-density response function at coupling constant $\lambda$. The KS density-density response function $\chi_{\lambda}(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'')$ reads, as a function of the KS orbitals $\varphi_{\pm}(\mathbf{r})$ and KS energies $\varepsilon_{\pm}$ (we assume a spin-compensated $N$-electron ground state):

$$\chi_{\lambda}(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'') = \sum_{j=1}^{N/2} \sum_{k} \frac{\varphi_{j}(\mathbf{r}) \varphi_{j}(\mathbf{r}) \varphi_{k}(\mathbf{r}') \varphi_{k}(\mathbf{r}')} { \mu^2 + \varepsilon_{j} - \varepsilon_{k} + \text{c.c.} } + \text{c.c.}$$ \hspace{1cm} (3)

Equations (1) and (2) are formally exact but $\chi_{\lambda}(\lambda \neq 0)$ needs to be approximated for practical purposes. The DFT-RPA functional follows from the time-dependent Hartree (or random-phase) approximation

$$\chi_{\lambda}^{\text{RPA}}(\mu) = \frac{1}{1 - \lambda \chi_{\lambda}(\mu) \mu^{-1} \chi_{\lambda}(\mu)}.$$ \hspace{1cm} (4)

Refined approximations for $\chi_{\lambda}(\mu)$, based on various time-dependent DFT kernels, can also be considered.\textsuperscript{25,32} In the RPA, Eq. (2) basically describes how KS density fluctuations correlate when they are allowed to interact dynamically at the time-dependent Hartree level. Backward substitution in Eq. (1) and integration over the coupling constant $\lambda$ finally yield the following expression for the DFT-RPA correlation energy:

$$E_{\text{c}}^{\text{RPA}}[\mu] = \frac{1}{2} \int \frac{d\mu}{2\pi} \text{Tr} \{ [1 - \nu(\mu) \mu^{-1} \nu(\mu)] + \nu(\mu) + \nu(\mu) \}.$$ \hspace{1cm} (5)

The total DFT-RPA energy of the system can thus be written

$$E_{\text{RPA}}[\mu] = E_{\text{0}}[\mu] + E_{\text{x}}[\mu] + E_{\text{c}}^{\text{RPA}}[\mu],$$ \hspace{1cm} (6)

Note that $E_{\text{x}}[\mu]$ and $E_{\text{c}}^{\text{RPA}}[\mu]$ are implicit functionals of the density through the KS orbitals and energies. The RPA exchange-correlation potential $\nu_{\text{xc}}^{\text{RPA}}(\mathbf{r}) = \delta E_{\text{c}}^{\text{RPA}}[\mu] / \delta n(\mathbf{r})$ hence satisfies an integral equation known as the linear-response Sham-Schlüter equation.\textsuperscript{6,33,34} Further details about the properties of the RPA potential can be found in Refs. 35–37.

III. THE DFT-RPA BANDGAP ENERGY

In this section, we calculate the DFT-RPA bandgap energy and compare with the KS bandgap energy $E_{\text{KS}} = E_{\text{g}} - E_{\text{c}}$, where $E_{\text{g}}$ and $E_{\text{c}}$ are the energies of the highest occupied and lowest unoccupied KS orbitals in the $N$-electron KS potential. We focus on perfect solids, and thus drop all terms that make a $O(\Omega^{-p/q})$ contribution ($p/q > 0$) when the volume $\Omega \rightarrow \infty$ (the average density being kept fixed).

The interacting bandgap energy of a $N$-electron system is the difference $E_{\text{g}} = I - A$ between its first ionization potential $I$ and its electron affinity $A$. These are defined as total energy differences between the $N$- and $(N\pm 1)$-electron systems

$$I = E_{\text{N}-1,N-1} - E_{\text{N},N} \approx E_{\text{N}-1,N-1} - E_{\text{N},N},$$ \hspace{1cm} (7a)

$$A = E_{\text{N},N} - E_{\text{N+1},N+1} = E_{\text{N},N} - E_{\text{N+1},N}.$$ \hspace{1cm} (7b)

$n_{\text{N}(\mathbf{r})}$ is the $N$-electron (spin-)density built upon the $N$ lowest KS orbitals of the $M$-electron system. In solids with delocalized highest occupied and lowest unoccupied orbitals,\textsuperscript{63} the rightmost (approximate) equality in both equations holds up to a $O(\Omega^{-1})$ correction thanks to the variational principle of DFT.\textsuperscript{2,46} The interacting bandgap energy of a solid can thus be calculated at constant (N-electron) KS potential $\nu_{\text{KS}}(\mathbf{r})$.

We first focus on the electron affinity $A$. We get from Eq. (7b)
\[ A = A_0 + A_s + A_c, \quad (8) \]

where \( A_0 = E_{\text{DFT}}[\rho_{N \chi}] - E_{\text{DFT}}[\rho_{N+1 \chi}] \) (with similar definitions for \( A_s \) and \( A_c \)). \( A_0 \) is easily calculated

\[ -A_0 = \langle \varphi \rvert \mathcal{L} \varphi \rangle + U_{cc}, \]

\[ = \varepsilon_c + U_{cc} - \langle \varphi \rvert [\mathcal{S}_c^{\text{RPA}}] \varphi \rangle. \quad (9) \]

\( \varphi(r) \) is the lowest unoccupied KS orbital, \( v_b(r) \) is the Hartree potential, and \( U_{cc} \) is the self-interaction integral for orbital \( \varphi_c \). \( A_s \) moreover reads:\(^{39}\)

\[ -A_s = \langle \varphi \rvert \Sigma_s \varphi \rangle - U_{cc}, \quad (10) \]

where \( \Sigma_s(r,r') \) is the KS exchange-only self-energy:

\[ \Sigma_s(r,r') = -\sum_{j=1}^{N/2} \varphi_j(r)\varphi_j^*(r'), \quad (11) \]

As for \( A_c \)—which is the part of most interest here—we get from Eq. (5)

\[ -A_c = \frac{1}{2} \int \frac{d\mathbf{u}}{2\pi} \text{Tr} \left[ \ln \left[ 1 - \nu \chi_0(iu) \right] - \ln \left[ 1 - \nu \chi_0(iu) + i\delta \chi_0(iu) \right] \right], \quad (12) \]

\( \delta \chi_0 \) is the change in \( \chi_0(iu) \) when adding one electron to either spin to the lowest unoccupied KS orbital. It is thus the KS response of an electron in this orbital

\[ \delta \chi_0(r,r';iu) = \varphi^*_c(r)G_0(r,r';e_c + iu)\varphi_c(r') + \ldots, \quad (13) \]

where the KS Green function \( G_0(r,r';z) \) is defined by

\[ G_0(r,r';z) = \sum_j \varphi_j(r)\varphi_j^*(r')/z - \varepsilon_j. \quad (14) \]

Using the identity \( \text{Tr} \left[ \ln A - \ln B \right] = \text{Tr} \left[ \ln A \times B^{-1} \right] \), we further get

\[ -A_c = \frac{1}{2} \int \frac{d\mathbf{u}}{2\pi} \text{Tr} \left[ \ln \left[ 1 - W(iu) + i\delta \chi_0(iu) \right] \right], \quad (15) \]

where \( W(iu) = [1 - \nu \chi_0(iu)]^{-1} \) is the RPA screened Coulomb interaction.

The physics behind \( A_c \) can be revealed by putting the first-order (\( \propto \delta \chi_0 \)) term aside from the others. Using the power series expansion of the logarithm \( \text{Tr} \left[ \ln (1 - F(iu)) \right] = -\text{Tr} \left[ F(iu) \right] + \ldots \), we can indeed split \( A_c = A_c^{\text{RPA}} + A_c' \) in two parts, where

\[ -A_c^{\text{RPA}} = -\frac{1}{2} \int \frac{d\mathbf{u}}{2\pi} \text{Tr} \left[ \ln \left[ W(iu) - \nu \right] \delta \chi_0(iu) \right], \quad (16a) \]

\[ -A_c' = +\frac{1}{2} \int \frac{d\mathbf{u}}{2\pi} \text{Tr} \left[ \ln \left[ 1 - W(iu) \right] \right] \delta \chi_0(iu) + W(iu) \delta \chi_0(iu)]. \quad (16b) \]

As we will next show, \( A_c^{\text{RPA}} \) is a \textit{GW}-like self-energy correction,\(^{48,49}\) while \( A_c' \) vanishes in solids.

Let us first discuss \( A_c^{\text{RPA}} \). Insertion of Eq. (13) into Eq. (16a) yields

\[ -A_c^{\text{RPA}} = \langle \varphi \rvert \Sigma_c(e_c) \varphi \rangle, \quad (17) \]

where \( \Sigma_c(r,r';\varepsilon) \) is the correlation part of the “\( G_0W_0 \)” self-energy (i.e., the \( \text{GW} \) self-energy\(^{38,49}\) calculated with KS orbitals and energies):

\[ \Sigma_c(r,r';\varepsilon) = -PV \int \frac{d\mathbf{u}}{2\pi} G_0(r,r';\varepsilon + iu)W_s(r,r';iu). \quad (18) \]

\( W_s(r,r';iu) = W(r,r';iu) - \nu \delta \chi_0(iu) \) is the screening part of the RPA screened Coulomb interaction. The symbol “PV” stands for Cauchy’s principal value. Contour deformations techniques can be used to show that this imaginary-frequency form of the \( \text{GW} \) self-energy is equal to the usual (real-frequency) expression\(^{48,49}\) as long as \( \varepsilon \) is in the KS bandgap (including \( \varepsilon = \varepsilon_c \) and \( \varepsilon = \varepsilon_c \)). We will further investigate the links with \( G_0W_0 \) calculations later and now focus on \( A_c' \).

We note at once that \( A_c' \) has the same functional form as \( E_{\text{RPA}} \) [Eq. (5)], but with \( \chi_0(iu) \) replaced by \( \delta \chi_0(iu) \) and \( \nu \) replaced by \( W(iu) \). \( A_c' \) thus formally appears as the correlation energy of one electron in the lowest unoccupied KS orbital, the interactions among density fluctuations in this orbital being screened by the other (valence) electrons. As a matter of fact, \( A_c' \) accounts for both the spurious response of the extra electron to its own contribution to the time-dependent Hartree potential, and for the response of the extra electron to the polarization it induces in the gas of valence electrons. A careful analysis however shows that \( A_c' \) vanishes as \( \Omega^{-1/4} \) in a KS insulator, and thus do not contribute to the bandgap energy of the solid (see Appendix A). Note that this exponent is consistent with the low-density behavior of the \( \text{DFT-RPA} \) correlation energy per particle in the homogeneous electron gas\(^{64,65} \varepsilon_{\text{RPA}}(n) \propto n^{1/4} \) (which yields \( \varepsilon_{\text{RPA}} \propto \Omega^{-1/4} \) for a fixed number of particles).

Let us now gather the results of the former paragraphs. The KS exchange-only self-energy [Eq. (11)] can also be cast in terms of the KS Green function \( G_0 \) [see, e.g., Eq. (14) of Ref. 36]; adding Eqs. (9), (10), and (17) then yields

\[ A_s = \varepsilon_c + \langle \varphi \rvert \Sigma_s(e_c) - v_{\text{xc}}^{\text{RPA}} \varphi \rangle + O(\Omega^{-1/4}), \quad (19) \]

where

\[ \Sigma_s(r,r';\varepsilon) = -PV \int \frac{d\mathbf{u}}{2\pi} e^{iu\delta} G_0(r,r';\varepsilon + iu)W_s(r,r';iu), \quad (20) \]

is the full \( G_0W_0 \) self-energy and \( \delta \to 0^+ \) is a positive infinitesimal. As for the first ionization energy, we get along the same lines

\[ -I = \varepsilon_c + \langle \varphi \rvert \Sigma_{\text{xc}}(e_c) - v_{\text{xc}}^{\text{RPA}} \varphi \rangle + O(\Omega^{-1/4}), \quad (21) \]

where \( \varphi(r) \) is the highest occupied KS orbital. Let us recall that the relation \( -I = \varepsilon_c \) holds\(^{38,65} \) for the exact exchange-correlation functional provided \( v_{\text{xc}}(r) \to 0 \) when \( r \to \infty \). As for the \( \text{DFT-RPA} \), one may show\(^{38} \) that \( \langle \varphi \rvert \Sigma_{\text{xc}}(e_c) \rangle \)
−υ^{\text{RPA}}(r)|ψ_e\rangle=0 \text{ if } υ_{\text{KS}}(r)\to 0 \text{ when } r\to \infty, \text{ which yields } I=−e_c+O(Ω^{-1/4}); \text{ the highest occupied KS energy tends to the negative of the DFT-RPA first ionization potential in a large system with a delocalized } ψ_e(r). \text{ This result only holds if } e_c \text{ has been calculated self-consistently; Eqs. (19) and (21) remain valid though if LDA/GGA orbitals, energies and potential are used as input for the calculation (which is customary). These equations show that the DFT-RPA bandgap energy of solids differs from the KS bandgap energy by a } G_0W_0\text{-like self-energy correction. We further discuss the implications of this result in the next section.}

IV. LINKS WITH } G_0W_0 \text{ QUASIPARTICLE BANDGAP CALCULATIONS}

In this section, we discuss the practical implications of Eqs. (19) and (21). We show that they provide a well-defined and consistent interpretation to } G_0W_0 \text{ quasiparticle bandgap calculations. We also discuss the accuracy of the DFT-RPA bandgap energy of the basis of the known deficiencies of the DFT-RPA functional.}

A. Interpretation of the } G_0W_0 \text{ quasiparticle bandgap energy within DFT}

As mentioned in the Introduction, the DFT, which is a ground-state theory, is not meant for the calculation of quasiparticle bands structures. Even the bandgap energy, a linear combination of ground-state total energies, may not be correctly given by the KS band structure.\textsuperscript{53,44-46} The quasiparticle band structure of a solid is thus usually computed with the GW method.\textsuperscript{48,49} In principle, the Dyson equation should be solved iteratively to find the self-consistent Green function } G \text{ and the self-consistent GW self-energy } \Sigma_{\text{xc}}. \text{ This would notably make the quasiparticle band structure independent of the initial guess for the Green function. Such a self-consistent GW calculation has however long been untractable for real materials. The quasiparticle energies } E_c \text{ are expected to be real (i.e., the quasiparticle lifetime is expected to diverge at the edges of the gap)\textsuperscript{71}}, while the exact solution of Eq. (22) may be complex, especially in semiconductors with small KS bandgaps.\textsuperscript{72,73} This challenges the use of Eqs. (22) and (23) for the calculation of the } G_0W_0 \text{ bandgap energy. We will further compare the values of the } r-G_0W_0 \text{ and DFT-RPA bandgap energies with the experimental bandgap energy in Secs. IV B and V.}

The choice of the exchange-correlation potential } ν_{\text{xc}}(r) \text{ used throughout the calculation is another practical but important issue. Indeed, the unrenormalized } G_0W_0 \text{ bandgap energy has a well-defined interpretation within DFT only if DFT-RPA orbitals and energies are used as input for the self-energy. The adequacy of } ν_{\text{xc}}^{\text{RPA}}(r) \text{ as a starting point for the computation of the whole } G_0W_0 \text{ quasiparticle band structure is further emphasized in Appendix B. The DFT-RPA potential satisfies the linear-response Sham-Schlüter equation\textsuperscript{6,33,34} in the GW approximation for the self-energy, which is unfortunately very difficult to solve. The works of Godby et al.\textsuperscript{41,42} and of Kotani,\textsuperscript{43} however, suggest that the DFT-RPA and LDA potentials are quite close in simple solids such as silicon. The use of LDA orbitals and energies as input for the self-energy should thus have limited impact on the bandgap energy in most semiconductors. Still, the case of materials such as Germanium (often quoted as a metal in the LDA)
might be worth a detailed investigation. The latter could be carried out with approximate DFT-RPA potentials such as those introduced in Refs. 43 and Refs. 35–37, which are much simpler to compute while being likely of reasonable accuracy.

To conclude, we have shown that the density functional theory itself provides a justification to $G_0W_0$ quasiparticle bandgap calculations in solids, but questions the use of renormalization factors in the calculation of the bandgap energy. In the next section, we will discuss the accuracy of the DFT-RPA bandgap energy on the basis of the known deficiencies of the DFT-RPA functional.

B. Some deficiencies of the DFT-RPA functional and their consequences on the bandgap energy

The performances of the $G_0W_0$ approach can now be analyzed in a consistent DFT framework and related to those of the DFT-RPA functional. The RPA density-density response function $\chi^{\text{RPA}}$ reasonably describes long-range screening but misses important short-range effects.21,30,31,48 As a consequence, the DFT-RPA on-top correlation hole is too deep, so that the correlation energies are too negative and the total energies thus too low. This has been evidenced in finite systems such as $\text{H}_2$ (Ref. 25) and in the homogenous electron gas (HEG).7,17,32,74 In the latter case, the total energy error per particle $\Delta E_c(n) = E_c^{\text{RPA}}(n) - E_c^{\text{HEG}}(n)$ weakly increases (in absolute value) with the density17,74 $[E_c^{\text{HEG}}(n)$ and $E_c^{\text{RPA}}(n)$ being, respectively, the exact and RPA correlation energy per particle]. The work function $\Phi = I + A$ of a metal should thus be overestimated by the DFT-RPA functional. We may expect similar trends in semiconductors, provided the total energy error steadily increases with the number of particles across the gap. The inclusion of LDA-like vertex corrections in the $G_0W_0$ self-energy for example indeed results in an upward shift of the quasiparticle energies in Si.75 The introduction of short-range corrections to the RPA within a local density approximation (RPA+) functional21,31 also shifts the quasiparticle energies upwards.76 These errors on I and A might mostly cancel in the bandgap energy. The accuracy of the $G_0W_0$ bandgap energy is, however, quite controversial. Indeed, pseudopotential calculations42,54,55 usually yield $r$-$G_0W_0$ bandgap energies in good agreement with the experiment, and thus significantly too large DFT-RPA bandgap energies. On the other hand, all-electron calculations52,77–80 generally yield much lower $r$-$G_0W_0$ bandgaps. The all-electron DFT-RPA bandgap energies (deduced from Refs. 78 and 79) are thus often found in better agreement with the experiment than the $r$-$G_0W_0$ values, although they might still be too low. These discrepancies between pseudopotential and all-electron calculations are not yet fully understood.52,80,81 Further comparison between the two approaches is thus needed to be conclusive.

V. KINETIC AND COULOMB CONTRIBUTIONS TO THE BANDGAP ENERGY

In this section, we further refine our interpretation and separate the kinetic from the Coulomb contributions to the DFT-RPA bandgap energy in solids. Indeed, we can split $E_c^{\text{RPA}} = E_c^{\text{int}} + E_c^{\text{kin}}$, where $E_c^{\text{int}} = \langle \Psi_{i} | V_c | \Psi_{i} \rangle - E_{c0}$ is the Coulomb correlation energy and $E_c^{\text{kin}} = T_c - T_s$ is the difference between the interacting kinetic energy $T_c$ and the non-interacting KS kinetic energy $T_s = -\sum_{\mu} n_{\mu} \langle \varphi_{\mu} | V_{\text{kin}} | \varphi_{\mu} \rangle$. $E_c^{\text{kin}}$ is expected negative, because the introduction of correlations further prevents the electrons from coming too close one to each other, thereby decreasing the Coulomb interaction energy with respect to the exchange-only theory. This is of course made at the expense of the kinetic energy of the system ($E_c^{\text{kin}} > 0$). Nonetheless, the introduction of correlations always results in a net decrease of the total energy ($E_c < 0$).

Accordingly, we may separate kinetic ($A_c^{\text{kin}}$) from Coulomb ($A_c^{\text{int}}$) contributions in $A_c$. $A_c^{\text{int}}$ is easily calculated from Eqs. (2) and (4). To that end, we introduce $F(iv) = \text{Tr}[\chi^{\text{RPA}}(iv) - \chi_{0}(iv)] = [W(iv) - iv]\chi_{0}(iv)$ and write, upon addition of one electron to the lowest unoccupied orbital

$$\delta F(iv) = [W(iv) - iv] \delta \chi_{0}(iv) + \delta W(iv) \chi_{0}(iv)$$

$$+ \delta W(iv) \delta \chi_{0}(iv),$$

(24)

where $\delta F(iv)$ and $\delta W(iv) = [1 - W(iv) \delta \chi_{0}(iv)]^{-1} W(iv) - W(iv)$ are, respectively, the changes in $F(iv)$ and $W(iv)$. The trace of $\delta F(iv)$ over spatial coordinates and frequency yields $\delta A_c^{\text{int}}$ through Eq. (2). The first term on the right-hand side of Eq. (24) gives rise to the $G_0W_0$ self-energy correction of Eq. (17). The second and third terms involve the coupling of the extra electron with the time-dependent Hartree potential. They will allow further relaxation of the system and decrease of the Coulomb energy. In a solid, the only non-vanishing contribution (beyond the first term) arises from the first-order variation of the screened Coulomb interaction $\delta W^{(1)}(iv) = W(iv) \delta \chi_{0}(iv) W(iv)$ in the second term. This contribution thus equals $A_c^{\text{kin}} = A_c - A_c^{\text{int}}$, which yields after straightforward algebra

$$- A_c^{\text{kin}} = \langle \varphi_{r} | \Sigma_{c}^{\text{kin}}(\varphi_{r}) | \varphi_{r} \rangle + O(\Omega^{-1/4}),$$

(25)

where

$$\Sigma_{c}^{\text{kin}}(\varphi_{r}, \varphi_{r}'; \varepsilon) = PV \int \frac{du}{2\pi} G_{0}(\varphi_{r}, \varphi_{r}'; \varepsilon + iv) \tilde{W}(\varphi_{r}, \varphi_{r}'; iv)$$

(26)

and

$$\tilde{W}(iv) = W(iv) \chi_{0}(iv) W(iv) = \varepsilon^{-1}(iv) W_{c}(iv),$$

(27)

$\varepsilon(iv) = 1 - \nu_{\chi_{0}}(iv)$ being the RPA dielectric function. A similar equation holds for the first ionization energy $I$, $\langle \varphi_{r} |$ and $\varepsilon_{c}$ being replaced with $| \varphi_{v} \rangle$ and $\varepsilon_{v}$. Note that $\Sigma_{c}^{\text{kin}}$ has the same functional form as the correlation part of the $G_0W_0$ self-energy [Eq. (18)], but with a (re)screened $W_{c}(iv)$.

We have evaluated the kinetic and Coulomb contributions to the bandgap energy in silicon and diamond. The calculation was performed with the ABINIT package,82 using Troullier-Martins83 pseudopotentials and a plasmon-pole approximation for $\varepsilon^{-1}(iv)$. The wave functions were expanded in a plane-wave basis set with cutoff energy 12 Ha for Si and
The quasiparticle energies have been shifted so that the top of the valence band is at zero energy in the DFT-RPA approximation. The total correlation $\Sigma_c$, kinetic $\Sigma_c^{\text{kin}}$, and Coulomb $\Sigma_c^{\text{int}}=\Sigma_c-\Sigma_c^{\text{kin}}$ contributions to the DFT-RPA are also given.

<table>
<thead>
<tr>
<th></th>
<th>KS</th>
<th>$r$-$G_0 W_0$</th>
<th>RPA</th>
<th>$\Sigma_c$</th>
<th>$\Sigma_c^{\text{kin}}$</th>
<th>$\Sigma_c^{\text{int}}$</th>
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</thead>
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<tr>
<td>Si</td>
<td>$E_g$</td>
<td>0.751</td>
<td>0.176</td>
<td>0.000</td>
<td>0.434</td>
<td>0.753</td>
</tr>
<tr>
<td></td>
<td>$E_c$ (Ref. 86)</td>
<td>1.232</td>
<td>1.325</td>
<td>1.351</td>
<td>-3.555</td>
<td>1.294</td>
</tr>
<tr>
<td></td>
<td>$E_g$</td>
<td>0.481</td>
<td>1.149</td>
<td>1.351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$E_g$</td>
<td>0.924</td>
<td>0.154</td>
<td>0.000</td>
<td>1.102</td>
<td>0.554</td>
</tr>
<tr>
<td></td>
<td>$E_c$ (Ref. 86)</td>
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<td>5.757</td>
<td>5.884</td>
<td>-4.753</td>
<td>1.904</td>
</tr>
<tr>
<td></td>
<td>$E_g$</td>
<td>4.150</td>
<td>5.603</td>
<td>5.884</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

30 Ha for diamond. Up to 200 bands and 256 $k$ points (full Brillouin zone) were included in the computation of the $181 \times 181$ dielectric matrices and self-energies. The KS band structure was calculated in the LDA parameterization at the experimental lattice parameter $a$ = 5.43 Å for Si and $a$ = 3.57 Å for C. The quasiparticle energies $E_c$, $E_\nu$, and the bandgap energy $E_g$ are reported in Table I. Both renormalized and unrenormalized (RPA) $G_0 W_0$ values are given. The quasiparticle energies have been shifted so that the top of the valence band is at zero energy in the DFT-RPA approximation. The total correlation $\Sigma_c$, kinetic $\Sigma_c^{\text{kin}}$, and Coulomb $\Sigma_c^{\text{int}}=\Sigma_c-\Sigma_c^{\text{kin}}$ contributions to the DFT-RPA are also given. We expect the quasiparticle energies and $\Sigma_c^{\text{kin}}$ to be converged (from above and from below, respectively) within 0.05 eV. The values of $\Sigma_c$, $\Sigma_c^{\text{kin}}$, and $\Sigma_c^{\text{int}}$ should be marginally affected by the use of the LDA instead of the DFT-RPA potential.

As discussed in Sec. IV B, the $r$-$G_0 W_0$ bandgap energies of silicon and diamond are found in good agreement with the experimental $E_g$ = 1.17 eV for Si and $E_g$ = 5.48 eV for C, at least in the pseudopotential framework. However, the DFT-RPA figures, that are higher by 202 meV in Si and 281 meV in diamond, significantly overestimate the experimental bandgap energy. The quasiparticle energies show the same trends in both materials. One would naively expect the absolute values of $E_c$, $E_\nu$, and $E_g^{\text{kin}}$ to increase with the number of particles, i.e., $\Sigma_c<0$, $\Sigma_\nu<0$, and $\Sigma_g^{\text{kin}}>0$. This is clearly the case on the conduction band side. However, $\Sigma_c$ is found positive at the valence band edge, which means that the correlation energy is more negative in both the $(N+1)$- and $(N-1)$-electron systems than in the $N$-electron system. The removal of one electron to the insulating ground state thus strongly enhances the efficiency of correlations. This is especially evidenced in diamond, where $\Sigma_g^{\text{kin}}$ itself is found positive. $\Sigma_g^{\text{kin}}$ is a significant part of $\Sigma_g$, but is much lower than the variations of the noninteracting kinetic energy $\Delta T = \langle \varphi_{\nu\nu} | -\frac{1}{2} \nabla^2 | \varphi_{\nu\nu} \rangle$ (typically a few tens of eV). Again, $\Sigma_g^{\text{kin}}$ is higher on the conduction than on the valence band side, because the enhancement of the correlations on the latter side comes with an increase of $E_g^{\text{kin}}$ that nearly compensates for the loss of one particle. We would last like to recall that these results are obtained in a pseudopotential framework and notably miss part of the (screened-)exchange effects. Their accuracy should thus be assessed by comparison with all-electron calculations.

VI. THE DERIVATIVE DISCONTINUITY IN THE DFT-RPA EXCHANGE-CORRELATION FUNCTIONAL

The difference between the KS bandgap energy $E_g$ and the interacting bandgap energy $E_g^{\text{int}}$ can be related to the existence of a derivative discontinuity in the exchange-correlation functional. In this section, we discuss the derivative discontinuity in the DFT-RPA functional, as well as the applicability of our results to other exchange-correlation functionals based on many-body perturbation theory.

The domain of definition of the DFT-RPA functional must first be extended to arbitrary (noninteger) number of particles. The ensemble approach is the most appropriate way to do so. It is basically the $T \to 0$ limit of Mermin’s DFT (Ref. 88) for finite temperature $T$ and fixed chemical potential $\mu$. In this approach, the $\tilde{N}=N+f$ electron system ($0 \leq f \leq 1$) is described as a statistical mixture of the $N$ and $(N+1)$-electron systems; the ground-state density and total energy thus read

$$\tilde{n}_{N+f}(\mathbf{r}) = f n_{N+1}(\mathbf{r}) + (1-f)n_N(\mathbf{r}),$$

$$\tilde{E}[\tilde{n}_{N+f}] = f E[N+1] + (1-f)E[N],$$

where $n_N(\mathbf{r})$ is the $N$-electron ground-state density. The exchange-correlation energy $E_{xc}[\tilde{n}_{N+f}]$ does not reduce to the weighted average of $E_{xc}[n_{N+1}]$ and $E_{xc}[n_{N+1}]$, but also includes nonlinear but straightforward kinetic and Hartree energy corrections. By construction, we may expect derivative discontinuities in $\tilde{E}_{xc}$ for integer values of $N$. We thus define

$$\Delta_{xc}(\mathbf{r}) = \lim_{\delta \to 0^+} \left[ v_{xc}^{N+\delta}(\mathbf{r}) - v_{xc}^{N-\delta}(\mathbf{r}) \right]$$

$$= \lim_{\delta \to 0^+} \left[ \left( \frac{\delta \tilde{E}_{xc}[\tilde{n}]}{\delta \tilde{n}(\mathbf{r})} \right)_{N+\delta} - \left( \frac{\delta \tilde{E}_{xc}[\tilde{n}]}{\delta \tilde{n}(\mathbf{r})} \right)_{N-\delta} \right].$$

where $v_{xc}^{N+\delta}(\mathbf{r})$ and $v_{xc}^{N-\delta}(\mathbf{r})$ are the exchange-correlation po-
In the ensemble approach, the derivative discontinuity in the exchange-correlation functional is thus the difference between the interacting and KS bandgap energies, whether the system is finite or not. The size of the derivative discontinuity in the exact exchange-correlation functional is somewhat controversial. The LDA and GGA for example have no such derivative discontinuities in solids, but yield too low bandgap energies. The KS exact-exchange (EXX) functional on the other hand yields much too large $E_g$'s in solids but shows a huge discontinuity that pulls the KS bandgap down to the experiment in many materials.90,91 There is, however, no clear physics behind this agreement.92 As for the DFT-RPA, one gets in solids

$$\Delta_{xc} = (I - e_i) - (A - e_i) = E_g - E_{g0} \quad \text{for the DFT-RPA}$$

where $\Sigma_0(r, r'; e)$ is the $G_0W_0$ self-energy. The DFT-RPA is one of the first known functionals that yields reasonable interacting bandgap energies while having a sizeable derivative discontinuity is solids—on the order of a few tenths of eV in most semiconductors, as suggested by Refs. 42 and 43. Whether this derivative discontinuity will decrease if further correlations are included is, however, an open question.

In principle, noninteger number of particles can also be handled within the fractional occupation number formalism. In this approach, each KS spin orbital $\phi_i(\mathbf{r})$ may be occupied with a fractional number of electrons $f_i$ ($0 < f_i \leq 1$). This allows a straightforward extension of any explicit functional of the density such as the LDA and GGA to arbitrary densities $n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2$. The derivative discontinuity in the fractional occupation number formalism is not in general equal to the difference between the interacting and KS bandgap energies, except presumably in solids. The introduction of fractional occupation numbers in implicit functionals of the density is much more involved.93 Casida has developed such a fractional occupation number formalism for a class of RPA-like functionals.94 We point out, however, that some energy denominators in the expression of the exchange-correlation energy may reduce to zero in this fractional occupation number formalism if the $f_i$'s are different from 0 or 1 [as can be seen (in another approximation for the exchange-correlation energy) in Eq. (2.8) of Ref. 94]. Hence Ref. 94 allows a formal extension of the RPA to fractional occupation numbers (that yields the same results as ours in solids), but is not meant for practical applications. We are not aware of any other extension of the RPA to fractional occupation numbers.

The results of Secs. III–VI may be applicable to the functionals discussed in Ref. 94 and first introduced in Ref. 6. These functionals are based on Nozières' expression95 for the total energy in many-body perturbation theory (Nozières' formula is a variant of the Luttinger Ward formula96). Each different approximation for the self-energy yields a particular functional of this class. The DFT-RPA functional, that can also be derived within many-body perturbation theory, actually follows from the $GW$ approximation for the self-energy. The calculation of the electron affinity $A$ and of the first ionization potential $I$ for any functional of this class yields results similar to Eqs. (19) and (21), with the appropriate self-energy operator and exchange-correlation potential (provided some higher-order contributions vanish in solids as in the RPA—see details in Appendix C). This provides a well-defined interpretation to quasiparticle bandgap calculations with KS-based self-energy operators in solids.

Last, we would like to mention that other ACFD functionals can be built upon the model of the RPA using a time-dependent exchange-correlation kernel in Eq. (4) such as the adiabatic LDA kernel97. The extension of the results of Sec. III to these functionals is, however, intricate, notably because the integration over the coupling constant $\lambda$ in Eq. (1) cannot be performed analytically any more. Work in this direction is still under way.

VII. CONCLUSION

In this paper, we have calculated the interacting bandgap energy of a solid in the random-phase approximation for the exchange-correlation energy (DFT-RPA functional). We have shown that the latter differs from the Kohn-Sham bandgap energy by an unrenormalized $G_0W_0$ self-energy correction, computed using Kohn-Sham orbitals and energies as input. This provides a clear rationale behind $G_0W_0$ quasiparticle bandgap calculations, that can be consistently interpreted and analyzed within density functional theory. This, however, questions the use of renormalization factors in the expression of the bandgap energy. We have also separated the kinetic from the Coulomb contributions to the DFT-RPA bandgap energy, and discussed the problem of the derivative discontinuity in the DFT-RPA functional. Last, we have discussed the applicability of our results to other functionals based on Nozière's expression for the total energy in many-body perturbation theory.

ACKNOWLEDGMENTS

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APPENDIX A: PROOF THAT $A' = O(\Omega^{-1/4})$ WHEN $\Omega \to \infty$

In this Appendix, we show that $A' = O(\Omega^{-1/4})$ when $\Omega \to \infty$. We also recover the low-density behavior of the DFT-
RPA correlation energy per particle in the homogeneous electron gas \( e_{c}^{\text{RPA}}(n) \sim -0.574n^{1/4} \), a result found numerically by Wang and Perdew.\(^{64}\) We consider a piece of crystalline solid with finite (but very large) volume \( \Omega \) and periodic boundary conditions.\(^{99}\) We thus index the KS orbitals \( \varphi_{n k}(r) = e^{-i k \cdot r} \Delta_{u k}(r) / \sqrt{\Omega} \) and the KS energies \( e_{n k} \) by their wave vector \( k \) in the first Brillouin zone (FBZ) and by their band index \( n \). \( \Delta_{u k}(r) \) has the periodicity of the underlying crystal lattice. We assume \( n_{v} \) occupied valence bands, a direct bandgap at \( k = 0 \), and no nondegenerate conducion band minimum (though this is not restrictive). We let \( c = n_{v} + 1 \) and take \( \varepsilon_{c} = e_{c,0} \) as the reference of energies. We also assume (for simplicity) that \( e_{n k} \sim k^{2}/(2m_{c}^{*}) \) around \( k = 0 \). We shall first discuss the long-wavelength behavior of \( \delta \chi_{0}(iu) \) and \( W(iu) \). The wave vector decomposition of \( \delta \chi_{0}(iu) \) reads

\[
\delta \chi_{0}(r, r'; iu) = \frac{i}{2(2\pi)^{3}} \sum_{G, G'} e^{i(q+G)\cdot r} \delta \chi_{0, GG'}(q; iu)e^{-i(q+G')\cdot r'},
\]

where \( q \) runs over the whole FBZ and \( G, G' \) are reciprocal lattice vectors. \( \delta \chi_{0, GG'}(q; iu) \) is easily calculated from Eq. (13):

\[
\delta \chi_{0, GG'}(q; iu) = -\frac{2}{\Omega} \sum_{u_{n k}=0}^{\Omega} \Phi_{e_{n k}}(G)\Phi^{*}_{e_{n k}}(G') \frac{e_{n k}}{u^{2}+e_{n k}^{2}}
\]

and \( \Omega_{0} \) is the volume of the unit cell of the crystal lattice. The small \( q \) behavior of \( \Phi_{e_{n k}}(G) \) [hence of \( \delta \chi_{0, GG'}(q; iu) \)] follows from the orthogonality between KS orbitals

\[
\Phi_{e_{n k}}(G=0) \propto q \quad (n \neq c), \quad \Phi_{e_{c n}}(G=0) \rightarrow 1,
\]

and

\[
\Phi_{e_{n k}}(G \neq 0) \rightarrow \text{const.}
\]

As for \( W(iu) \), one typically gets\(^{99}\) in a KS insulator, when \( q \rightarrow 0 \):

\[
W_{00}(q; iu) \propto \frac{1}{q^{2}},
\]

\[
W_{0G}(q; iu), W_{G0}(q; iu) \propto \frac{1}{q} \quad (G \neq 0),
\]

\[
W_{GG'}(q; iu) \rightarrow \text{const} \quad (G \neq 0, G' \neq 0).
\]

We now prove that \( A' = O(\Omega^{-1/4}) \) when \( \Omega \rightarrow \infty \). We start from the wave vector decomposition of \( A' \) [see Eq. (16b)]:

\[
-A' = \Omega \left( \frac{d}{2\pi} \int du \int d\Omega' \text{Tr}[\ln[1 - W(q; iu)\delta \chi_{0}(q; iu)]}
\]

\[
+ W(q; iu)\delta \chi_{0}(q; iu)],
\]

where \( \delta \chi_{0}(q; iu) \) and \( W(q; iu) \) are the matrices with elements \( \delta \chi_{0, GG'}(q; iu) \) and \( W_{GG'}(q; iu) \) respectively. The trace of the logarithm can also be written

\[
\text{Tr}[\ln[1 - W(q; iu)\delta \chi_{0}(q; iu)]]
\]

\[
= \ln \text{det}[1 - W(q; iu)\delta \chi_{0}(q; iu)].
\]

Now, Eqs. (A4) and (A5) can be used to show that the integrand in Eq. (A6) is finite except around \( q = 0, u = 0 \). Moreover, \( \delta \chi_{0}(q; iu) \) scales as \( 1/\Omega \). Hence, for any \( q_{0} > 0 \) and any \( u_{0} > 0 \), there exists \( \Omega_{0} \) large enough such that the power-series expansion of \( \text{Tr}[\ln[1 - W(q; iu)\delta \chi_{0}(q; iu)]] \) is convergent for \( \Omega \geq \Omega_{0}, q > q_{0} \) and \( |u| > u_{0} \). This yields

\[
\text{Tr}[\ln[1 - W(q; iu)\delta \chi_{0}(q; iu)]]
\]

\[
= -\text{Tr}[W(q; iu)\delta \chi_{0}(q; iu)] + O\left( \frac{1}{\Omega_{0}^{2}} \right).
\]

The contribution to \( A' \) coming from the domain \( q > q_{0}, |u| > u_{0} \) will thus vanish as \( 1/\Omega \) when \( \Omega \rightarrow \infty \). We must last deal with the contribution \( \delta A'(q_{0}, u_{0}) \) coming from the domain \( q \leq q_{0}, |u| \leq u_{0} \).

The divergence of the integrand in this region comes from the lowest conduction band contribution to \( \delta \chi_{0, GG'}(q; iu) \). We can discard the contribution from all the other bands for the purpose of our demonstration. \( \delta \chi_{0}(q; iu) \) then reads

\[
\delta \chi_{0}(q; iu) = -\frac{1}{\Omega} \frac{q^{2}m_{e}^{*}}{u^{2} + q^{4}/(2m_{c}^{*})^{2}} |\Phi_{c eq}|(\Phi_{c eq}^{*}),
\]

where \( |\Phi_{c eq}| \) is the vector with components \( \Phi_{c eq}(G) \). This yields

\[
\text{Tr}[W(q; iu)\delta \chi_{0}(q; iu)] = -\frac{1}{\Omega} \frac{q^{2}m_{e}^{*}}{u^{2} + q^{4}/(2m_{c}^{*})^{2}} \times \langle |\Phi_{c eq}|W(q; iu)|\Phi_{c eq}^{*} \rangle
\]

\[
= \text{det}[1 - W(q; iu)\delta \chi_{0}(q; iu)] = 1 - \text{Tr}[W(q; iu)\delta \chi_{0}(q; iu)].
\]

The small \( q \) behavior of \( \langle |\Phi_{c eq}|W(q; iu)|\Phi_{c eq}^{*} \rangle \) is driven by \( W_{00}(q; iu) \); we thus get when both \( q \rightarrow 0 \) and \( u \rightarrow 0 \)

\[
\langle |\Phi_{c eq}|W(q; iu)|\Phi_{c eq}^{*} \rangle \sim \frac{4\pi}{e_{s}q^{2}},
\]

where \( e_{s} \) is the static dielectric constant.

If we now plug Eqs. (A10) and (A11) into Eq. (A6) and make the following change of variables:

\[
u' = (e_{s}m_{e}^{*}/\Omega)^{1/2}u,
\]

\[
A' = O(\Omega^{-1/4})\]
BAND-GAP ENERGY IN THE RANDOM-PHASE...

\[ q' = \left( \frac{e_s \Omega}{m_e} \right)^{1/4} q. \]  

(A12b)

we get

\[ -\delta A'_s(q_0, u_0) \sim \frac{1}{2e_r} \left( \frac{m_s}{e_s \Omega} \right)^{1/4} \int_{-q_0}^{q_0} \frac{du'}{2\pi} \int_{B_{q_0}} \frac{d^3q'}{(2\pi)^3} \times \ln \left( 1 + \frac{4\pi}{u'^2 + q'^4/4} \right) - \frac{4\pi}{u'^2 + q'^4/4}, \]

(A13)

where \( u_0' = (e_s m_s^2 \Omega)^{1/2} u_0 \) and \( B_{q_0} \) is the domain \( q \leq q_0 \) with \( q_0' = (e_s m_s \Omega)^{1/2} q_0 \). The above integral has a finite limit when \( u_0' \to \infty \) and \( q_0' \to \infty \), which finally yields the expected result

\[ A'_s = -\frac{K}{e_r} S \left[ \frac{m^*}{e_s \Omega} \right]^{1/4}, \]

(A14)

where, after a few transformations on Eq. (A13):

\[ K = \frac{2}{\pi^{3/2}} \int_{0}^{+\infty} x^4 \left[ 1 - \sqrt{1 + \frac{1}{x^2}} \right]^2 dx = 0.574(4). \]  

(A15)

Equation (A14) is consistent with the low-density behavior of the RPA correlation energy per particle in the homogeneous electron gas \( e_r^{RPA}(n) \). Let us indeed add an electron to an otherwise empty box of large volume \( \Omega \). The RPA (self-) correlation energy of this electron will be given by \( -A'_s \). If we now think of this system as a realization of a spin-polarized homogeneous electron gas with low (with \( n=1/\Omega \), we get from Eq. (A14) \( e_r^{RPA}(n) \sim -0.574n^{1/4} \) [the low-density behavior of \( e_r^{RPA}(n) \) is independent of the spin polarization]. This is precisely the result obtained numerically by Wang and Perdew.

APPENDIX B: FIRST-ORDER APPROXIMATION TO THE SELF-CONSISTENT QUASIPARTICLE ENERGIES

In this Appendix, we show that Eqs. (19) and (21) are first-order approximations to the quasiparticle energies in an appropriate treatment of the self-consistent quasiparticle equation. First of all, the quasiparticle energies can be considered as functionals of the ground-state density, up to an additive constant [since \( n_r \) yields \( v_{xc}\left(r\right) \) up to an additive constant, which then yields the interacting Green function \( G_{\alpha} \) up to a shift along the frequency axis]. This motivates a tentative expansion of the quasiparticle energies in terms of the KS orbitals and energies. We thus consider the following quasiparticle equation:

\[ -\frac{1}{2}\nabla^2 \Psi_{\alpha}(r) + v_{xc}\left(r\right) \Psi_{\alpha}(r) = E_{\alpha} \Psi_{\alpha}(r) \]

(B1)

\[ v_{xc}(r) \] is the external (ionic) potential and \( G_{\alpha}(r,r';E) \) is the GW self-energy calculated with the self-consistent Green function \( G_{\alpha} \) at coupling constant \( \alpha \). \( v_{xc}(r) \) is a local potential such that \( v_{xc}\left(r,1\right) = 0 \) and such that the density \( n_r = n_\alpha(r) \) is held constant along the way from the KS Hamiltonian (\( \alpha = 0 \)) to the self-consistent quasiparticle equation (\( \alpha = 1 \)).

We now make a power series expansion of \( v_{xc}(r) \) of the form \( v_{xc}(r) = \sum \left( 1 - \alpha^2 \right) v_{xc}^{\left(2\right)}(r) \) and calculate \( v_{xc}^{\left(2\right)}(r) \) so that the \( k \)th order variation of the density \( \partial v_{xc}^{\left(k\right)}(r) \) is zero. \( \delta \theta^{\left(1\right)}(r) \) reads \( \delta \theta^{\left(1\right)}(r) \) (the limits \( r' \to r \) and \( \delta \to 0^+ \) are understood)

\[ \delta \theta^{\left(1\right)}(r) = 0 = \int_0^{2\pi} \frac{d\omega}{2\pi} e^{i\omega \delta'} \delta G^{\left(1\right)}(r,r';\omega), \]

(B2)

where \( \delta G^{\left(1\right)}(\omega) = G_0(\omega) \sum_{\alpha} \left[ G_{\alpha}(\omega) - v_{xc}^{\left(1\right)}(r) \right] G_0(\omega) \) is the first-order variation of the Green function. Equation (B2) is no more than the linear-response Sham-Schlüter equation, meaning that \( v_{xc}^{\left(1\right)}(r) \) is the DFT-RPA potential \( v_{xc}^{\left(RPA\right)}(r) \).

Let \( \Psi_0(r) = \phi(r) \) be a zero-order KS orbital with KS energy \( E_0 = \phi \). We then easily get

\[ \left( \frac{dE_{\alpha}}{d\alpha} \right)_{\alpha=0} = \langle \phi | \sum_{\alpha} [ G_{\alpha}(\epsilon) - v_{xc}^{\left(1\right)}(r) ] | \phi \rangle, \]

(B3)

where we have taken into account the fact that \( \delta \theta^{\left(1\right)}(r) \) is zero. We thus end up at first-order with

\[ E = \phi + \langle \phi | \sum_{\alpha} [ G_{\alpha}(\epsilon) ] | \phi \rangle - v_{xc}^{\left(RPA\right)}(r). \]

(B4)

This result is valid in finite systems as well as solids, and for any KS orbital \( \phi(r) \). In particular, the first-order approximations to the conduction and valence band edges in the first-order potential \( v_{xc}(r) = v_{xc}^{\left(RPA\right)}(r) \) are given by Eqs. (19) and (21), respectively. The DFT-RPA potential \( v_{xc}^{\left(RPA\right)}(r) \) moreover appears as the adequate starting point for the computation of the whole \( G_0 W_0 \) quasiparticle band structure. We acknowledge, though, that a higher-order expansion of \( E_0 \) is not practical and may even break down due to nonanalyticities in the self-energy.

APPENDIX C: APPLICATION TO OTHER FUNCTIONALS

In this Appendix, we discuss the applicability of our results to other functionals based on many-body perturbation theory. Indeed, the total energy of a system can be calculated from the interacting Green function \( G \) using the well-known Galitskii-Midgal formula or variational functionals such as Luttinger-Ward’s or Nozières’ formula. The latter two formulae notably make use of the expansion of the self-energy in a series of “skeleton diagrams” only involving the interacting Green function \( G \) and the bare Coulomb interaction \( v \). As variational functionals, they are much more robust with respect to errors in the Green function than is the Galitskii-Midgal formula. We can thus expect reasonable total energies if we use the KS Green function \( G_0 \) instead of the interacting Green function \( G \) as input for the calculation. Evaluating Nozières’ functional at the KS Green function \( G_0 \) yields (we still work with spinless Green functions for the sake of simplicity)
where $\delta \rightarrow 0^+$ and $\Sigma_{xc}(G_0)(\mathbf{r}, \mathbf{r}'; \omega)$ is the sum of all skeleton diagrams of order $n$ (that involve $n$ interaction lines), the interacting Green function lines being replaced with $G_0$ lines. The KS Green function $G_0$ reads on the real frequency axis

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_j \frac{\varphi_j(\mathbf{r}) \varphi_j^{*}(\mathbf{r}')}{\omega - \varepsilon_j \pm i \eta},$$

where $\eta$ is a positive infinitesimal and the sign $(-)$ holds for occupied (empty) KS states. The exchange-correlation potential $v_{xc}(\mathbf{r})$ that derives from Eq. (C1) can be shown to satisfy the linear-response Sham-Schlüter equation. This follows from a particular property of the $\Phi$ functional defined in Eq. (C1):

$$\frac{\delta \Phi[\Sigma_{xc}]}{\delta G_0(\mathbf{r}, \mathbf{r}'; \omega)} = \frac{1}{2 \pi} \Sigma_{xc}(G_0)(\mathbf{r}, \mathbf{r}'; \omega).$$

As an example, the DFT-RPA functional of Sec. II can also be derived within many-body perturbation theory and is actually equivalent to Eq. (C1) in the $GW$ approximation for the self-energy. Let us now consider any well-defined self-energy approximation in solids and calculate the electron affinity $A$ with approximation (C1) for the exchange-correlation energy. The variation of $G_0(\mathbf{r}, \mathbf{r}'; \omega)$ upon addition of one electron to the lowest unoccupied orbital is [see Eq. (C2)]

$$\delta G_0(\mathbf{r}, \mathbf{r}'; \omega) = \varphi_i(\mathbf{r}) \left( \frac{1}{\omega - \varepsilon_i - i \eta} - \frac{1}{\omega - \varepsilon_i + i \eta} \right) \varphi_i^{*}(\mathbf{r}')$$

$$- \frac{1}{2 \pi} \varphi_i(\mathbf{r}) \varphi_i^{*}(\mathbf{r}') \delta(\omega - \varepsilon_i).$$

Following the lines of Sec. III, we split $A_{xc}$ in two parts $A_{xc} = \Phi[G_0] - \Phi[G_0 + \delta G_0]$ where $A_{xc}^{\Phi}$ is the contribution from the diagrams that contain only one $\delta G_0$ line, and $A_{xc}'$ is the remainder. The first-order variation of the $\Phi$ functional

$$A_{xc}^{\Phi} = \int d^3r \int d^3r' \int \frac{d\omega}{2 \pi} e^{i \omega \delta} \frac{\delta \Phi[\Sigma_{xc}(\varepsilon_c)]}{\delta G_0(\mathbf{r}, \mathbf{r}'; \omega)}.$$ 

Equations (C3) and (C4) thus yield

$$A_{xc}^{\Phi} = 2 \varepsilon_c + \langle \varphi_i | A_{xc}(\varepsilon_c) | \varphi_i \rangle.$$ 

We last get from Eqs. (8) and (9):

$$-A = \varepsilon_c + \langle \varphi_i | A_{xc}(\varepsilon_c) - v_{xc}(\varepsilon_c) | \varphi_i \rangle - A_{xc}' + O(\Omega^{-1}),$$

with a similar result for the first ionization potential $I$. We expect $A_{xc}'$ to vanish in solids as in the RPA (but not necessarily as $\Omega^{-1/2}$), though we did not prove it whatever the self-energy. If so, Eq. (C7) provides a clear and consistent interpretation for quasiparticle bandgap calculations with KS-based self-energy operators in solids.

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6Electronic address: yniquet@cea.fr


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As a matter of fact, the exact solution of Eq. (22) is real only if it falls within the interval \([E_c - E_{KS}^0, E_c + E_{KS}^0]\) [see e.g., B. Farid, in *Electron Correlations in the Solid State* (edited by N. H. March (Imperial College Press, London, 1999, p. 212)]. In metals notably, the Fermi energy according to Eq. (22) will always be complex in the \(G_0W_0\) approximation.

Note that the values of \(E_c\) and \(E_F\) computed from Eqs. (19) and (21) are always real, as expected from their interpretation as the electron affinity and first ionization potential, respectively (see previous note). Although the \(r\rightarrow\) \(G_0W_0\) values of \(E_c\) and \(E_F\) are also real (because \(Z_e\) and \(Z_n\) are), the higher-order solutions of Eq. (22) may be complex.


The RPA+ functional is defined as

\[
E_{\text{RPA+}}^0[n] = E_{\text{RPA}}^0[n] + E_{\text{LDA}}^0[n],
\]

where

\[
E_{\text{SR}}^0[n] = E_{\text{LDA}}^0[n] - E_{\text{RPA}}^0[n] \quad \text{and} \quad E_{\text{SR}}^0[n] = E_{\text{LDA}}^0[n] - E_{\text{RPA}}^0[n]
\]

being the local density approximations based on the "exact" and RPA correlation energies of the homogeneous electron gas (Refs. 21 and 31). The electron affinity and first ionization potential in the RPA+ approximation are still given by Eqs. (19) and (21), the KS orbitals and energies being now calculated in the RPA+ exchange-correlation potential

\[
E_{\text{xc}}^0(r) = E_{\text{RPA}}^0(r) + E_{\text{SR}}^0(r).
\]

This LDA-like short-range correction shifts the quasiparticles upwards by about 50 meV in silicon and diamond, but leaves the gap unaffected.


The values of the self-energy corrections at the conduction band minimum along \(\Gamma X\) are interpolated from neighboring \(k\) points.


M. Städele, J. A. Majewski, P. Vogl, and A. Göring, Phys. Rev.
As a matter of fact, the KS orbitals cannot be reconstructed from a trial density \( n(\mathbf{r}) = \sum f_i |\varphi_i(\mathbf{r})|^2 \) if the \( f_i \)'s are not known. The introduction of fractional occupation numbers into orbital-dependent approximations for the exchange-correlation energy such as KS-EXX or DFT-RPA thus yields functionals of both the density and \( (\text{independently}) \) the \( f_i \)'s. That is notably why KS-EXX or the RPA do not satisfy the usual form of Janak’s theorem \[ J. F. Janak, Phys. Rev. B 18, 7165 (1978) \] \( dE/df_i = e_i \), except for the highest occupied KS orbital.

We could as well consider a piece of solid with properly saturated surfaces so that there are no defect states left in the gap.

Of course, a “one electron in a box” system is not physically equivalent to a low-density electron gas; this equivalence should nonetheless hold in the RPA because the electron \( (s) \) only respond to the time-dependent Hartree potential (which is a non-self-interaction free average).

Equation (5) can be recovered from Eq. (C1) in the GW approximation for the self-energy by analytic continuation from the real frequency axis to the imaginary frequency axis.